

Ruthenium(III)-catalyzed oxidation of 2-phenylethylamine with sodium *N*-chlorobenzenesulphonamide in hydrochloric acid solution: A kinetic and mechanistic study

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Abstract

The kinetics of ruthenium(III)-catalyzed oxidation of 2-phenylethylamine (PEA) with sodium *N*-chlorobenzenesulphonamide or chloramine-B (CAB) in hydrochloric acid solution has been studied at 313 K. The reaction rate shows first-order dependence each on [CAB], [H⁺] and [Ru(III)Cl₃] and fractional order on [PEA] and [Cl⁻]. Variation of ionic strength and addition of the reduction product of CAB has no significant effect on the rate. There is a negative effect of dielectric constant of the solvent. The stoichiometry of the reaction was found to be 1:1 and the oxidation product of 2-phenylethylamine was identified as phenyl acetaldehyde. The reaction was studied at different temperatures and the activation parameters have been evaluated from the Arrhenius plot. The reaction constants involved in the mechanisms were computed. RN⁺H₂Cl has been postulated as the reactive oxidizing species. Mechanisms consistent with the observed kinetic data have been proposed and discussed.

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Keywords: 2-Phenylethylamine; Chloramine-B; Ru(III)chloride catalysis; Oxidation kinetics

1. Introduction

Aromatic *N*-halosulphonamides are mild oxidants containing a strongly polarized *N*-linked halogen in its +1 oxidation state. The prominent compound of this group is chloramine-T and the mechanistic aspects of many of its reactions have been documented [1,2]. The benzene analogue chloramine-B (C₆H₅SO₂NCINa·1.5H₂O or CAB) is being important and received considerable attention as an oxidimetric reagent [3–5]. Conductometric studies of the interaction of CAB with some metal ion solutions [6] and photolysis of aqueous solution of CAB have been reported [7].

2-Phenylethylamine (PEA) is a naturally occurring endogenous amine, which is present in several mammalian tissues [8] including the brain [9]. 2-Phenylethylamine is formed by decarboxylation of amino acid, L-phenylalanine [10]. It crosses the presynaptic membrane and potentiates the postsynaptic effects

of dopamine [11]. 2-Phenylethylamine may act as neuromodulator of catecholamine neurotransmission in the brain [11]. This bioactive amine is also present in certain foodstuffs such as chocolate, cheese and wine and may cause undesirable side effects in susceptible individuals [12]. After reviewing the literature, we found that there was no information available on the oxidation kinetics of 2-phenylethylamine with any oxidant. There was a need for understanding the oxidation mechanism of this bioactive compound in acidic solution, so that the study could throw some light on the fate of the compound in biological systems.

In light of the available information and of our continued interest on mechanistic studies on haloaminometric reactions in general and bioactive compounds in particular the present studies are undertaken. The present paper reports the kinetics of Ru(III)chloride catalyzed oxidation of 2-phenylethylamine with CAB in HCl medium at 313 K in order to (i) elucidate the reaction mechanism in the biological system, (ii) put forward an appropriate rate law and (iii) identify the reactive species. The reaction of 2-phenylethylamine with CAB in the presence of HCl medium without a catalyst was found to be sluggish,

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but the reactions were facile in the presence of ruthenium(III) chloride catalyst.

2. Experimental

2.1. Materials

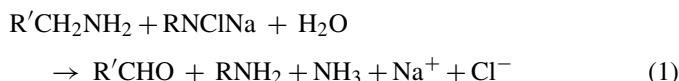
Chloramine-B was prepared by passing chlorine through a solution of benzenesulfonamide in 4 mol dm^{-3} NaOH for 1 h. The product was collected, dried and recrystallized from water (mp 170°C with decomposition). Its purity was checked by iodometry for its active chlorine content and also by its IR, ^1H NMR and ^{13}C NMR spectra. An aqueous solution of CAB was standardized iodometrically and stored in brown bottles to prevent photochemical deterioration. Analar grade 2-phenylethylamine (Himedia) was used as received. Aqueous solution of the compound was prepared freshly each time. A solution of Ru(III)Cl_3 (Arora Mathey) in a solution of hydrochloric acid was used as catalyst. The final concentrations of HCl and Ru(III)Cl_3 were 1.0×10^{-2} and $8.86 \times 10^{-3} \text{ mol dm}^{-3}$, respectively. Allowance was made for the amount of HCl present in catalyst solution while preparing for kinetic runs. All other chemicals were of analytical grade. Doubly distilled water was used throughout.

2.2. Kinetic measurements

Kinetic runs were performed under pseudo first-order conditions by taking known excess of $[\text{PEA}]_0$ over $[\text{CAB}]$ at 313 K. The reaction was carried out in stoppered Pyrex boiling tubes whose outer surfaces were coated black to eliminate photochemical effects. For each run, requisite amount of solutions of PEA, HCl, RuCl_3 , NaClO_4 , and water (to keep the total volume constant for all runs) were taken in the tube and thermally equilibrated at 313 K. A measured amount of CAB solution also pre-equilibrated at the same temperature was rapidly added to the mixture and stirred well. The progress of the reaction was monitored by the iodometric determination of unreacted CAB in 5 ml aliquots of the reaction mixture withdrawn at different time intervals. The course of the reaction was studied for at least two half-lives. The pseudo first-order rate constants (k') calculated from the linear plots of $\log[\text{CAB}]$ versus time were reproducible within $\pm 4\%$. Regression analysis of the experimental data to obtain regression coefficient, r , was performed using a fx-570MS scientific calculator.

2.3. Stoichiometry and product analysis

Reaction mixtures containing varying ratios of CAB to PEA in the presence of HCl and Ru(III)Cl_3 were equilibrated at 313 K for 48 h. Estimation of unreacted CAB showed that 1 mol of PEA consumed 1 mol of oxidant, confirming the following stoichiometry,



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

The products in the reaction mixture were extracted several times with diethyl ether. The combined ether extract was evaporated and subjected to the column chromatography on silica gel (60–200 mesh) using gradient elutions (from dichloromethane to chloroform). After initial separation, the products were further purified by recrystallization. The reduction product of CAB, benzenesulfonamide (RNH_2) was detected by paper chromatography [13]. Benzyl alcohol saturated with water was used as the solvent with 0.5% vanillin in 1% HCl solution in ethanol as spray reagent ($R_f = 0.88$). It was further confirmed by its melting point $149\text{--}150^\circ\text{C}$ (lit. mp = $150\text{--}152^\circ\text{C}$). The oxidation product of PEA was found to be phenyl acetaldehyde. The aldehyde was detected by conventional spot tests and also by 2,4-DNP derivative. Furthermore, the presence of the aldehyde was confirmed by its IR absorption bands at 1720 cm^{-1} for $\text{C}=\text{O}$ stretching mode and at 2852 cm^{-1} for aldehydic $\text{C}-\text{H}$ stretching mode (IR spectrum was recorded on JASCO FT-IR spectrometer using KBr pellets).

3. Results

The oxidation of PEA by CAB has been kinetically investigated at different initial concentrations of the reactants in the presence of HCl and Ru(III)chloride at 313 K.

3.1. Effect of varying reactant concentrations on the rate

With the substrate in excess at constant $[\text{HCl}]$, $[\text{PEA}]$, $[\text{Ru(III)Cl}_3]$ and temperature, the $[\text{CAB}]_0$ was varied. Plots of $\log[\text{CAB}]$ versus time were linear ($r > 0.990$) indicating a first-order dependence of the rate on $[\text{CAB}]_0$. The pseudo first-order rate constants (k') calculated from the slopes are given in Table 1. The values of k' are unaltered with variation of $[\text{CAB}]_0$.

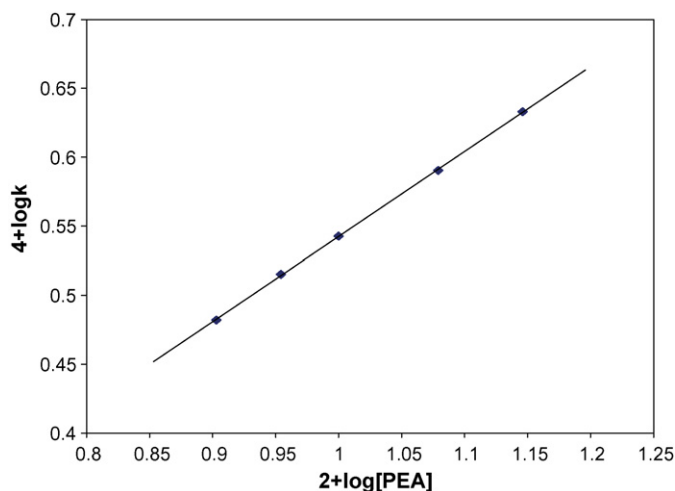
Table 1
Effect of varying concentrations of oxidant, substrate and acid on the reaction rate at 313 K

$10^4 [\text{CAB}]$ (mol dm^{-3})	$10^3 [\text{PEA}]$ (mol dm^{-3})	$10^5 [\text{HCl}]$ (mol dm^{-3})	$10^4 k'$ (s^{-1})
3.0	10.0	50.0	3.52
5.0	10.0	50.0	3.49
7.0	10.0	50.0	3.53
9.0	10.0	50.0	3.49
10.0	10.0	50.0	3.50
5.0	8.0	50.0	3.03
5.0	9.0	50.0	3.27
5.0	10.0	50.0	3.49
5.0	12.0	50.0	3.89
5.0	14.0	50.0	4.29
5.0	10.0	30.0	1.42
5.0	10.0	40.0	2.34
5.0	10.0	50.0	3.49
5.0	10.0	60.0	4.99
5.0	10.0	70.0	6.55
5.0*	10.0	50.0	3.53
5.0**	10.0	50.0	3.50

$[\text{Ru(III)Cl}_3] = 10.0 \times 10^{-5} \text{ mol dm}^{-3}$; $\mu = 0.8 \text{ mol dm}^{-3}$.

* In presence of benzenesulfonamide.

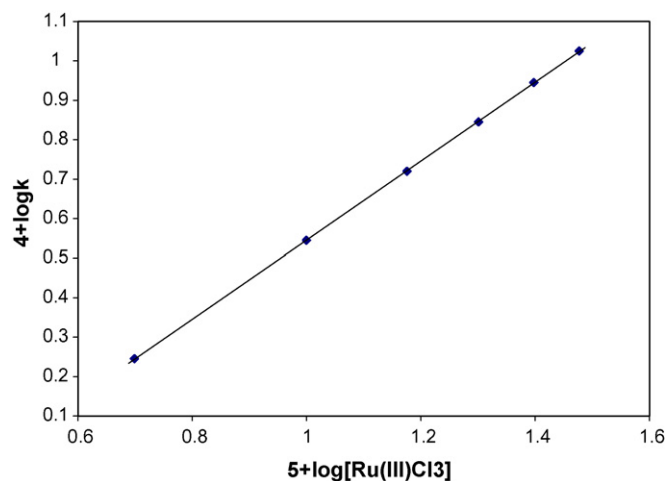
** At ionic strength of 1.0 mol dm^{-3} .

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

confirming the first order dependence of the rate on $[\text{oxidant}]_0$. Under the similar experimental conditions, an increase in $[\text{PEA}]_0$ increased the k' values (Table 1). Plots of $\log k'$ versus $\log [\text{PEA}]_0$ was linear (Fig. 1; $r = 0.997$) with a slope of 0.63 indicating a fractional order dependence on $[\text{PEA}]_0$. Furthermore, a plot of k' versus $[\text{PEA}]_0$ was linear ($r = 0.998$) with a Y -intercept confirming the fractional order dependence on $[\text{PEA}]_0$.

3.2. Effect of varying HCl and Ru(III)Cl₃ concentrations on the rate

The rate increased with increase in $[\text{HCl}]$ (Table 1) and a plot of $\log k'$ versus $\log [\text{HCl}]$ was linear ($r = 0.999$) with a slope of 1.73. The reaction rate increases with increase in $[\text{Ru(III)Cl}_3]$ (Table 2). Plot of $\log k'$ versus $\log [\text{Ru(III)Cl}_3]$ was linear (Fig. 2;

Fig. 2. Plot of $4 + \log k$ vs. $5 + \log [\text{Ru(III)Cl}_3]$.

$r = 0.997$) with a slope of 0.99 indicating first-order dependence on $[\text{Ru(III)Cl}_3]$.

3.3. Effect of varying $[\text{H}^+]$ and $[\text{Cl}^-]$ on the rate

The total $[\text{Cl}^-]$ in the reaction mixture was kept constant at 0.8 mol dm^{-3} by adding NaCl, then $[\text{H}^+]$ was varied using HCl. The rate increased with increase in $[\text{H}^+]$ (Table 2). A plot of $\log k'$ versus $\log [\text{H}^+]$ was linear (Fig. 3; $r = 0.999$) with unit slope indicating first-order dependence on $[\text{H}^+]$. At constant $[\text{H}^+] = 0.5 \text{ mol dm}^{-3}$ maintained with HCl, addition of Cl^- in the form of NaCl increases the reaction rate (Table 2). From a plot of $\log k'$ versus $\log [\text{Cl}^-]$ (Fig. 3; $r = 0.998$), the order with respect to $[\text{Cl}^-]$ is found to be 0.72.

3.4. Effect of benzenesulphonamide on the rate

The addition of reduced product, benzenesulphonamide (1×10^{-4} to $8 \times 10^{-4} \text{ mol dm}^{-3}$) had no effect on the rate, indicating that it is not involved in pre-equilibrium step before the rate-determining step.

Table 2

Effect of varying H^+ , Cl^- and Ru(III)Cl_3 concentrations on the reaction rate at 313 K

$10^2 [\text{H}^+]$ (mol dm^{-3})	$10^2 [\text{Cl}^-]$ (mol dm^{-3})	$10^5 [\text{Ru(III)Cl}_3]$ (mol dm^{-3})	$10^4 k'$ (s^{-1})
10.0	80.0	10.0	1.31
15.0	80.0	10.0	1.93
20.0	80.0	10.0	2.56
30.0	80.0	10.0	3.79
40.0	80.0	10.0	4.98
50.0	80.0	10.0	6.30
50.0	50.0	10.0	3.49
50.0	60.0	10.0	3.99
50.0	70.0	10.0	4.48
50.0	80.0	10.0	4.90
50.0	90.0	10.0	5.36
50.0	50.0	5.0	1.76
50.0	50.0	10.0	3.51
50.0	50.0	15.0	5.25
50.0	50.0	20.0	7.01
50.0	50.0	25.0	8.82
50.0	50.0	30.0	10.60

$[\text{CAB}]_0 = 5.0 \times 10^{-4} \text{ mol dm}^{-3}$; $[\text{PEA}]_0 = 10.0 \times 10^{-3} \text{ mol dm}^{-3}$; $\mu = 0.8 \text{ mol dm}^{-3}$.

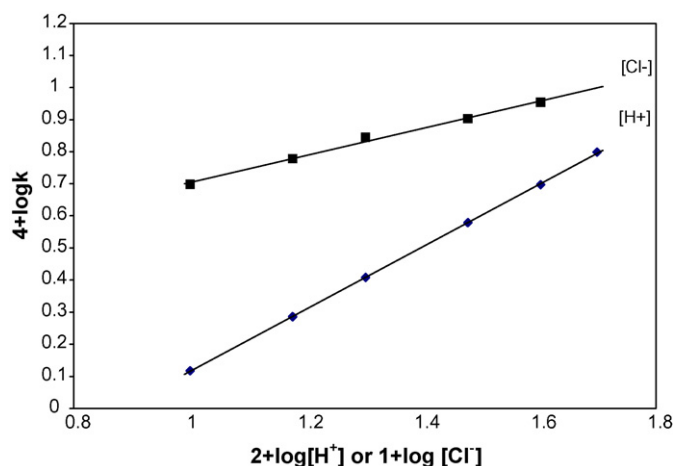
Fig. 3. Plot of $4 + \log k$ vs. $2 + \log [\text{H}^+]$ or $1 + \log [\text{Cl}^-]$.

Table 3
Effect of solvent composition and temperature on the reaction rate

Temperature (K)	CH ₃ CN (% v/v)	10 ⁴ k' (s ⁻¹)
313	0	3.49
313	5	2.66
313	10	2.06
313	15	1.58
313	20	1.20
308	–	2.08
313	–	3.49
318	–	5.36
323	–	8.53
328	–	12.68

[CAB]₀ = 5.0 × 10⁻⁴ mol dm⁻³; [PEA]₀ = 10.0 × 10⁻³ mol dm⁻³; [HCl] = 0.5 mol dm⁻³; [Ru(III)Cl₃] = 10.0 × 10⁻⁵ mol dm⁻³; μ = 0.8 mol dm⁻³.

3.5. Effect of varying ionic strength and dielectric permittivity of the medium on the rate

The reaction rate remained unaffected by varying ionic strength of the medium through addition of NaClO₄ (0.7–1.0 mol dm⁻³). The dielectric permittivity of the medium was varied by adding different proportions (0–20%, v/v) of acetonitrile to the reaction mixture. The rate decreased with decrease in dielectric permittivity of the reaction mixture (Table 3). Plot of log k' versus 1/D, where D is the dielectric permittivity of the medium (D values are taken from the literature [14–16]), gave a straight line with a negative slope. Blank experiments performed showed that CAB did not oxidize acetonitrile under the experimental conditions employed.

3.6. Effect of varying temperature on the rate

The reaction was studied at different temperatures (308–328 K) (Table 3), keeping other experimental conditions constant. From the linear Arrhenius plot of log k' versus 1/T (Fig. 4; r = 0.998), activation energy and other thermodynamic parameters for the composite reaction were found to be E_a = 75.7 kJ mol⁻¹; ΔH[‡] = 73.2 kJ mol⁻¹; ΔG[‡] = 97.7 kJ mol⁻¹ and ΔS[‡] = -79.6 J K⁻¹ mol⁻¹.

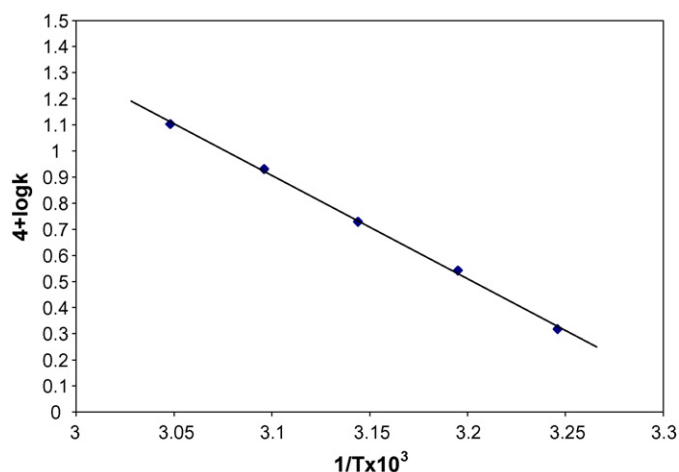


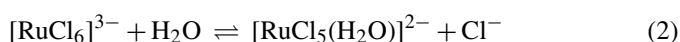
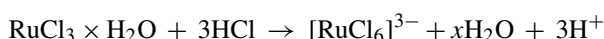
Fig. 4. Plot of 4 + log k vs. 10³/T.

3.7. Test for free radicals

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

4. Discussion

Cady and Connick [17] and Connick and Fine [18] based on the ion exchange properties and UV-spectral studies have shown that the octahedral complexes such as [RuCl₅(H₂O)]²⁻, [RuCl₄(H₂O)₂]⁻, [RuCl₃(H₂O)₃], [RuCl₂(H₂O)₄]⁺ and [RuCl(H₂O)₅]²⁺, may not exist in aqueous solutions of RuCl₃, however other studies [19–21] have shown that the following ligand substitution equilibrium exists in acidic solutions,



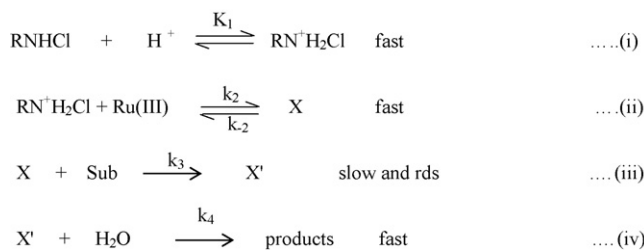
Singh et al. [22,23] have employed the above equilibrium in the ruthenium(III) chloride catalyzed oxidation of primary alcohols with bromamine-T and ethylene glycols with *N*-bromoacetamide in HClO₄ medium. In the present studies, increasing effect of added chloride ion on the reaction rate suggests that [RuCl₆]³⁻ is the more likely catalyzing species [18,21], which interacts with the oxidant to form a complex intermediate [24,25].

Pryde and Soper [26], Morris et al. [27] and Bishop and Jennings [28] 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 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 behaviour of CAB is identical with that of CAT [29–31], while the pH-titration curves observed are similar to those noted by Morris et al. [27]. The possible equilibria in acidified CAB solutions are,



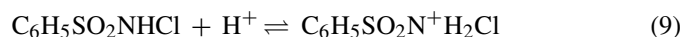
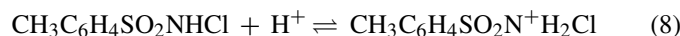
where R = C₆H₅SO₂.

Therefore, the possible oxidizing species in acidic solutions of CAB are the free acid (RNHCl), RNCl₂, HOCl and H₂OCl⁺. The involvement of RNCl₂ in the mechanism leads to a second-order rate law and negative effect of RNH₂ according to Eq. (6), which is contrary to the experimental observations. If HOCl were the primary oxidizing species, a first-order retardation of the rate by the added RNH₂ would be expected. However no



Scheme 1.

such effect is noticed. Hardy and Johnston [32], who studied the pH-dependent relative concentrations of the species present in acidified chloramine-T solutions of comparable molar concentrations have shown that $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{NHCl}$ is the probable oxidizing species in acid medium. Narayanan and Rao [33] and Subhashini et al. [34] have reported that monochloroamines can be further protonated at $\text{pH} < 2$, as shown in the Eqs. (8) and (9) and the values of the second protonation constants are 102 and $61 \pm 2 \text{ mol}^{-1}$ at 25°C for chloramine-T and chloramine-B, respectively.



In the present studies, the first-order in $[\text{H}^+]$ indicates that the protonation of RNHCl results in the formation of $\text{RN}^+\text{H}_2\text{Cl}$, which is likely to be the active oxidizing species, involved in the mechanism. In the proposed mechanism (Scheme 1), the ruthenium(III)- $\text{RN}^+\text{H}_2\text{Cl}$ complex (X) reacts with the substrate to form an intermediate (X') which then disproportionate to the products.

UV-spectral measurements showed that a sharp absorption band was noticed at 216 nm for Ru(III)Cl_3 , 226.5 nm for CAB solution and 214 nm for PEA in the presence of 0.5 mol dm^{-3} HCl. A mixture of CAB and Ru(III)Cl_3 solution in the presence of HCl showed an absorption band at 268 nm, while for a mixture of PEA and Ru(III)Cl_3 solution an absorption band was noticed at 214 nm. The spectral evidence showed that complex formation takes place only between Ru(III)Cl_3 and oxidant. Based on the preceding discussion the following mechanistic interpretation (Scheme 1) is proposed for the reaction.

In Scheme 1, Sub represents the substrate, X and X' represent the complex intermediate species whose structures are shown in Scheme 2 where a detailed mechanism of Ru(III)chloride catalyzed oxidation of PEA with CAB in HCl medium is illustrated. An initial equilibrium involves protonation of RNHCl forming an active oxidizing species of CAB ($\text{RN}^+\text{H}_2\text{Cl}$) (shown in Scheme 1). In the next step, the oxygen atom of the oxidant is coordinated to the metal centre of the active catalyst species, $[\text{RuCl}_6]^{3-}$ to form a loosely bound metal complex, X (step i in Scheme 2) trapped in a solvent cage. This is similar to an associative interchange mechanism involving a fast pre-equilibrium in a ligand substitution reaction of metal complexes. Then follows an electrophilic attack by Cl at the nitrogen atom of PEA to form intermediate X' , RNH_2 and releasing $[\text{RuCl}_6]^{3-}$ (steps ii and iii of Scheme 2). The intermediate X' undergoes intermolecular

rearrangement (step iv) forming phenyl acetaldehyde.

$$\text{From Scheme 1,} \quad \text{rate} = k_3[\text{Sub}][\text{X}] \quad (10)$$

Applying steady state condition for X, it can be shown that,

$$[\text{X}] = \frac{K_1 k_2 [\text{CAB}][\text{H}^+][\text{Ru(III)}]}{k_{-2} + k_3[\text{Sub}]} \quad (11)$$

Since the iodometric titre corresponds to both CAB and RNHCl, and CAB is consumed in the formation of RNHCl, it is reasonable to assume that $[\text{RNHCl}] = [\text{CAB}]$.

On substituting Eq. (11) in Eq. (10) it can be shown that,

$$\text{rate} = \frac{K_1 k_2 k_3 [\text{CAB}][\text{H}^+][\text{Ru(III)}][\text{Sub}]}{k_{-2} + k_3[\text{Sub}]} \quad (12)$$

The rate law (12) is in complete agreement with the experimental results. Since $\text{rate} = k'[\text{CAB}]$, Eq. (12) can be transformed into Eqs. (13) and (14).

$$k' = \frac{K_1 k_2 k_3 [\text{H}^+][\text{Ru(III)}][\text{Sub}]}{k_{-2} + k_3[\text{Sub}]} \quad (13)$$

$$\frac{1}{k'} = \frac{k_{-2}}{K_1 k_2 k_3 [\text{Sub}][\text{H}^+][\text{Ru(III)}]} + \frac{1}{K_1 k_2 [\text{H}^+][\text{Ru(III)}]} \quad (14)$$

Based on Eq. (14), a plot of $1/k'$ versus $1/[\text{sub}]$ was found to be linear and the value of $(K_1 k_2)$ was calculated from the intercept. From Eq. (13), plot of k' versus $[\text{H}^+]$ and k' versus $[\text{Ru(III)}]$ were found to be linear passing through the origin. The value of $(K_1 k_2)$ was again calculated from the slopes of the plots and the two values were found to be same (from Eqs. (13) and (14)). The constancy of $(K_1 k_2)$ values indirectly supports the proposed mechanism for the oxidation of PEA.

In the presence of chloride ion at constant $[\text{H}^+]$, Scheme 3 is proposed for the reaction mechanism. From the slow steps in Scheme 3

$$\text{rate} = k_8[\text{X}][\text{Sub}] \quad (15)$$

Applying steady state approximation for [X], it can be shown that,

$$[\text{X}] = \frac{K_6 k_7 [\text{RNHCl}][\text{H}^+][\text{C}_2]}{k_{-7} + k_8[\text{Sub}]} \quad (16)$$

If $[\text{Ru(III)}]_t$ represents the total concentration of Ru(III),
Then

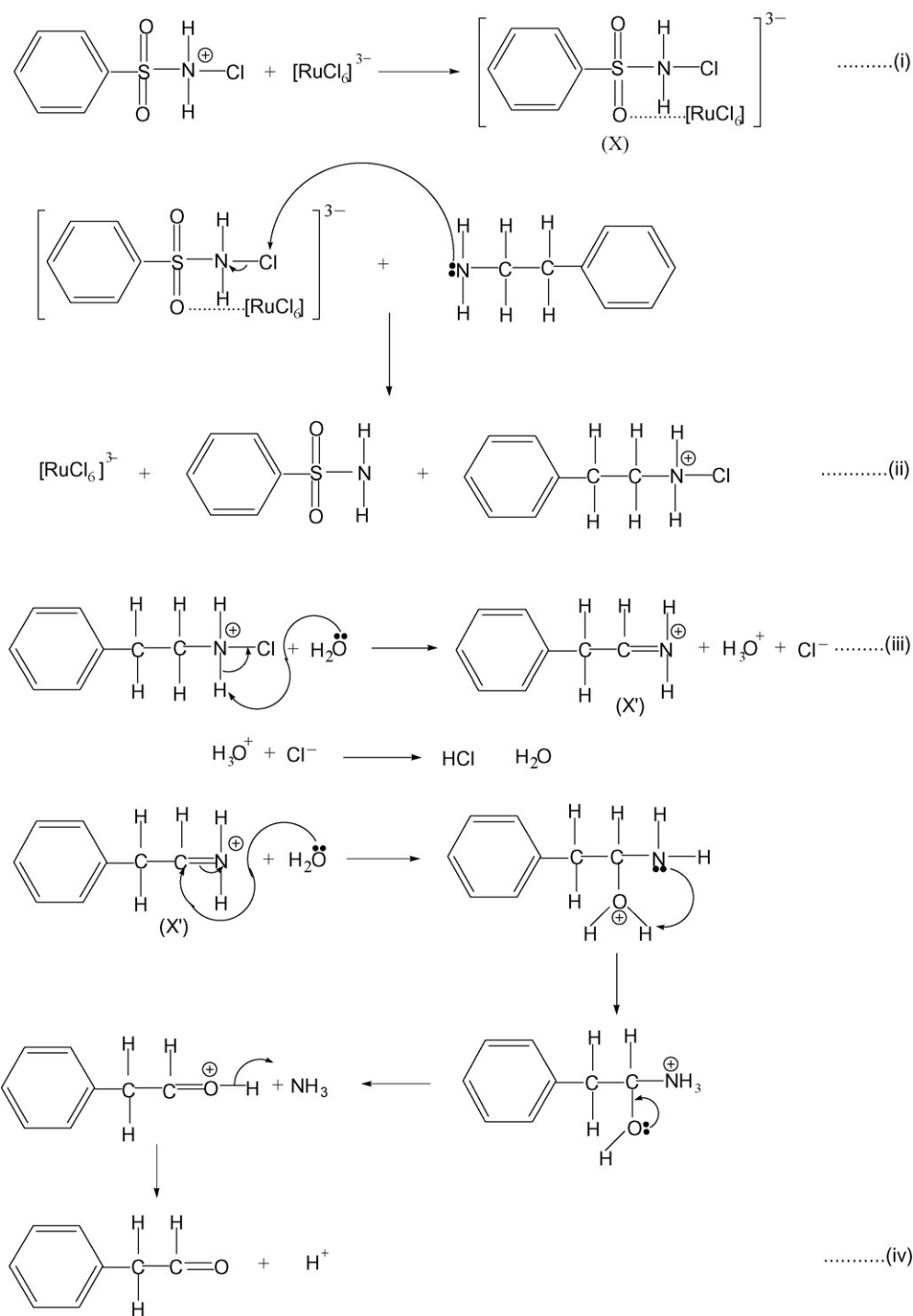
$$[\text{Ru(III)}]_t = [\text{C}_1] + [\text{C}_2] \quad (17)$$

By substituting for $[\text{C}_1]$ from equilibrium step (i) in Eq. (17), one obtains,

$$[\text{Ru(III)}]_t = \frac{[\text{C}_2][\text{H}_2\text{O}]}{K_5[\text{C}_2]} + [\text{C}_2]$$

Or

$$[\text{C}_2] = \frac{K_5[\text{Ru(III)}]_t[\text{Cl}^-]}{[\text{H}_2\text{O}] + K_5[\text{Cl}^-]} \quad (18)$$



Scheme 2.

By substituting Eq. (18) in Eq. (16), Eq. (19) is obtained,

$$[\text{X}] = \frac{K_5 K_6 k_7 [\text{RNHCl}][\text{H}^+][\text{Ru(III)}]_t [\text{Cl}^-]}{\{k_{-7} + k_8 [\text{Sub}]\} [\text{H}_2\text{O}] + K_5 [\text{Cl}^-]} \quad (19)$$

By substituting Eq. (19) in Eq. (15), the following rate law is obtained,

$$\text{rate} = \frac{K_5 K_6 k_7 k_8 [\text{CAB}][\text{H}^+][\text{Ru(III)}]_t [\text{Cl}^-][\text{Sub}]}{\{k_{-7} + k_8 [\text{Sub}]\} [\text{H}_2\text{O}] + K_5 [\text{Cl}^-]} \quad (20)$$

The rate expression (20) clearly demonstrates the fractional-order dependence of rate on $[\text{Cl}^-]$ and $[\text{Sub}]$, and is in good agreement with the experimental results.

A decrease in the rate with decreasing dielectric permittivity (D) of the medium supports the proposed mechanism. Amis and Jaffe [35] have shown that,

$$\log k'_D = \frac{\log k' + Z e \mu}{2.303 k T r^3 D} \quad (21)$$

