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Mechanistic investigation of the oxidation of vitamin B_1 with sodium *N*-chlorobenzenesulfonamide in presence of ruthenium(III) catalyst in hydrochloric acid medium: a kinetic approach

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Abstract The oxidative cleavage of vitamin B_1 (thiamine hydrochloride, *THM*) with sodium *N*-chlorobenzenesulfonamide (chloramine-B, *CAB*) has been kinetically investigated in HCl medium in presence of ruthenium(III) catalyst at 308 K. The oxidation reaction follows the rate law, $-d[CAB]/dt = k\,[CAB]\,[Ru(III)]\,[H^+]\,[THM]^a\,[Cl^-]^b$, where a and b are less than unity. Variation of ionic strength of the medium and addition of the reaction product, benzenesulfonamide (*BSA*) had no significant effect on the reaction rate. The change in relative permittivity of the medium affected by changing the solvent composition with acetonitrile has been studied. The stoichiometry of the reaction was found to be 1:1, and *N*-[(4-amino-2-methylpyrimidine-5-yl)methyl]benzensulfonamide and 2-(4-methylthiazol-5-yl)ethanol were identified as the oxidation products of vitamin B_1. The reaction constants involved in the mechanism were computed. The reaction was studied at different temperatures and the overall activation parameters have been evaluated. $C_6H_5SO_2NHCl$ has been postulated as the reactive oxidizing species. The observed results have been explained by plausible mechanisms and the relative rate laws have been deduced.

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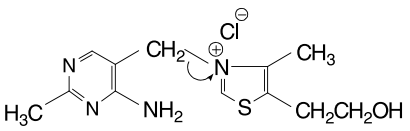
Keywords Vitamin B_1; Chloramine-B; Ruthenium(III) catalysis; Oxidation kinetics.

Introduction

Vitamin B_1 (thiamine, *THM*) was the first member of vitamin B complex to be isolated and identified as vitamin. Vitamin B_1 occurs in the outer coats of the seeds of many plants including cereal grains. Thiamine is fundamentally associated with carbohydrate metabolism. It is phosphorylated in the body to the active coenzyme, thiamine pyrophosphate that functions as co-carboxylase for various reactions in carbohydrate metabolism including the transketolase reaction in the direct oxidative pathway of glucose metabolism [1]. Thiamine might also serve as a modulator of neuromuscular transmission. It binds to isolated nicotinic cholinergic receptors, and neurotransmission is impaired by pyrithiamine, a thiamine antimetabolite [2]. In thiamine deficiency, the oxidation of α-keto acid is impaired, resulting in an increase in the concentration of pyruvate in blood. The requirement of thiamine is related to metabolic rate and is greatest when carbohydrate is a source of en-



Vitamin B_1 (*THM*)

ergy [3]. The oxidation kinetics and mechanism of vitamin B_1 are thus important to the process *in vitro*.

The chemistry of *N*-halogeno compounds containing the halogen in the +1 oxidation state has received considerable attention. The most prominent member of this group is chloramine-T (*CAT*), which is a byproduct in the manufacture of saccharin. It is well known as an analytical reagent for determining diverse substrates, and the mechanistic aspects of these reactions have been documented [4–6]. The benzene analogue chloramine-B ($C_6H_5SO_2NClNa \cdot 1.5\ H_2O$, *CAB*) is also important and received considerable attention as an oxidimetric reagent [7–9]. Conductometric studies of the interaction of *CAB* with some metal ion solutions [10] and photolysis of aqueous solution of *CAB* have been reported [11].

After reviewing the literature, we found that there was no information available on the oxidation kinetics of *THM* with any oxidant. However, oxidation of *THM* with alkaline potassium ferricyanide [12], hypoiodide [13], and chlorite [14] showed the formation of an intense blue fluorescent compound, thiochrome. In view of varied nature of *N*-haloamines and extensive biological importance of vitamin B_1, it was felt important and interesting to investigate the oxidative behavior of *CAB* towards vitamin B_1. The reaction of vitamin B_1 with *CAB* in presence of HCl medium without a catalyst was found to be sluggish, but the reaction was found to be facile in the presence of micro-amounts of ruthenium(III) catalyst. Therefore the present paper reports the results of the investigation on the mechanistic and kinetic aspects of oxidation of vitamin B_1 with *CAB* in the presence of HCl and ruthenium(III) catalyst. The objectives of the present investigation are to (i) elucidate the reaction mechanism in the biological system, (ii) put forward appropriate rate law, (iii) ascertain the reactive species, and (iv) identify the oxidation products.

Results and discussion

Effect of varying reactant concentrations on the rate

The reaction was performed in the presence of $RuCl_3$ catalyst and HCl under pseudo-first-order conditions ($[PYX]_0 \gg [CAB]_0$). Plots of log[*CAB*] *versus* time were linear ($r > 0.991$). The linearity of these plots, together with the constancy of slope for various $[CAB]_0$, indicates a first-order dependence of the reaction rate on [*CAB*]. The pseudo-first-order rate constants, k_{obs} obtained at 308 K are listed in Table 1. Under similar experimental conditions, an increase in $[THM]_0$ increased the rate. Plot of $\log k_{obs}$ *versus* log[*THM*] was linear ($r = 0.998$) with a slope of 0.45 indicating a fractional-order dependence on $[THM]_0$.

Table 1 Effect of varying concentrations of reactants and acid on the reaction rate at 308 K $[RuCl_3] = 4 \times 10^{-4}$ mol dm^{-3}, $\mu = 0.2$ mol dm^{-3}

$10^4[CAB]$ / mol dm^{-3}	$10^3[THM]$ / mol dm^{-3}	$10^2[HCl]$ / mol dm^{-3}	$10^4 k_{obs}$ / s^{-1}
3.0	8.0	5.0	4.11
5.0	8.0	5.0	4.09
7.0	8.0	5.0	3.97
8.0	8.0	5.0	3.99
9.0	8.0	5.0	4.13
5.0	6.0	5.0	3.61
5.0	10.0	5.0	4.39
5.0	12.0	5.0	4.72
5.0	14.0	5.0	5.18
5.0	8.0	4.0	2.71
5.0	8.0	6.0	5.95
5.0	8.0	7.0	7.45
5.0	8.0	8.0	9.44
5.0*	8.0	5.0	4.10
5.0**	8.0	5.0	3.98

* In presence of benzensulfonamide
** At ionic strength 0.5 mol dm^{-3}

Effect of varying [HCl] and [Ru(III)] on the rate

At constant $[CAB]_0$, $[THM]_0$, $[RuCl_3]$, and temperature, the reaction rate increased with increasing

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

$10^2[H^+]$ / mol dm^{-3}	$10^2[Cl^-]$ / mol dm^{-3}	$10^4[RuCl_3]$ / mol dm^{-3}	$10^4 k_{obs}$ / s^{-1}
4.0	15.0	4.0	6.06
5.0	15.0	4.0	7.52
6.0	15.0	4.0	9.08
7.0	15.0	4.0	10.76
8.0	15.0	4.0	12.11
5.0	5.0	4.0	4.09
5.0	7.0	4.0	5.53
5.0	9.0	4.0	6.83
5.0	10.0	4.0	7.29
5.0	11.0	4.8	7.77
5.0	5.0	2.0	2.01
5.0	5.0	3.0	2.99
5.0	5.0	5.0	5.26
5.0	5.0	6.0	6.45

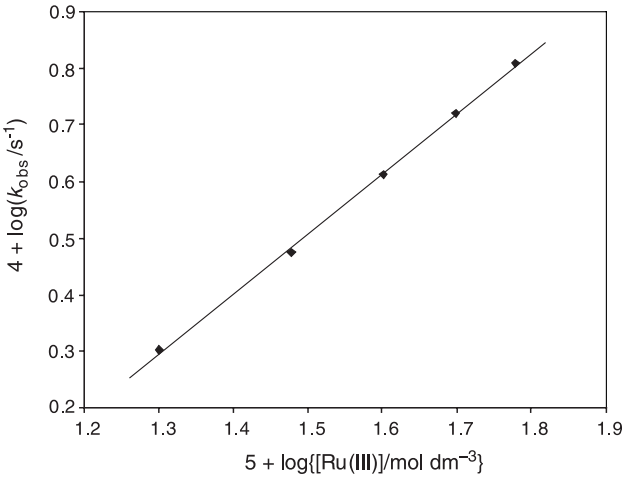


Fig. 1 Plot of $4+\log(k_{obs}/s^{-1})$ *versus* $5+\log\{[Ru(III)]/mol\,dm^{-3}\}$ at $[CAB]=5\times10^{-4}$, $[THM]=8\times10^{-3}$, [HCl] = 0.05, and $[Ru(III)]=4\times10^{-4}\,mol\,dm^{-3}$

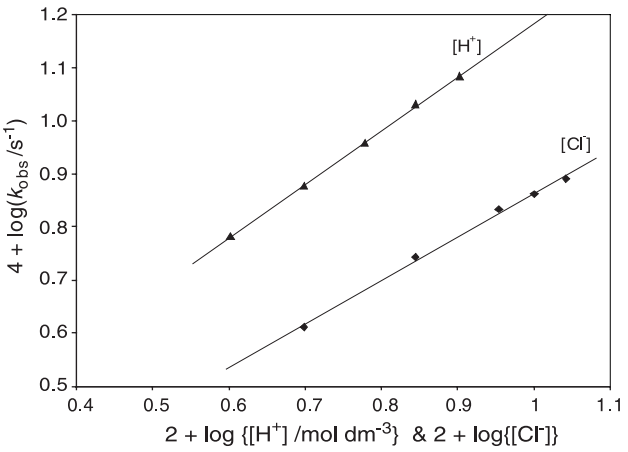


Fig. 2 Plot of $4+\log(k_{obs}/s^{-1})$ *versus* $2+\log\{[H^+]/mol\,dm^{-3}\}$ and $2+\log\{[Cl^-]/mol\,dm^{-3}\}$ at $[CAB]=5\times10^{-4}$, $[THM]=8\times10^{-3}$ and $[Ru(III)]=4\times10^{-4}mol\,dm^{-3}$

[HCl] (Table 1). A plot of $\log k_{obs}$ *versus* log[HCl] was linear ($r=0.997$) with a slope of 1.83. The rate increased with increasing [$RuCl_3$] (Table 2). Plot of $\log k_{obs}$ *versus* log[Ru(III)] (Fig. 1; $r=0.999$) was linear with a slope equal to 1.02, confirming first-order dependence on [Ru(III)].

Effect of varying [H^+] and [Cl^-] on the rate

At constant $[Cl^-]=0.15\,mol\,dm^{-3}$ maintained with NaCl, increase in the concentration of H^+ using HCl increased the rate (Table 2). A plot of $\log k_{obs}$ *versus* log[H^+] was linear (Fig. 2; $r=0.997$) with unit slope indicating first-order dependence on [H^+]. Addition of Cl^- in the form of NaCl keeping [H^+] constant ($0.05\,mol\,dm^{-3}$) increases the reaction rate (Table 2). From a plot of $\log k_{obs}$ *versus* log[Cl^-] (Fig. 2; $r=0.996$), the order with respect to [Cl^-] is found to be 0.82.

Effect of added benzenesulfonamide on the rate

The addition of reduced product, benzenesulfonamide had no effect on the rate, indicating that it is not involved in the pre-equilibrium step prior to the rate-determining step.

Effect of varying ionic strength and relative permittivity of the medium

The reaction rate remained unaffected by varying ionic strength of the medium through addition of sodium perchlorate ($0.2–0.5\,mol\,dm^{-3}$). The dielectric permittivity of the medium was varied by adding different proportions of CH_3CN (0–20%, v/v), but no significant change in the rate was observed when increasing the CH_3CN content in the reaction mixture. The values of relative permittivity were computed from the values of the pure liquids [15].

Effect of temperature on the rate

The reaction was studied at different temperatures (303–321 K) (Table 3), keeping other experimental conditions constant. From the *Arrhenius* plot of $\log k_{obs}$ *versus* $1/T$ ($r=0.998$), activation energy and other thermodynamic parameters were found to be $E_a=95.69\,kJ\cdot mol^{-1}$, $\Delta^{\neq}H^0=93.11\,kJ\cdot mol^{-1}$, and $\Delta^{\neq}S^0=-7.88\,J\cdot K^{-1}\cdot mol^{-1}$.

Table 3 Effect of temperature and solvent composition on the reaction rate $[CAB]_0=5\times10^{-4}\,mol\,dm^{-3}$, $[THM]_0=8\times10^{-3}\,mol\,dm^{-3}$, $[HCl]=0.05\,mol\,dm^{-3}$, $[RuCl_3]=4\times10^{-4}\,mol\,dm^{-3}$, $\mu=0.2\,mol\,dm^{-3}$

Temperature/K	CH_3CN/%, (v/v)	$10^4k_{obs}/s^{-1}$
303	–	2.16
308	–	4.09
313	–	7.30
318	–	13.01
321	–	18.28
308	5	4.01
308	10	3.98
308	15	4.12
308	20	3.96

Test for free radicals

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

Postulated mechanism

Bishop and *Jennings* [16], *Morris et al.* [17], and *Higuchi* and co-workers [18] 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* [19, 20], while the *pH* titration curves observed are similar to those noted by *Morris et al.* [17]. The possible equilibria in acidified *CAB* solutions are,

$$R\mathrm{NClNa} \rightleftharpoons R\mathrm{NCl}^- + \mathrm{Na}^+ \quad (1)$$

$$R\mathrm{NCl}^- + \mathrm{H}^+ \rightleftharpoons R\mathrm{NHCl} \quad (2)$$

$$R\mathrm{NHCl} + \mathrm{H_2O} \rightleftharpoons R\mathrm{NH_2} + \mathrm{HOCl} \quad (3)$$

$$2R\mathrm{NHCl} \rightleftharpoons R\mathrm{NH_2} + R\mathrm{NCl_2} \quad (4)$$

$$\mathrm{HOCl} + \mathrm{H}^+ \rightleftharpoons \mathrm{H_2O^+Cl} \quad (5)$$

where *R* is $C_6H_5SO_2$.

Therefore the possible oxidizing species in acid solution of *CAB* are the free acid (*R*NHCl), $R\mathrm{NCl_2}$, HOCl, and $\mathrm{H_2OCl^+}$. The involvement of $R\mathrm{NCl_2}$ in the mechanism leads to a second-order rate law and negative effect of $R\mathrm{NH_2}$ according to Eq. (4), which is contrary to the experimental observations. If HOCl were the primary oxidizing species, a first-order retardation of the rate by the added $R\mathrm{NH_2}$ would be expected. However, no such effect is noticed. *Hardy* and *Johnston* [21] have determined the *pH* dependent relative concentrations of the species present in acidified bromamine-B solutions of comparable molarities indicating that $C_6H_4SO_2NHBr$ is the likely oxidizing species in acid medium.

Electronic spectral studies by *Cady* and *Connick* [22] and *Connick* and *Fine* [23] have shown that the octahedral complexes such as $[RuCl_5(H_2O)]^{2-}$, $[RuCl_4(H_2O)_2]^-$, $[RuCl_3(H_2O)_3]$, $[RuCl_2(H_2O)_4]^+$, and $[RuCl(H_2O)_5]^{2+}$ do not exist in aqueous solutions of $RuCl_3$, however, other studies [24–26] have shown that the following ligand substitution equilibrium exists in acidic solutions.

$$\mathrm{RuCl_3 \cdot xH_2O + 3HCl \longrightarrow [RuCl_6]^{3-} + xH_2O + 3H^+}$$

$$\mathrm{[RuCl_6]^{3-} + H_2O \rightleftharpoons [RuCl_5(H_2O)]^{2-} + Cl^-} \quad (6)$$

Singh et al. [27, 28] have employed the above equilibrium in the ruthenium(III)-catalyzed oxidation of primary alcohols with bromamine-T and ethylene glycols with *N*-bromocetamide in $HClO_4$ medium. In the present studies, increasing effect of added chloride ion on the rate suggests that $[RuCl_6]^{3-}$ is the more likely catalyzing species [23, 26] which interacts with the oxidants to form a complex intermediate.

Further, UV-spectral measurements showed that a sharp absorption band was noticed at 220 nm for $RuCl_3$, 224 nm for *CAB* solution, and 216 nm for *THM* in presence of 0.5 mol dm^{-3} HCl. A mixture of *CAB* and $RuCl_3$ solution in the presence of HCl showed an absorption band at 268 nm, while for a mixture of *THM* and $RuCl_3$ solution an absorption band was noticed at 214 nm. The spectral evidence showed that complex formation takes place only between $RuCl_3$ and oxidant. Based on the preceding discussion, a detailed mechanistic interpretation (Scheme 1) for the Ru(III)-catalyzed *THM-CAB* reaction in acid medium has been proposed to substantiate the observed kinetics.

From Scheme 1,

$$\mathrm{rate} = k_3[X][Sub] \quad (7)$$

Applying steady state conditions to *X*, then

$$k_2[R\mathrm{NHCl}][\mathrm{Ru(III)}] - k_{-2}[X] - k_3[X][Sub] = 0 \quad (8)$$

From step (i) of Scheme 1,

$$K_1 = \frac{[R\mathrm{NHCl}]}{[R\mathrm{NCl}^-][\mathrm{H}^+]}$$

$$R\mathrm{NCl}^- + \mathrm{H}^+ \overset{K_1}{\rightleftharpoons} R\mathrm{NHCl} \quad \text{fast} \quad \text{(i)}$$

$$R\mathrm{NHCl} + \mathrm{Ru(III)} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} X \quad \text{fast} \quad \text{(ii)}$$

$$X + Sub \xrightarrow{k_3} X' \quad \text{slow and thus r.d.s.} \quad \text{(iii)}$$

$$X' \xrightarrow{k_4} \text{products} \quad \text{fast} \quad \text{(iv)}$$

Scheme 1

substituting in Eq. (8), it can be shown that

$$[X] = \frac{K_1 k_2 [R\mathrm{NCl}^-][\mathrm{H}^+][\mathrm{Ru(III)}]}{k_{-2} + k_3[Sub]} \quad (9)$$

Since the iodometric titre corresponds to both *CAB* and $R\mathrm{NCl}^-$, and *CAB* is consumed in the formation of $R\mathrm{NCl}^-$, it is reasonable to assume that $[R\mathrm{NCl}^-] = [CAB]$, on substituting Eq. (9) in Eq. (7), the following rate law (Eq. (10)) is obtained.

$$\text{rate} = \frac{K_1 k_2 k_3 [CAB][H^+][\mathrm{Ru(III)}][Sub]}{k_{-2} + k_3[Sub]} \quad (10)$$

The rate law (Eq. (10)) is in complete agreement with the experimental results. Since rate $= k_{\mathrm{obs}}[CAB]$, Eq. (10) can be transformed into Eqs. (11) and (12).

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

$$\frac{1}{k_{\mathrm{obs}}} = \frac{k_{-2}}{K_1 k_2 k_3 [Sub][H^+][\mathrm{Ru(III)}]} + \frac{1}{K_1 k_2 [\mathrm{H}^+][\mathrm{Ru(III)}]} \quad (12)$$

Based on Eq. (12), a plot of $1/k_{\mathrm{obs}}$ *versus* $1/[Sub]$ at standard concentrations of $[\mathrm{H}^+]$ and [Ru(III)], was found to be linear (Fig. 3; $r = 0.985$) and the value of K_1k_2 was calculated from the intercept of the plot ($K_1k_2 = 36.1$).

In the presence of chloride ion at constant $[\mathrm{H}^+]$, Scheme 2 is proposed for the reaction mechanism.

From slow step of Scheme 2,

$$\text{rate} = k_7[X][Sub] \quad (13)$$

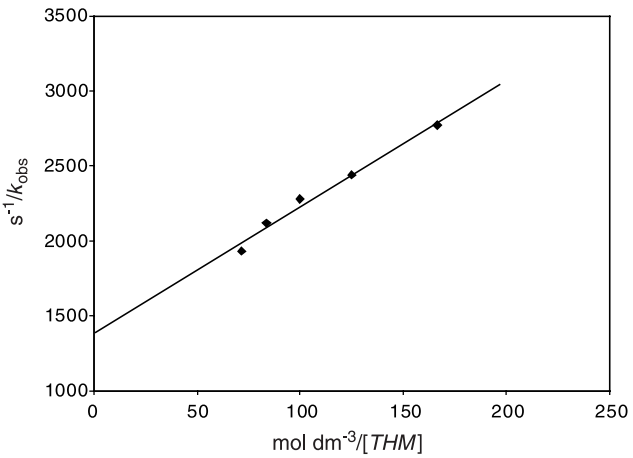


Fig. 3 Plot of s^{-1}/k_{obs} *versus* mol dm^{-3}/[*THM*] at standard concentrations of H^+ and $RuCl_3$

$$[RuCl_5(H_2O)]^{2-} + Cl^- \underset{}{\overset{K_5}{\rightleftharpoons}} [RuCl_6]^{3-} + H_2O \quad \text{fast} \quad \text{(i)}$$
(C_1 → C_2)

$$R\mathrm{NCl}^- + H^+ \overset{K_1}{\rightleftharpoons} R\mathrm{NHCl} \quad \text{fast} \quad \text{(ii)}$$

$$R\mathrm{NHCl} + C_2 \overset{k_6}{\underset{k_{-6}}{\rightleftharpoons}} X \quad \text{fast} \quad \text{(iii)}$$

$$X + Sub \xrightarrow{k_7} X' \quad \text{slow and thus r.d.s.} \quad \text{(iv)}$$

$$X' \xrightarrow{k_8} \text{products} \quad \text{fast} \quad \text{(v)}$$

Scheme 2

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

$$[X] = \frac{K_1 k_6 [R\mathrm{NCl}^-][\mathrm{H}^+[\mathrm{C}_2]}{k_{-6} + k_7[Sub]} \quad (14)$$

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

$$[\mathrm{Ru(III)}]_t = [C_1] + [C_2] \quad (15)$$

By substituting for $[C_1]$ from equilibrium step (i) of Scheme 2 in Eq. (15), one obtains

$$[\mathrm{Ru(III)}]_t = \frac{[C_2][\mathrm{H_2O}]}{K_5[\mathrm{Cl}^-]} + [C_2]$$

or

$$[C_2] = \frac{K_5[\mathrm{Ru(III)}]_t[\mathrm{Cl}^-]}{[\mathrm{H_2O}] + K_5[\mathrm{Cl}^-]} \quad (16)$$

By substituting Eq. (16) in Eq. (14), Eq. (17) is obtained.

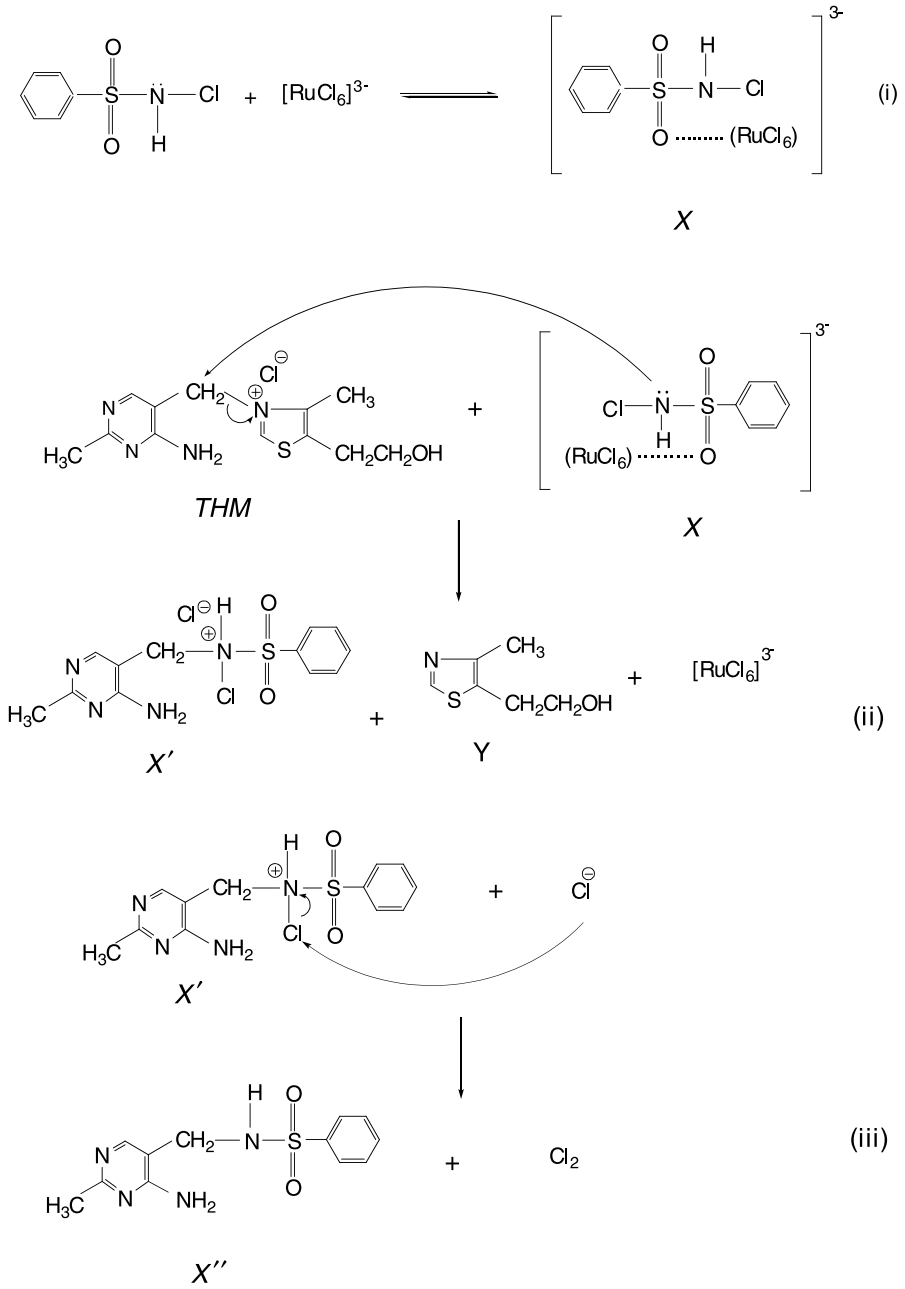
$$[X] = \frac{K_1 K_5 k_6 [R\mathrm{NCl}^-][\mathrm{H}^+][\mathrm{Ru(III)}]_t[\mathrm{Cl}^-]}{\{k_{-6} + k_7[Sub]\}\{[\mathrm{H_2O}] + K_5[\mathrm{Cl}^-]\}} \quad (17)$$

By substituting Eq. (17) in Eq. (13), the following rate law is obtained.

$$\text{rate} = \frac{K_1 K_5 k_6 k_7 [CAB][\mathrm{H}^+][\mathrm{Ru(III)}]_t[\mathrm{Cl}^-][Sub]}{\{k_{-6} + k_7[Sub]\}\{[\mathrm{H_2O}] + K_5[\mathrm{Cl}^-]\}} \quad (18)$$

The rate expression (Eq. (18)) clearly demonstrates the fractional-order dependence of rate on $[\mathrm{Cl}^-]$ and [*Sub*], and is in good agreement with the experimental results.

In Schemes 1 and 2, *Sub* represents the substrate, *X* and *X*′ represent the complex intermediate species whose structures are shown in Scheme 3, where a detailed mechanism of Ru(III)-catalyzed oxidation of *THM* with *CAB* in HCl medium is illustrated. An initial equilibrium involves protonation of $R\mathrm{NCl}^-$ forming an active oxidizing species of *CAB*



Scheme 3

(*R*NHCl). In the next step, the oxygen atom of the oxidant is coordinated to the metal center of the active catalyst species, $[RuCl_6]^{3-}$ to form a loosely bound metal complex, *X* (step (i) in Scheme 3) 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 nucleophilic attack of the sulfonamide nitrogen on the methylene group of thiamine to form intermediate *X′*, *Y* and releasing $[RuCl_6]^{3-}$ (step (ii) of Scheme 3). Then reorganization of the intermediate (*X′*) to form products with the release of chlorine.

Laidler [29] and *Amis* [30] have described the effect of solvent composition on the reaction kinetics. For limiting case of zero angle of approach between two dipoles or an ion-dipole system, *Amis* [30] has shown that a plot of $\log k_{obs}$ *versus* $1/D$

gives a straight line with a positive slope for a reaction involving a positive ion and a dipole and a negative slope for a negative ion-dipole or dipole–dipole interactions. In the present investigations, variation of dielectric permittivity of the medium does not affect the rate supports the proposed mechanisms. The reduction product of the oxidant, benzenesulfonamide did not influence the rate showing that it is not involved in any pre-equilibrium. The proposed mechanism is also supported by the values of energy of activation and other activation 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 high negative value of entropy of activation accounts for the formation of a compact transition state in which several degrees of freedom are lost.

Conclusions

Oxidative cleavage of vitamin B_1 with chloramine-B in hydrochloric acid medium using a $RuCl_3$ catalyst has been studied. The stoichiometry of the reaction was found to be 1:1 and the oxidation products of *THM* were identified by spectral studies. Oxidation of *THM* with *CAB* in acid medium will become facile in presence of micro-quantities of ruthenium(III) catalyst. $C_6H_5SO_2NHCl$ was found to be the reactive oxidizing species. Activation parameters were computed from the *Arrhenius* plot. The observed results have been explained by plausible mechanisms and the related rate laws have been deduced.

Experimental

Materials

Chloramine-B was prepared and purified by the method described earlier [31]. An aqueous solution of the compound was standardized iodometrically and preserved in brown bottles to prevent its photochemical deterioration. Vitamin B_1 (Himedia) was used as received. An aqueous solution of the compound was prepared freshly each time. A solution of $RuCl_3$ (Arora Mathey) in a solution of hydrochloric acid was used as catalyst. The final concentrations of HCl and $RuCl_3$ were 1.0×10^{-2} and 8.86×10^{-3} mol dm^{-3}. Allowance was made for the amount of HCl present in catalyst solution while preparing for kinetic runs. All other chemicals used were of accepted grades of purity. 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.

Kinetic measurements

Mixtures containing requisite amounts of the *THM*, $RuCl_3$, HCl, and $NaClO_4$ were taken in stoppered Pyrex glass tubes whose outer surfaces were coated black. Required amount of water was added to maintain a constant total volume. The tube was thermostated in a water bath 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. Under pseudo-first-order conditions, rate constants k'_{obs} were reproducible within $\pm 3\%$. Regression analysis of the experimental data to obtain regression coefficient, *r*, was performed using MS Excel.

Stoichiometry and product analysis

Reaction mixtures containing various ratios of *THM* and *CAB* were equilibrated in the presence of 0.05 mol dm^{-3} HCl and 5×10^{-4} mol dm^{-3} $RuCl_3$ catalysts at 308 K for 48 h. Iodometric estimation of unconsumed *CAB* in the mixture revealed that one mole of *CAB* was consumed per mole of *THM*. Accordingly, the following stoichiometric equation can be formulated,

$$C_{12}H_{17}N_4ClOS + RNClNa + HCl \longrightarrow C_{12}H_{14}N_4SO_2 + C_6H_9NSO + NaCl + Cl_2 \quad (19)$$

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 the column chromatography on silica gel (60–200 mesh) using gradient elusion (chloroform). After initial separation, the products were further purified by recrystallization. The oxidation products of *THM* were detected by conventional spot tests [32], and identified as *N*-[(4-amino-2-methylpyrimidine-5-yl)methyl] benzensulfonamide (*X″*) and 2-(4-methylthiazol-5-yl)-ethanol (*Y*) by ^{1}H NMR spectral studies. *X″* (D_2O): $\delta = 2.3$ (s, 3H, CH_3), 7.7 (s, H, *Ar*–H), 7.5–8.0 (bm, 5H, *Ar*–H), 3.8 (s, 2H, NH_2) ppm; *Y* ($CDCl_3$): $\delta = 2.5$ (s, 3H, CH_3), 3.9 (t, 2H, CH_2), 2.8 (t, 2H, CH_2), 8.5 (s, H, *Ar*–H). ^{1}H NMR spectra were recorded on a BRUKER 400 MHz spectrometer using $D_2O/CDCl_3$ as solvent and *TMS* as internal reference.

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References

1. Dougherty HW, Pollak PI (1970) Medicinal Chemistry, 3rd edn. Wiley-Interscience, New York, Ch 30
2. Waldenlind I (1978) Acta Physiol Scand 1:459
3. Marcus R, Coulsfon AM (1991) The Pharmacological Basis of Therapeutics, 8th edn. Pergamon press, New York, Ch 63

4. Campbell MM, Johnson G (1978) Chem Rev 78:65
5. Banerji KK, Jayaram B, Mahadevappa DS (1987) J Sci Ind Res 46:65
6. Bremner DH (1986) Synthetic Reagents 6:9
7. Revathi SK, Ananda S, Mohana KN, Rangaswamy (2004) Collect Czech Chem Commun 69:1577
8. Mahadevappa DS, Sayeed Ahmed M, Madegowda NM (1983) Int J Chem Kinet 15:775
9. Mohana KN, Rangaswamy, Lokanatha Rai KM (2005) Oxid Commun 28:394
10. Usha BN, Rangaswamy, Yathirajan HS (1984) J Indian Chem Soc 61:812
11. Raju CR, Mohana KN, Yathirajan HS, Rangappa KS (2001) Indian J Chem 40A:613
12. Garger G, Barger F, Todd AR (1935) Nature 136:259
13. Jaroensanti J, Panijan B (1981) Experientia 37:1248
14. Kawasaki C, Horio TJ (1954) Pharm Soc Jpn 74:904
15. Lide DR (1992) CRC Hand Book of Chemistry and Physics, 73rd edn. CRC Press, London, p 8
16. Bishop E, Jennings VJ (1958) Talanta 1:197
17. Morris JC, Salazar JR, Winemann MA (1948) J Am Chem Soc 70:2036
18. Higuchi T, Ikeda K, Hussain A (1967) J Chem Soc (B): 546
19. Mahadevappa DS, Rangaswamy (1977) Rev Roumaine de Chimie 22:1233
20. Rangaswamy, Mahadevappa DS (1976) Indian J Chem 14A:463
21. Hardy FF, Johnston JP (1973) J Chem Soc Perkin Trans 2:742
22. Cady HH, Connick RE (1958) J Am Chem Soc 80:2646
23. Connick RE, Fine DA (1960) J Am Chem Soc 82:4187
24. Davfokratova T (1963) Analytical Chemistry of Ruthenium. Academy of Sciences, USSR, pp 54, 71 and 97
25. Backhours JR, Dwyer FD, Shales N (1950) Proc Roy Soc 53:146
26. Griffith WP (1967) The Chemistry of Rare Platinum metals. Interscience, New York, p 4
27. Singh B, Singh NB, Saxena BBL (1984) J Indian Chem Soc 61:319
28. Singh B, Singh DK, Singh D (1988) J Mol Cat 78:207
29. Laidler KJ (1963) Reaction Kinetics. Pergaman, New York
30. Amis ES (1966) Solvent Effects on Reaction Rates and Mechanisms. Academic Press, New York
31. Yathirajan HS, Rangaswamy, Mahadevappa DS (1982) Collect Czech Chem Commun 47:1826
32. Feigl F (1966) Spot Tests in Organic Analysis. Elsevier, Amsterdam, New York, p 244