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Ruthenium(III) mediated Oxidation of Tripelennamine hydrochloride by Cerium(IV) in Aqueous Sulfuric Acid Medium: A Kinetic and Mechanistic Approach

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Abstract

The micro amounts (10^{-5} mol dm^{-3}) of ruthenium(III) mediated oxidation of tripelennamine hydrochloride by cerium(IV) in aqueous sulfuric acid medium is studied spectrophotometrically at 25°C and at I = 0.16 mol dm^{-3}. The observed stoichiometry is 1:2, [TPA]: [Ce(IV)]. The oxidation products were identified by spot test and TLC techniques and characterized by IR and GC-MS spectra. The reaction showed first order kinetics in cerium(IV), ruthenium(III) concentration and an apparent less than unit order dependence in tripelennamine hydrochloride concentration. Increase in sulphuric acid concentration decrease the rate of reaction. The active species of oxidant and catalyst are $Ce(OH)^{3+}$ and $[Ru(H_2O)_6]^{3+}$ respectively. Based on experimental results a possible mechanism is proposed and suitable rate law is derived. The reaction constants involved in the mechanism are calculated by using these constants, theoretical rate constants are calculated and are in good agreement with experimental values under different experimental conditions. The activation parameters are also calculated with respect to the slow step of the proposed mechanism.

1. Introduction

Tripelennamine hydrochloride is a psychoactive drug, and member of the pyridine and ethylenediamine classes. It is used as an antipruritic and first-generation antihistamine. It is also used in the treatment of asthma, hay fever, rhinitus and urticaria. Tripelennamine acts primarily as an antihistamine, or H^1 receptor antagonist. In addition to its antihistamine properties, tripelennamine also acts as a weak serotonin reuptake inhibitor (SRI) and dopamine reuptake inhibitor (DRI) [1-4]. Additionally, due to its DRI properties, it is occasionally abused as a recreational drug.

Cerium(IV) is a well known oxidant in acid media [5], having the reduction potential 1.70V of the couple Ce(IV)/Ce(III) [6]. Cerium(IV) is stable only in high acid concentration. The oxidation of organic compounds by cerium(IV) usually proceeds via an intermediate complex [7,8]. In sulphuric acid- sulphate media, cerium(IV) forms several sulphate complexes [9].

Ruthenium(III) acts as an efficient catalyst in the oxidations of many organic and inorganic substrates [10,11], although the mechanism of the catalysis depends on the nature of the substrate, oxidant and experimental conditions. It was shown that metal ions act as catalysts by one of several paths, such as the formation of complexes with reactants, oxidation of the substrate itself or through the formation of free radicals. Ruthenium(III) catalysis in redox reactions involves different degrees of complexity, due to the formation of different intermediate complexes and the different oxidation states of ruthenium.

The oxidation of tripelennamine by cerium(IV) in sulfuric acid medium is very slow. To the best of our knowledge there are no reports on the ruthenium(III) mediated oxidation of tripelennamine by cerium(IV). A micro amount (10^{-5} mol dm^{-3}) of ruthenium(III) is sufficient for this purpose. Such studies are of significance in understanding the mechanistic profile of tripelennamine in redox reactions and provide an insight into the interaction of metal ions. To compute the activity of the catalyst and the complexity of the reaction, a detailed study of the title reaction becomes important. Hence, the present investigation in this work explores the reactivity of tripelennamine towards cerium(IV) in the presence of ruthenium(III) catalyst, and to arrive at a plausible mechanism on the basis of kinetic and spectral results.

2. Material and Methods

2.1. Plant material

The used chemicals were of reagent grade and double distilled water was used throughout the experiment. A stock solution of tripelennamine was prepared by dissolving the appropriate amount of tripelennamine hydrochloride in double distilled water. The cerium(IV) solution was prepared by dissolving ceric ammonium sulphate (Trizma chemicals Co., India) in double distilled water in the presence of 1.0 mol dm^{-3} H_2SO_4. It was standardized by a known method [12]. The cerium(III) solution was prepared by dissolving cerium(III) sulphate (Trizma chemicals Co., India) in double distilled water. H_2SO_4 and Na_2SO_4 were used to provide the required acidity and ionic strength respectively.

2.2. Kinetic measurements

The kinetic measurements were performed under pseudo-first order condition with tripelennamine, in at least 10-fold excess over cerium(IV) concentration at a constant ionic strength and acidity. The reaction was initiated by mixing previously thermostatted solutions of cerium(IV) and tripelennamin which also contained the necessary quantities of catalyst, Ru(III), H_2SO_4 and Na_2SO_4 at 25 ± 0.1°C. The course of reaction was followed by monitoring the decrease in absorbance of cerium(IV) in a 1 cm quartz cell placed in the thermostatted compartment of a Varian carry 50 Bio UV–Vis spectrophotometer, at its absorption maximum of 360nm, as a function of time. Application of Beer's law under reaction conditions was verified between 1.0×10^{-4} and 1.0×10^{-3} moldm^{-3} of cerium(IV) at 360 nm. The molar extinction coefficient of cerium(IV) at 360 nm was found to be $\varepsilon = 3{,}500 \pm 40$ dm^{3}mol^{-1}cm^{-1}.

During the kinetic studies it was observed that under the present experimental conditions in the absence of catalyst ruthenium(III), the oxidation of tripelennamine by cerium(IV) occurs very slowly, but in a measurable quantity. Hence, during the calculation of pseudo-first order rate constants, k_C, in the presence of catalyst, the uncatalyzed rate was also been taken into account. Therefore, in each ruthenium(III) catalyzed kinetic run, a parallel kinetic run under similar conditions in the absence of ruthenium(III) was also carried out. In both cases the pseudo-first order rate constants (k_U and k_C) were obtained from the plots of log(absorbance) versus time. The pseudo-first order plots were linear over 70% completion of the reaction. Thus, the total rate constant (k_T) is equal to the sum of the rate constants in the absence (k_U) and in the presence (k_C) of catalyst, i.e.,

$$k_T = k_C + k_U$$

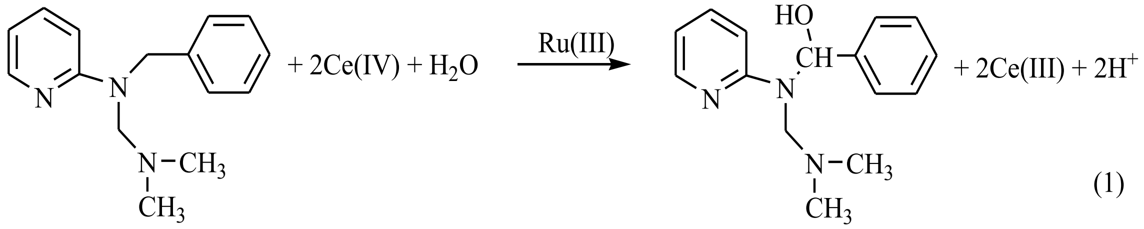
Therefore
$$k_C = k_T - k_U$$

The k_C values were reproducible to within±5% and are the average of at least three independent kinetic runs (Table 1).

3. Results and discussion

3.1. Stoichiometry and analysis of reaction products

The reaction mixture containing the excess cerium (IV) concentration over tripelennamine concentration was mixed in the presence of constant H_2SO_4, catalyst ruthenium(III) concentration and ionic strength. The reaction mixture was allowed to react for half day at 25°C. The remaining unreacted cerium(IV) concentration was analyzed spectrophotometrically at 360nm. By these results an one mole of TPA requires two moles of cerium(IV) according to Equation (1).



(1)

The reaction products were eluted with solvent ether and organic products were submitted to spot test [13] and chromatographic analysis (TLC) [14], which revealed the presence of (N-((dimethylamino) methyl)-N-(pyridine-2-yl)amino)(phenyl)methanol. The observed product was characterized by FTIR and GC-MS spectra. **FT-IR** - The IR spectrum displayed the peaks at 2958 cm^{-1}, 1620 cm^{-1} and 1284 cm^{-1} indicates the alcoholic –OH stretching, -NH and -CN stretching respectively (Figure 1).

GC-MS-The mass spectrum showed a base peak at 44 amu and molecular ion peak at 257amu confirming (N-((dimethylamino)methyl)-N-(pyridine-2-yl)amino)(phenyl)methanol (Figure 2) cerium(III) was recorded in UV spectrum and it had three λ_{max} and most pronounced peak at λ_{max} 252 nm.

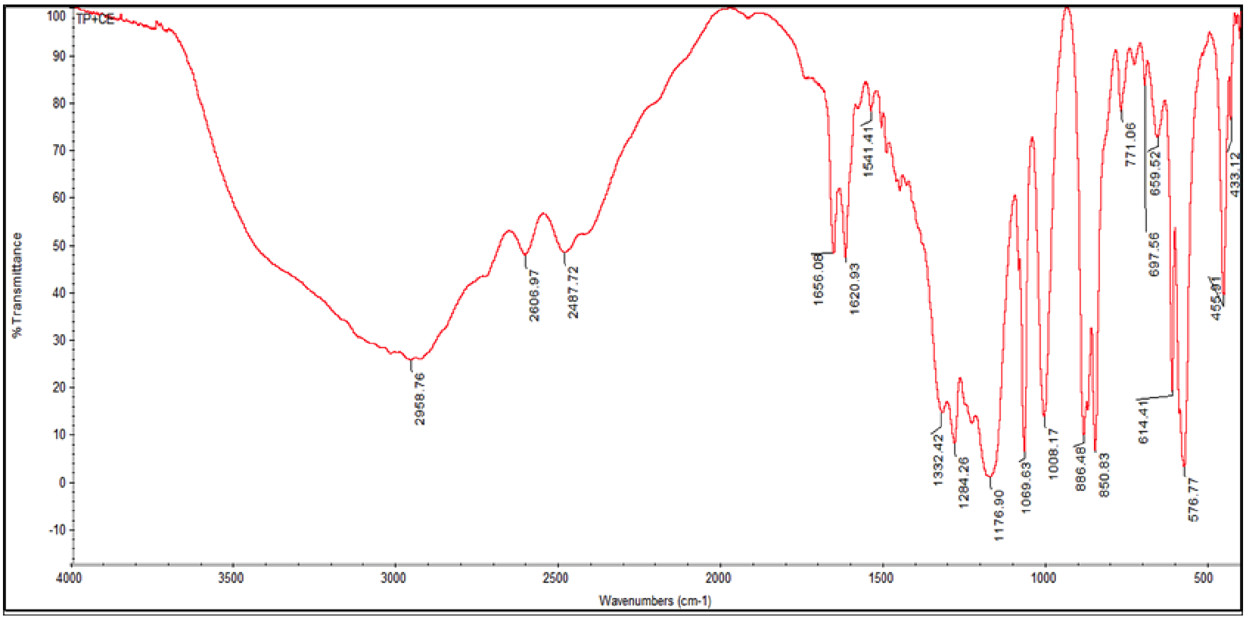


Figure 1: FT-IR spectra of oxidation product, (N-((dimethylamino)methyl)-N-(pyridine-2-yl)amino)(phenyl)methanol.

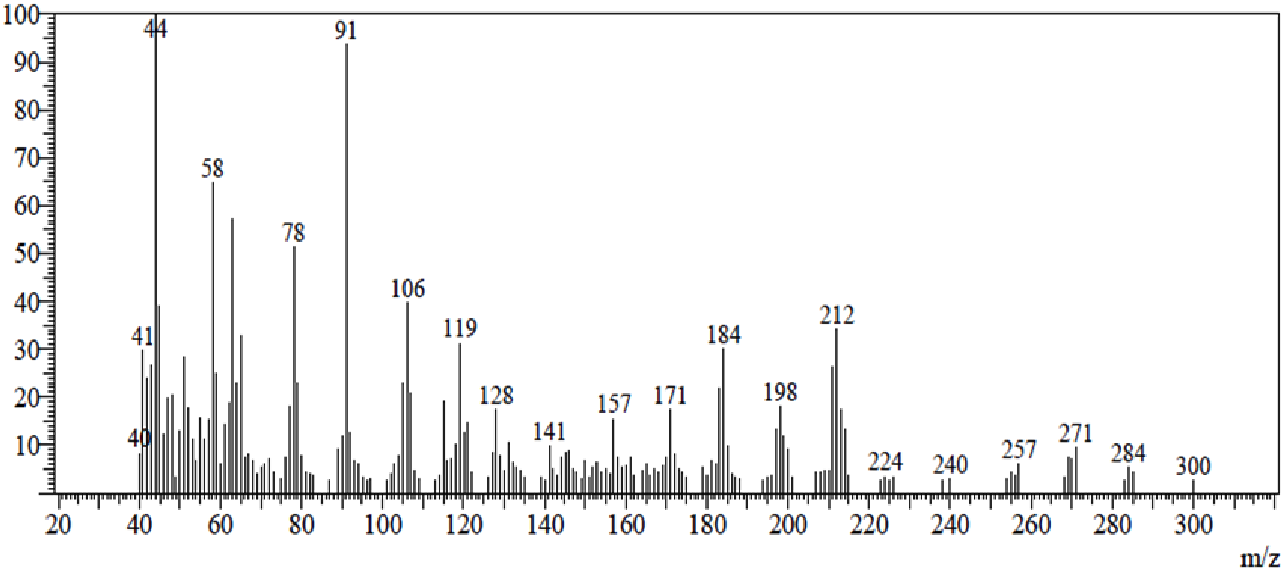


Figure 2: GC-MS spectra of the product (N-((dimethylamino) methyl)-N-(pyridine-2-yl)amino)(phenyl)methanol showed molecular ion peak at m/z 257.

3.2. Reaction orders

The reaction orders were determined from the slopes of logk_C versus log(concentration) plots by varying the concentrations of tripelennamine, acid and catalyst in turn while keeping all other concentrations and conditions constant.

3.3. Effect of cerium(IV) concentration

At constant concentration of tripelennamine, acid, catalyst ruthenium(III) and at constant ionic strength, I = 0.16 mol dm^{-3}, the cerium(IV) concentration was varied from 0.50 × 10^{-4} to 5.0 × 10^{-4} mol dm^{-3}. The calculated k_C values are almost constant (Table 1) which indicates unit order with respect to cerium(IV) concentration. The plots of log [Ce(IV)] versus time are straight line for more than 70% completion of the reaction which also indicates unit order in cerium(IV) concentration.

3.4. Effect of tripelennamine concentration

The tripelennamine concentration was varied in the concentration range of 1.0 × 10^{-3} mol dm^{-3} to 1.0 × 10^{-2} mol dm^{-3} at 25˚C, keeping all other concentration and conditions constant. The rate constant, k_C, increased with increase in the concentration of tripelennamine (Table 1). From the slope of the plot of log k_C versus log[TPA], the order with respect to tripelennamine concentration was found to be less than unity (0.82).

3.5. Effect of ruthenium(III) concentration

At constant, oxidant, 2.0 × 10^{-4} mol dm^{-3}, reductant, 5.0 × 10^{-3} mol dm^{-3}, and acid, 4.0×10^{-2} mol dm^{-3}, concentrations and at I = 0.16 mol dm^{-3}, the catalyst, ruthenium(III) concentration was varied between 4.0 × 10^{-6} and 4.0 × 10^{-5} mol dm^{-3}. As the catalyst concentration increases the rate of reaction also increases (Table 1). The order with respect to ruthenium(III) concentration was found to be unity (Figure 3).

Table 1: Effect of variation of cerium(IV), tripelennamine and ruthenium(III) concentrations on the ruthenium(III)-mediated oxidation of tripelennamine by cerium(IV) in aqueous sulfuric acid medium at 25˚C

$[H^+]=4.0\times10^{-2}$ mol dm^{-3} I = 0.160 moldm^{-3}

$[Ce(IV)]\times10^4$ (mol dm^{-3})	$[TPA] \times 10^3$ (mol dm^{-3})	$[Ru(III)]\times10^5$ (mol dm^{-3})	$k_T \times 10^2$ (s^{-1})	$k_U \times 10^3$ (s^{-1})	$k_C \times 10^3$ Exptl(s^{-1})	$k_C \times 10^3$ Calc(s^{-1})
0.50	5.0	1.0	1.08	2.24	8.56	8.62
1.0	5.0	1.0	1.08	2.32	8.48	8.51
2.0	5.0	1.0	1.07	2.44	8.26	8.16
3.0	5.0	1.0	1.06	2.38	8.22	8.26
4.0	5.0	1.0	1.07	2.26	8.44	8.48
5.0	5.0	1.0	1.05	2.34	8.16	8.19
2.0	1.0	1.0	0.25	0.70	1.87	1.87
2.0	2.0	1.0	0.51	1.11	4.07	4.07
2.0	3.0	1.0	0.67	1.72	5.07	5.07
2.0	5.0	1.0	1.07	2.44	8.26	8.16
2.0	7.0	1.0	1.29	2.99	9.99	9.99
2.0	10.0	1.0	1.62	3.37	12.84	12.84
2.0	5.0	0.0	---	2.44	---	---
2.0	5.0	0.4	0.46	2.44	2.2	3.51
2.0	5.0	0.6	0.64	2.44	4.0	5.61
2.0	5.0	0.8	0.85	2.44	6.1	6.89
2.0	5.0	1.0	1.07	2.44	8.26	8.16
2.0	5.0	2.0	1.99	2.44	17.5	16.90
2.0	5.0	4.0	3.99	2.44	37.5	32.92

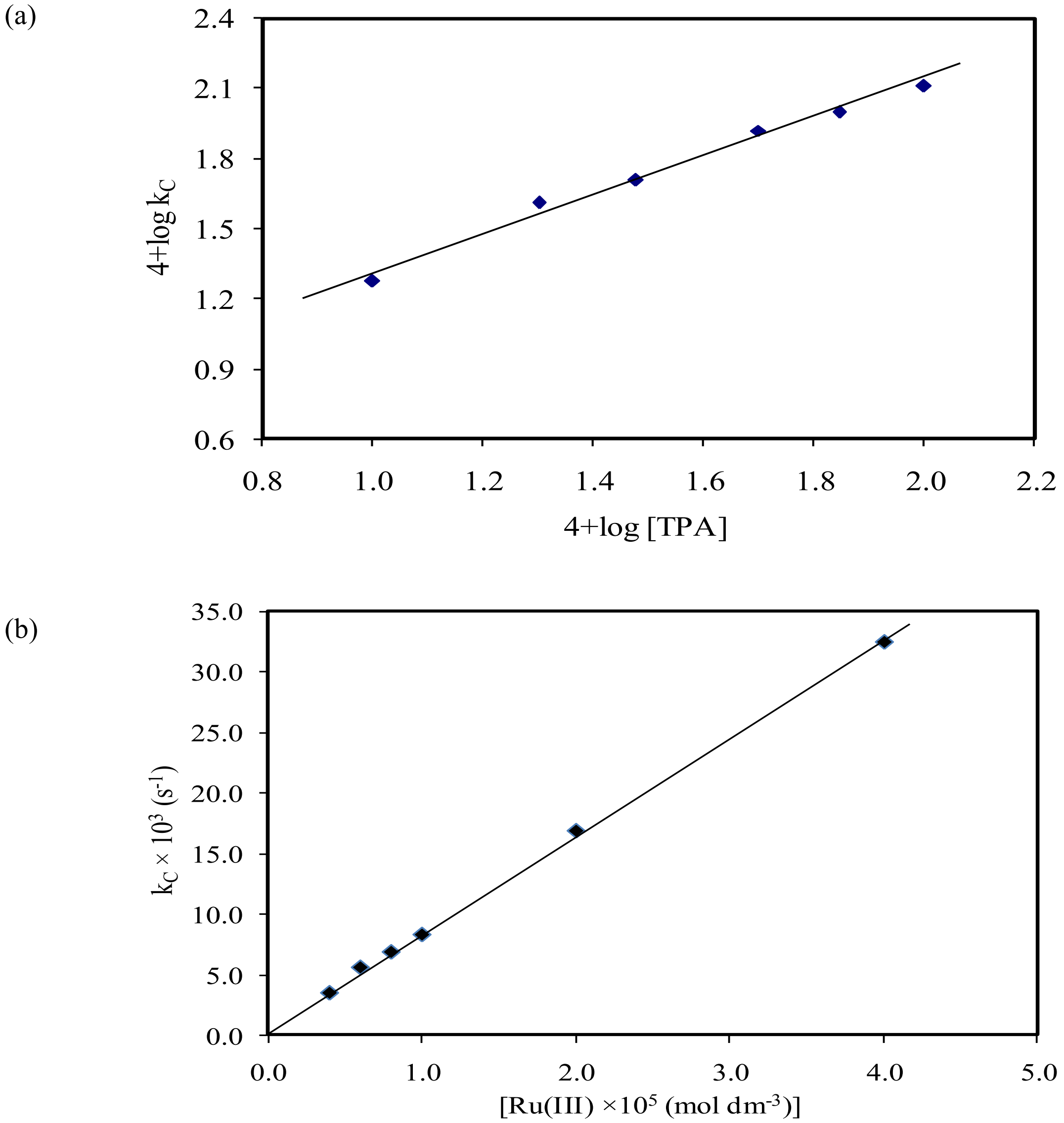


Figure 3: Order with respect to (a) tripelennamine concentration; (b) ruthenium(III) concentration on ruthenium(III) mediated oxidation of tripelennamine by cerium(IV) in aqueous sulfuric acid medium at 25˚C (Conditions as in Table (i))

3.6. Effect of sulphuric acid concentration

The effect of sulphuric acid on the reaction was studied at constant concentrations of cerium(IV), tripelennamine, catalyst, ruthenium(III) and at constant ionic strength in the concentration range 1.0×10^{-2} – 5.0×10^{-2} and it was found that rate decreases with increase in the sulphuric acid concentration (Table 2). The in situ $[H^+]$ concentration in the sulphuric acid–sulphate media was calculated using the known ionization constant [15] of acid sulphate as in an earlier study [16]. An example calculation of $[H^+]$ in case of 0.04 mol dm^{-3} added $H_2SO_4^-$ is given below. From the knowledge of the added acidity and at constant amount of sulphate, the concentration of HSO_4^- was calculated from the quadratic equation. Thus in case of 0.04mol dm^{-3} H_2SO_4 and 0.06 mol dm^{-3} added sulphate to maintain the constant ionic strength.

$$\underset{(a-x)}{H^+} \quad + \quad \underset{(b-x)}{SO_4^{2-}} \quad \rightleftharpoons \quad \underset{x}{HSO_4^-} \qquad K = \frac{[HSO_4^-]}{[H^+][SO_4^{2-}]}$$

where ‘a’ and ‘b’ are the concentrations of acid, (0.04 + 0.04) = 0.08 mol dm^{-3} and sulphate, (0.04 + 0.06) = 0.1 mol dm^{-3} respectively and ‘x’ that of bisulphate,

Therefore,

$$8.3 = \frac{x}{(a-x)(b-x)} \qquad \text{or} \qquad 8.3x^2 - 2.494x + 0.0664 = 0$$

and

$$[\mathrm{HSO_4^-}] = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$
$$= 0.2709 \text{ or } 0.0295$$

Thus,

$$[H^+] = (a - x) = (0.08 - 0.0295) = 0.0504$$
$$[SO_4^{2-}] = (b - x) = (0.10 - 0.0295) = 0.0704$$

Similarly, other $[H^+]$ were calculated and are given in Table 2. The order in $[H^+]$ was inverse less than unity, as found from a plot of log k_C versus log $[H^+]$ (Figure 4). Cerium(IV) is known to form [17] several complexes in acid sulphate media, namely $Ce(OH)^{3+}$, $Ce(SO_4)^{2+}$, $Ce(SO_4)_2$, $Ce(SO_4)_2(HSO_4^-)$ and $H_3Ce(SO_4)_4^-$ as shown in equilibria (2) to (6):

$$Ce^{4+} + H_2O \overset{K_{OH}}{\rightleftharpoons} Ce(OH)^{3+} + H^+ \qquad (2)$$

$$Ce^{4+} + SO_4^{2-} \overset{K_1}{\rightleftharpoons} Ce(SO_4)^{2+} \qquad (3)$$

$$Ce(SO_4)^{2+} + SO_4^{2-} \overset{K_2}{\rightleftharpoons} Ce(SO_4)_2 \qquad (4)$$

$$Ce(SO_4)_2 + HSO_4^- \overset{K_3}{\rightleftharpoons} Ce(SO_4)_2\,HSO_4^- \qquad (5)$$

$$Ce(SO_4)_2\,HSO_4^- + HSO_4^- + H^+ \overset{K_4}{\rightleftharpoons} H_3Ce(SO_4)_4^- \qquad (6)$$

The concentration of cerium(IV) species vary with acidity. The formation of $Ce(OH)_2^{2+}$ occurs to a much lesser extent in comparison with the others and is therefore neglected. The total cerium(IV) concentration is the sum of different cerium(IV) species concentrations, $[Ce^{4+}]$, $[Ce(OH)^{3+}]$, $Ce(SO)_2^{4+}$, $[Ce(SO_4)_2]$, $[Ce(SO_4)_2HSO_4^-]$ and $[H_3Ce(SO_4)_4^-]$, the complexes having the cumulative equilibrium constants, K_{OH}, β_1, β_2, β_3, and β_4 as shown in equation 7:

$$[Ce^{4+}]_t = [Ce^{4+}]_f\left\{1 + \frac{K_{OH}}{[H^+]} + \beta_1[SO_4^{2-}] + \beta_2[SO_4^{2-}]^2 + \beta_3[SO_4^{2-}]^2[HSO_4^-] + \beta_4[SO_4^{2-}]^2[HSO_4^-]^2[H^+]\right\} \qquad (7)$$

where $K_{OH} = 15$, $\beta_1 = K_1 = 3.85 \times 10^2$, $\beta_2 = K_1K_2 = 1.69 \times 10^2$, $\beta_3 = K_1K_2K_3 = 1.01 \times 10^2$ and $\beta_4 = K_1K_2K_3K_4 = 2.03 \times 10^2$. The approximate concentrations of cerium sulphate complexes can be calculated from the know concentrations of dissolved Ce^{4+}, H^+, HSO_4^-, and SO_4^{2-} from the equilibria and their constants [18].

A sample calculation of different cerium(IV) species in 0.04 mol dm^{-3} sulphuric acid is given below:

$[H^+] = 0.0504$ mol dm^{-3}; $[SO_4^{2-}] = 0.0704$ mol dm^{-3}

$[Ce(IV)]_t = 2.0\times10^{-4}$

$$= [Ce^{4+}]_f\left\{1 + \frac{15}{0.0504} + 384.6\times(0.0704) + 169.49(0.0704)^2 + 101.17(0.0704)^2(0.0295) + 203.4(0.0704)^2(0.0295)^2(0.0504)\right\}$$

$$= [Ce^{4+}]_f\{1 + 297.17 + 27.106 + 0.8418 + 0.01483 + 0.0000444\}$$

$$[Ce^{4+}]_t = [Ce^{4+}]_f\times326.138$$

$$[Ce^{4+}]_f = \frac{2.0\times10^{-4}}{326.138} = 6.1323\times10^{-7}$$

$$\alpha_0 = \frac{6.1323\times10^{-7}}{2.0\times10^{-4}} = 3.066\times10^{-3}$$

Similarly,

$$[\mathrm{Ce(OH)}^{3+}] = 297.176\times6.1323\times^{-7} = 1.82\times10^{-4}$$

$$\alpha_{\mathrm{OH}} = \frac{0.000182}{2.0\times10^{-4}} = 0.911$$

$$[\mathrm{Ce(SO_4)}^{2+}] = 27.106\times6.1323\times10^{-7} = 1.66\times10^{-5}$$

$$\alpha_1 = \frac{0.0000166}{2.0\times10^{-4}} = 8.31\times10^{-2}$$

$$[\mathrm{Ce(SO_4)_2}] = 0.84181\times6.1323\times10^{-7} = 5.162\times^{-7}$$

$$\alpha_2 = \frac{5.162\times10^{-7}}{2.0\times10^{-4}} = 2.58\times10^{-3}$$

$$[\mathrm{HCe(SO_4)_3^-}] = 0.01483\times6.1323\times10^{-7} = 9.097\times10^{-9}$$

$$\alpha_3 = \frac{9.097\times10^{-9}}{2.0\times10^{-4}} = 4.55\times10^{-5}$$

$$[\mathrm{H_3Ce(SO_4)_4^-}] = 0.00004445\times6.1323\times10^{-7} = 2.725\times10^{-11}$$

$$\alpha_4 = \frac{2.725\times10^{-11}}{2.0\times10^{-4}} = 1.36\times10^{-7}$$

where α_0, α_{OH}, α_1, α_2, α_3 and α_4 are the fraction of total cerium(IV) of the species Ce^{4+}, $Ce(OH)^{3+}$, $Ce(SO_4)_2^+$, $Ce(SO_4)_2$, $Ce(SO_4)_2HSO_4^-$ and $H_3Ce(SO_4)_4^-$ respectively. In the same way the calculations were made for other $[H^+]$ and the results are given in Table 2. The results of such calculations are utilized to draw the Figure 5 and it is seen that, of the concentrations of different species, the variation of only $Ce(OH)^{3+}$ with H^+ ion concentration showed parallelism with the variation of rate with H^+ ion concentration (Table 2). Hence, we conclude that $Ce(OH)^{3+}$ is the active species in the present experimental condition.

Table 2: Variation of different cerium(IV) species with H^+ ion concentration on ruthenium(III) mediated oxidation of tripelennamine by cerium(IV) in aqueous sulfuric acid medium at 25°C

$[H_2SO_4]$ mol dm^{-3}	$[H^+]$ mol dm^{-3}	$[SO_4^{2-}]$ mol dm^{-3}	$\alpha_o\times10^3$	$\alpha_{OH}\times10$	$\alpha_1\times10^2$	$\alpha_2\times10^3$	$\alpha_3\times10^6$	$\alpha_4\times10^8$	$k_U\times10^3$ (s^{-1})	$k_T\times10^2$ (s^{-1})	$k_C\times10^3$ Exp (s^{-1})	$k_C\times10^3$ Calc (s^{-1})
0.01	0.012	0.077	0.79	9.74	2.35	0.80	3.72	0.071	3.57	1.67	13.27	12.65
0.02	0.024	0.074	1.56	9.51	4.50	1.48	13.5	1.03	3.12	1.45	11.49	10.69
0.03	0.037	0.072	2.32	9.30	6.47	2.06	27.8	4.72	2.76	1.20	9.26	9.25
0.04	0.050	0.070	3.06	9.11	8.31	2.58	45.4	13.62	2.44	1.07	8.26	8.16
0.05	0.063	0.068	3.79	8.92	10.0	3.03	65.7	30.60	2.18	0.99	7.79	7.30

α_0, α_{OH}, α_1, α_2, α_3 and α_4 are the fractions of the total cerium(IV) species, Ce_f^{4+}, $Ce(OH)^{3+}$, $Ce(SO_4)^{2+}$, $Ce(SO_4)_2$, $HCe(SO_4)_3^-$, and $H_3Ce(SO_4)_4^-$ respectively.

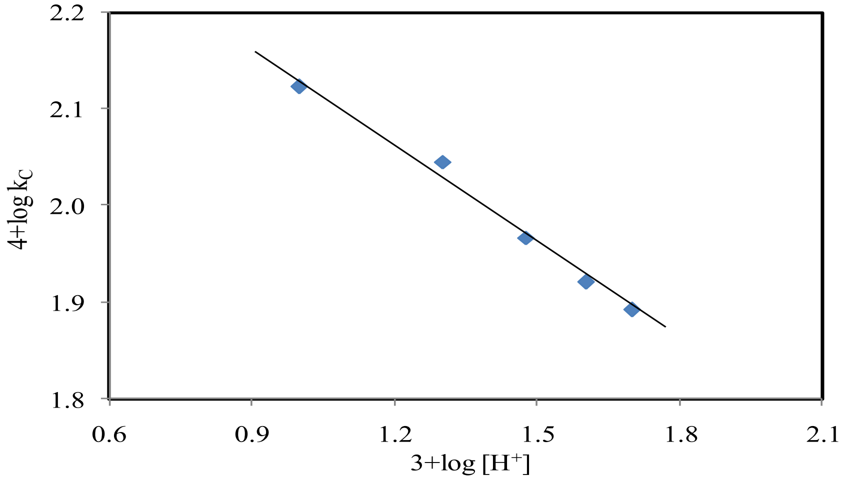


Figure 4: Order with respect to $[H^+]$ concentration on ruthenium(III) mediated oxidation of tripelennamine by cerium(IV) in aqueous sulfuric acid medium at 25°C.

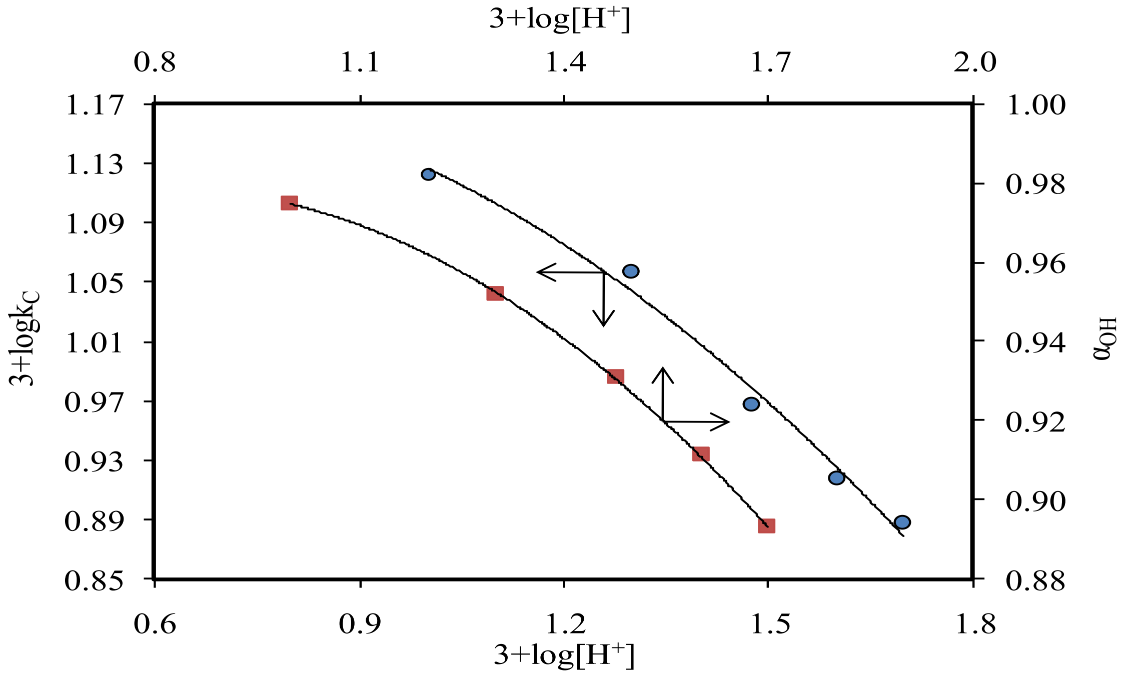


Figure 5: Plots of log k_C versus log$[H^+]$ and α_{OH} versus log$[H^+]$, (conditions as in Table (II)).

3.7. Effect of added product

The initially added product, cerium(III) concentration did not show any significant effect on the rate of the reaction.

3.8. Effect of ionic strength and solvent polarity

The effect of ionic strength was studied by varying the sodium sulphate concentration in the reaction medium. The ionic strength of the reaction medium was varied from 0.05 to 0.5 mol dm^{-3} at constant concentrations of cerium(IV), tripelennamine and sulphuric acid. It was found that the rate constant decreased marginally with the increase in Na_2SO_4 concentration (Table 3) and (Figure 6). The relative permittivity (D) effect was studied by varying the acetic acid–water volume fraction from 0 to 40% in the reaction mixture, all other conditions being maintained constant [19]. The rate constant, k_C decreased with increase in the acetic acid concentration (Table 4). The plot of log k_C versus 1/D is linear with a negative slope (Figure 7).

Table 3 Effect of ionic strength on ruthenium(III) mediated oxidation of tripelennamine by cerium(IV) in aqueous sulfuric acid medium at 25˚C

$[Ce(IV)] = 2.0 \times 10^{-4}$; $[TPA] = 5.0 \times 10^{-3}$; $[Ru(III)] = 1.0\times10^{-5}$; $[H_2SO_4] = 4.0\times10^{-2}$/ mol dm^{-3}

I	√I	$k_U\times10^3$ (s^{-1})	$k_T\times10^2$ (s^{-1})	$k_C\times10^2$ (s^{-1})	3 + log k_C
0.05	0.2236	3.96	1.92	1.52	1.182
0.10	0.3162	3.23	1.44	1.12	1.050
0.16	0.4000	2.44	1.07	0.83	0.916
0.25	0.5000	2.09	0.82	0.61	0.786
0.35	0.5916	1.71	0.60	0.44	0.638
0.50	0.7071	1.45	0.40	0.26	0.409

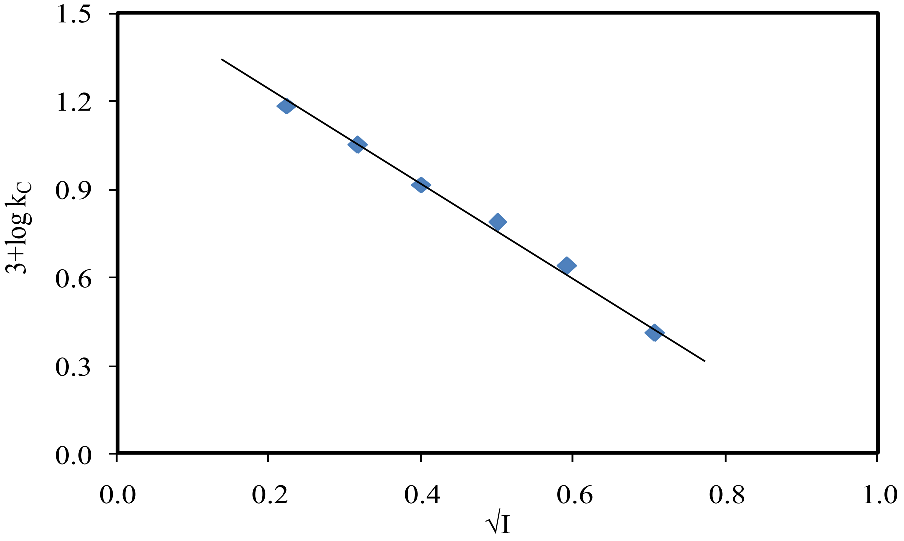


Figure 6: Effect of ionic strength on ruthenium(III) mediated oxidation of tripelennamine by cerium(IV) in aqueous sulfuric acid medium at 25˚C

Table 4: Effect of variation of solvent polarity on ruthenium(III) mediated oxidation of tripelennamine by cerium(IV) in aqueous sulfuric acid medium at 25˚C
[Ce(IV)] = 2.0×10^{-4}; [TPA] = 5.0×10^{-3}; [H_2SO_4] = 4.0×10^{-2}; [Ru(III)] =1.0×10^{-5};
I = 0.16/ mol dm^{-3}

% of t-butyl alcohol-water (v/v)	D	$1/D\times10^2$	$k_U\times10^3$ (s^{-1})	$k_T\times10^2$ (s^{-1})	$k_C\times10^3$ (s^{-1})	3 + log k_C
0	78.50	1.27	2.44	1.07	8.26	0.916
10	71.74	1.39	2.20	1.00	7.891	0.897
20	64.98	1.53	2.01	0.95	7.50	0.875
30	58.22	1.71	1.80	0.88	7.05	0.848
40	51.46	1.94	1.59	0.82	6.63	0.821

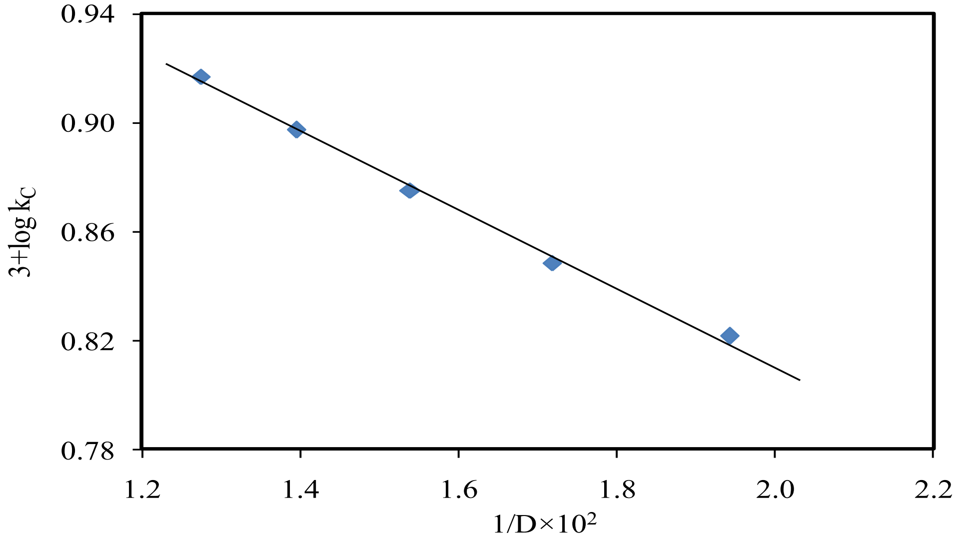


Figure 7: Effect of dielectric constant on ruthenium(III) mediated oxidation of tripelennamine by cerium(IV) in aqueous sulfuric acid medium at 25˚C

3.9. Polymerization study

The reaction mixture containing acrylonitrile was kept for 4 h in a nitrogen atmosphere. On diluting the reaction mixture with methanol precipitate resulted indicating the presence of free radical intervention in the reaction. The initial addition of acrylonitrile leads to a decrease in the rate of reaction also indicates involvement of free radical in the reaction.

3.10. Effect of temperature

The rate of reaction was studied at four different temperatures 15, 25, 35 and 45˚C under varying the concentration of tripelennamine, sulphuric acid, cerium(IV) and ruthenium(III), keeping other condition constant. The rate constant, k with respect to slow step of Scheme 1 was found to increase with increase in temperature. The rate constant, k, of the slow step of Scheme 1 was obtained from the intercept of the plots of $1/k_C$ versus 1/[TPA] at different temperatures (Table 5a). The energy of activation corresponding to rate constant k_C was evaluated by least square method of plot of log k_C (Y* Calc) versus 1/T (Figure 8) and the other activation parameters were calculated by using the Eyring equation and are tabulated in Table 5b.

Table 5 (a): Effect of temperature on slow step of the mechanism for the ruthenium(III)-mediated oxidation of tripelennamine by cerium(IV) in aqueous sulfuric acid medium

T (K)	$k \times 10^{-3}$ (s^{-1})	Log k (Y)	$1/T \times 10^3$ (X)	Y^*_{calc} (log k)
288	4.56	3.658	3.47	3.646
298	8.69	3.938	3.35	3.948
308	16.2	4.210	3.24	4.231
318	32.7	4.514	3.14	4.496

*Calculated

(b): Activation parameters with respect to the slow step of Scheme 1

Parameters	Values
Ea (kJ mol^{-1})	50±3
$\Delta H^{\#}$ (kJ mol^{-1})	47±3
$\Delta S^{\#}$ (J $K^{-1}mol^{-1}$)	-11 ±2
$\Delta G^{\#}$ (kJ mol^{-1})	51±3
log A	12.6 ± 0.2

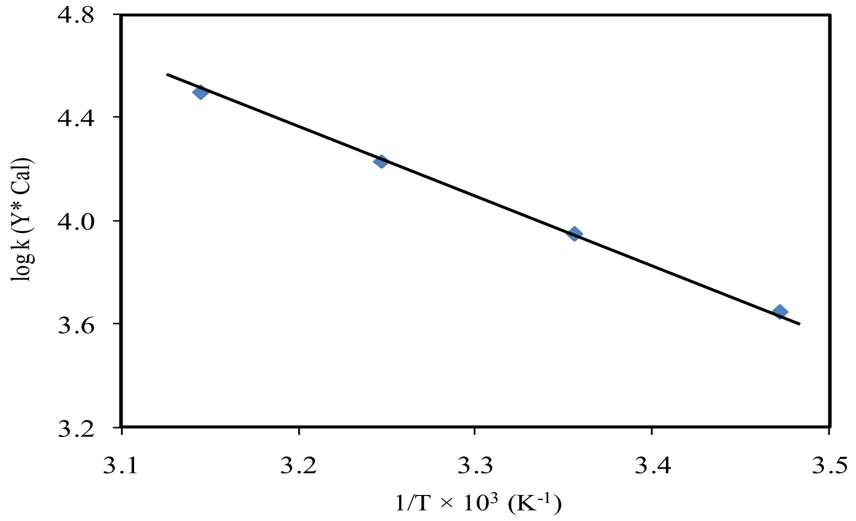


Figure 8: Effect of temperature on ruthenium(III) mediated oxidation of tripelennamine by cerium(IV) in aqueous sulfuric acid medium (Condition as in Table (v a))

3.11. Catalytic activity

Molelwyn-Hughes [20] pointed out that in the presence of catalyst, the uncatalyzed and catalyzed reactions proceed simultaneously, so that,

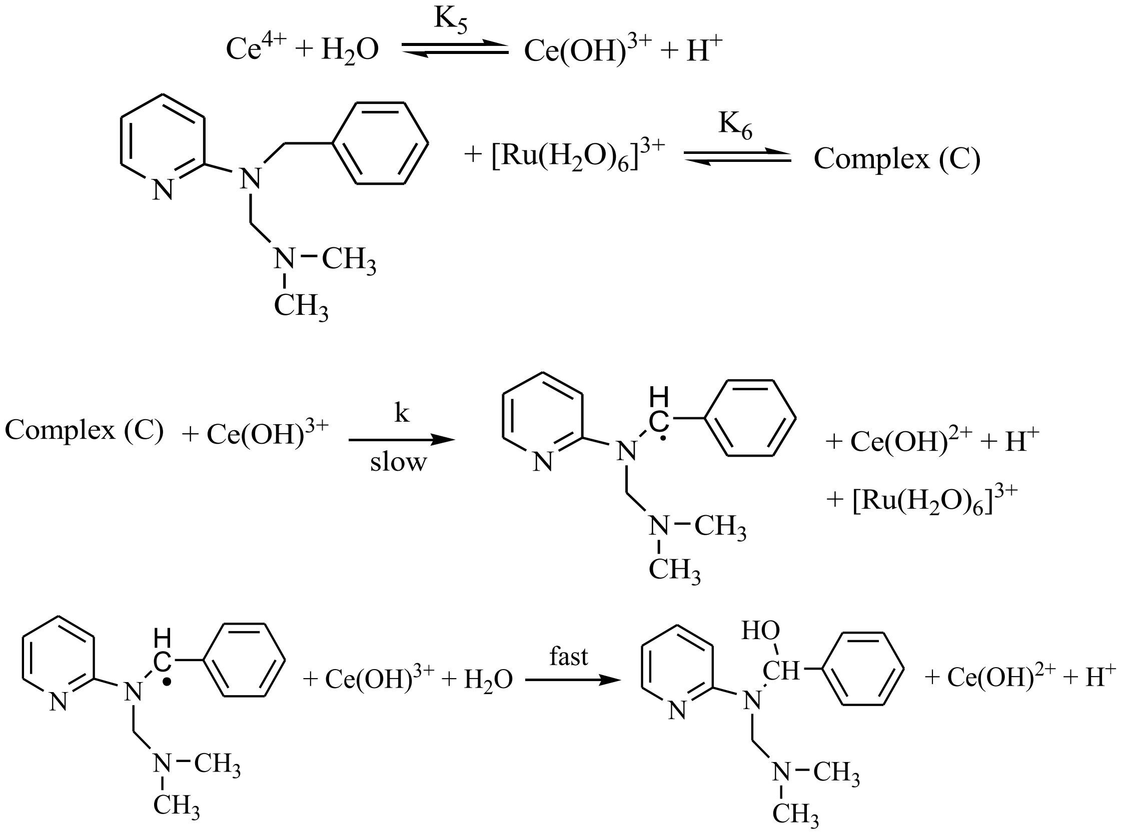
$$k_T = k_U + K_C[\text{Ru(III)}]^x$$

where k_T is the total rate constant, k_U is the pseudo-first order rate constant for the uncatalyzed path, K_C the catalytic constant, and x the order of the reaction with respect to catalyst. In the present investigations the x value is unity. The value of K_C is calculated using the following equation.

(Where $k_T - k_U = k_C$)
$$K_C = \frac{k_T - k_U}{[\text{Ru(III)}]^X} = \frac{k_C}{[\text{Ru(III)}]} \qquad (8)$$

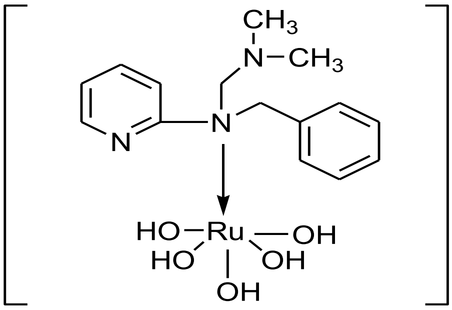
The value of K_C was calculated at 25°C and the value is 8.26×10^2 s^{-1} dm^3 mol^{-1}.

The cerium(IV) oxidation of tripelennamine was slow in aqueous sulfuric acid under the present experimental condition, but in a measurable quantity. The reaction is catalysed in the presence of micro amounts of ruthenium(III) in aqueous sulfuric acid-sulphate media. The reaction between tripelennamine and cerium(IV) has a 1:2 stoichiometry with negative less than unit order dependence on sulphuric acid, less than unit order dependence on tripelennamine, first-order dependence on Ce(IV) and ruthenium(III) concentrations. No effect of added cerium(III) was observed. The variation of rate with acidity was shown (results section), to parallel the trend of variation of concentration of the $Ce(OH)^{3+}$ species with the acidity (Table 2) (Figure 4). The results indicate that cerium(IV) on hydrolysis, first gives $Ce(OH)^{3+}$ species with deprotonation [21]. In the second equilibrium step the substrate, tripelennamine combines with ruthenium(III) species to form a complex, which then reacts in a rate determining step with one mole of $Ce(OH)^{3+}$ species to give a free radical derived from tripelennamine, the product cerium(III) with regeneration of the catalyst, ruthenium(III). This free radical reacts with another mole of $Ce(OH)^{3+}$ in a fast step to yield the products as shown in Scheme 1.



Scheme 1- Ruthenium(III)-mediated oxidation of tripelennamine by cerium(IV) in aqueous sulfuric acid medium

The probable structure of the complex(C) is



Spectroscopic evidence for the complex formation between oxidant and substrate was obtained from UV-visible spectra of tripelennamine (5.0×10^{-3} mol dm^{-3}), cerium(IV) (2.0×10^{-4} mol dm^{-3}), $[H_2SO_4] = 4.0\times10^{-2}$ mol dm^{-3} and mixture of both. A bathochromic shift of about 13.0 nm from 326.0 to 339.0 nm was observed (Figure 9). The formation of the complex is also proven kinetically by the non-zero intercept (Michaelis-Menten plot) of $[\mathrm{Ru(III)}]/k_C$ versus 1/ [TPA] (Figure 10).

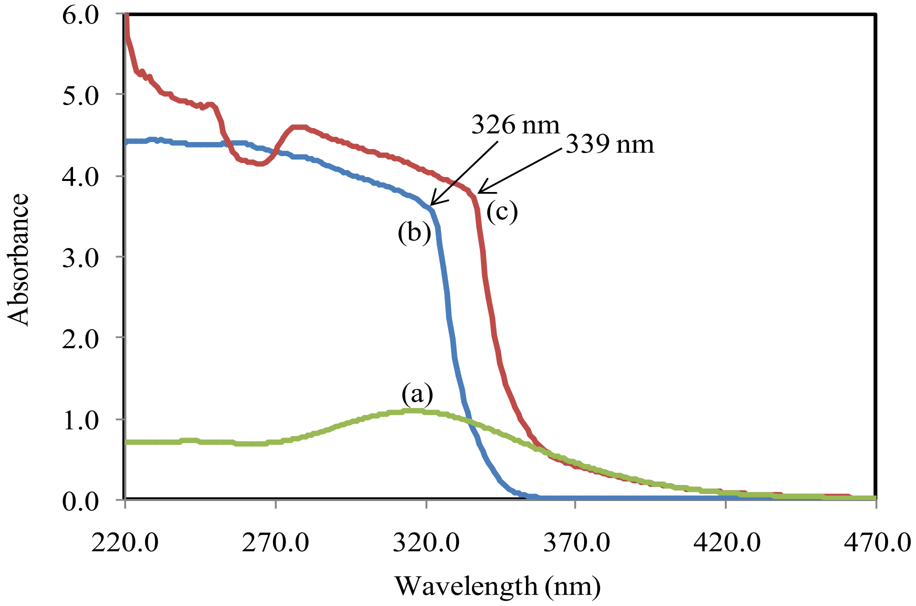


Figure 9: Spectroscopic evidence for the complex formation between tripelennamine and [Ce(IV)] (a) UV-vis spectra of [Ce(IV)] complex, (b) UV-vis spectra of tripelennamine and (c) UV-vis spectra of mixture of [Ce(IV)] and tripelennamine

From Scheme 1, the rate law (14) can be derived as:

$$\mathrm{Rate} = \frac{-\mathrm{d}[\mathrm{Ce(IV)}]}{\mathrm{dt}} = \mathrm{k}\,[\mathrm{Complex}][\mathrm{Ce(OH)^{3+}}]$$

$$= \mathrm{k}K_6[\mathrm{Ru(III)}][\mathrm{TPA}][\mathrm{Ce(OH)^{3+}}]$$

$$= \frac{\mathrm{k}K_6K_5[\mathrm{Ce(IV)}]_f[\mathrm{TPA}]_f[\mathrm{Ru(III)}]}{[\mathrm{H^+}]} \qquad (9)$$

The total concentration of cerium(IV) is given by

$$[\mathrm{Ce(IV)}]_t = [\mathrm{Ce(IV)}]_f + [\mathrm{Ce(OH)^{3+}}]$$

$$= [\mathrm{Ce(IV)}]_f + \frac{K_5[\mathrm{Ce(IV)}]_f}{[\mathrm{H^+}]}$$

$$= [\mathrm{Ce(IV)}]_f\left\{1 + \frac{K_5}{[\mathrm{H^+}]}\right\}$$

Therefore,

$$[\mathrm{Ce(IV)}]_\mathrm{f} = \frac{[\mathrm{Ce(IV)}]_\mathrm{t}}{1+\frac{\mathrm{K}_5}{[\mathrm{H}^+]}} = \frac{[\mathrm{Ce(IV)}]_\mathrm{t}[\mathrm{H}^+]}{[\mathrm{H}^+]+\mathrm{K}_5} \tag{10}$$

where subscripts'‘t' and’f' stands for total and free respectively.
Similarly, the total concentration of TPA is given by

$$\begin{aligned}[\mathrm{TPA}]_\mathrm{t} &= [\mathrm{TPA}]_\mathrm{f} + [\mathrm{Complex}]\\ &= [\mathrm{TPA}]_\mathrm{f} + \mathrm{K}_6[\mathrm{Ru(III)}][\mathrm{TPA}]_\mathrm{f}\end{aligned}$$

Therefore,

$$[\mathrm{TPA}]_\mathrm{f} = \frac{[\mathrm{TPA}]_\mathrm{t}}{(1+\mathrm{K}_6[\mathrm{Ru(III)}])} \tag{11}$$

As we have used low concentration of ruthenium(III) in the experiment, hence the term (1+K_6[Ru(III)]) can be neglected in the denominator of equation (11).
So,

$$[\mathrm{TPA}]_\mathrm{f} = [\mathrm{TPA}]_\mathrm{t} \tag{12}$$

Similarly,

$$\begin{aligned}[\mathrm{Ru(III)}]_\mathrm{t} &= [\mathrm{Ru(III)}]_\mathrm{f} + [\mathrm{Complex}]\\ &= [\mathrm{Ru(III)}]_\mathrm{f} + \mathrm{K}_6[\mathrm{Ru(III)}]_\mathrm{f}[\mathrm{TPA}]_\mathrm{f}\\ &= [\mathrm{Ru(III)}]_\mathrm{f}(1+\mathrm{K}_6[\mathrm{TPA}]_\mathrm{f})\end{aligned}$$

Therefore,

$$[\mathrm{Ru(III)}]_\mathrm{f} = \frac{[\mathrm{Ru(III)}]_\mathrm{t}}{1+\mathrm{K}_6[\mathrm{TPA}]} \tag{13}$$

Substituting equations (10), (12) and (13) in equation (9) and omitting the subscripts, we have

$$\mathrm{Rate} = -\frac{d[\mathrm{Ce(IV)}]}{dt} = \frac{\mathrm{k}\mathrm{K}_5\mathrm{K}_6[\mathrm{Ce(IV)}][\mathrm{H}^+][\mathrm{TPA}][\mathrm{Ru(III)}]}{[\mathrm{H}^+]([\mathrm{H}^+]+\mathrm{K}_5)(1+\mathrm{K}_6[\mathrm{TPA}])} \tag{14}$$

or

$$\frac{\mathrm{Rate}}{[\mathrm{Ce(IV)}]} = \mathrm{k_C} = \frac{\mathrm{k}\mathrm{K}_5\mathrm{K}_6[\mathrm{TPA}][\mathrm{Ru(III)}]}{([\mathrm{H}^+]+\mathrm{K}_5)(1+\mathrm{K}_6[\mathrm{TPA}])}$$

$$\mathrm{k_C} = \frac{\mathrm{k}\mathrm{K}_5\mathrm{K}_6[\mathrm{TPA}][\mathrm{Ru(III)}]}{[\mathrm{H}^+]+\mathrm{K}_5+\mathrm{K}_6[\mathrm{H}^+][\mathrm{TPA}]+\mathrm{K}_5\mathrm{K}_6[\mathrm{TPA}]} \tag{14}$$

Equation (14) can be rearranged in the form of the following equation (15), which is suitable for verification:

$$\frac{[\mathrm{Ru(III)}]}{\mathrm{k_C}} = \frac{[\mathrm{H}^+]}{\mathrm{k}\mathrm{K}_5\mathrm{K}_6[\mathrm{TPA}]} + \frac{[\mathrm{H}^+]}{\mathrm{k}\mathrm{K}_5} + \frac{1}{\mathrm{k}\mathrm{K}_6[\mathrm{TPA}]} + \frac{1}{\mathrm{k}} \tag{15}$$

According to equation (15), the plots of [Ru(III)]/$\mathrm{k_C}$ versus 1/[TPA] and [Ru(III)]/$\mathrm{k_C}$ versus[H^+] should be linear and are found to be so (Figure 10a and 10b).
From the first plot, [Ru(III)]/$\mathrm{k_C}$ versus 1/[TPA]:

$$(\mathrm{slope})_1 = \frac{[\mathrm{H}^+]}{\mathrm{k}\mathrm{K}_5\mathrm{K}_6} + \frac{1}{\mathrm{k}\mathrm{K}_6}$$

$$(\mathrm{intercept})_1 = \frac{[\mathrm{H}^+]}{\mathrm{k}\mathrm{K}_5} + \frac{1}{\mathrm{k}} \tag{16}$$

Therefore,

$$\frac{(\mathrm{intercept})_1}{(\mathrm{slope})_1} = \mathrm{K}_6 = \text{formation constant of complex (C)}$$

$$\frac{2.24\times10^{-4}}{5.0\times10^{-6}} = \mathrm{K}_6 = 44.72$$

From the second plot, [Ru(III)]/$\mathrm{k_C}$ versus [H^+]:

$$(\mathrm{slope})_2 = \frac{1}{\mathrm{k}\mathrm{K}_6\mathrm{K}_5[\mathrm{TPA}]} + \frac{1}{\mathrm{k}\mathrm{K}_5}$$

$$(\text{intercept})_2 = \frac{1}{kK_6[\text{TPA}]} + \frac{1}{k} \quad (17)$$

Therefore,

$$\frac{(\text{intercept})_2}{(\text{slope})_2} = K_5 = \text{hydrolysis constant of } \text{Ce(OH)}^{3+}$$

$$\frac{6.20\times10^{-4}}{1.39\times10^{-2}} = K_5 = 4.45\times10^{-2}$$

By knowing the values of $(\text{intercept})_1$, $(\text{slope})_1$, $(\text{intercept})_2$ and $(\text{slope})_2$ we determine the values of K_6 and K_5 respectively. Substituting the values of K_5, $[H^+]$ and $(\text{intercept})_1$ in the equation (16), the rate constant, k with respect to slow step of Scheme 1 can be obtained. From the same procedure, the values of equilibrium constant, K_5, K_6 and rate constant, k values are 4.45×10^{-2}, 44.7 $dm^3\ mol^{-1}$ and $8.69\times10^3\ dm^3 mol^{-1}\ s^{-1}$ respectively at 25°C. The K_5 value obtained is in the neighborhood of the earlier reported value [22, 23] at 25°C. Similarly the values of K_5 and K_6 were calculated at 15, 35 and 45°C and are given in Table 6 a. Using the values of k, K_5 and K_6 at 25°C in equation (14), the rate constants were calculated over a range of different conditions and compared with experimental values (Table 1); (Table 2). There is reasonable agreement between calculated and experimental rate constants, supporting the assumptions of Scheme 1. The effect of ionic strength on the rate qualitatively explains the reaction between a positive and neutral species as shown in Scheme 1. The effect of solvent on the rate of reaction has been discussed [24]. A decrease in the rate of the reaction with decrease in dielectric constant may be due to stabilization of the complex (C) at low dielectric constant values which is less solvated than cerium(IV) at lower dielectric constant. Perhaps this effect is countered substantially by the formation of active reaction species to a greater extent in a high relative permittivity media leading to the net increase in reaction rate [25].

The thermodynamic quantities were calculated as follows: A van't Hoff plot was made for the variation in K_5 and K_6 with temperature (log K_5 versus 1/T and log K_6 versus 1/T). The values of enthalpy of reaction ΔH, entropy of reaction ΔS, and free energy of reaction ΔG were calculated for the first and second equilibrium steps of Scheme 1 and the values are given in Table 6b.

The comparison of the ΔH value (11.5 $kJmol^{-1}$) from K_5 with that of $\Delta H^{\neq}$ (47.2 $kJmol^{-1}$) of the rate limiting step shows that the reaction before the rate determining step is fairly fast as it involves a low activation energy [26]. The negative value of $\Delta S^{\neq}$ indicates the formation of complexes in the reaction as shown in Scheme 1 and small negative value of $\Delta S^{\neq}$ value suggests that the complex is less ordered than the reactants and has been ascribed to loss of degrees of freedom, formerly available in reactions involving formation of a rigid transition state. The observed modest enthalpy of activation and the higher rate constant of the slow step indicate that oxidation presumably occurs by inner-sphere mechanism. This conclusion is supported by the results of earlier work [27].

Conclusions

The reaction between cerium(IV) and tripelennamine hydrochloride is slow in sulfuric acid medium at room temperature but in a measurable speed. The reaction is mediated in the presence of a minute quantity (10^{-5} mol dm^{-3}) of ruthenium(III). The main active species of cerium(IV) is considered as Ce(OH)^{3+}, although other species might be active to much lesser extent, and $[\text{Ru}(H_2O)_6]^{3+}$ is considered as the active species of the catalyst, ruthenium(III). Ruthenium(III) catalyzed oxidation of tripelennamine hydrochloride by cerium(IV) in aqueous sulfuric acid medium has a stoichiometry 1:2 in reductant to oxidant. The reaction product was identified as (N-((dimethylamino) methyl)-N-(pyridine-2-yl) amino)(phenyl)methanol and characterised by UV–Vis, GC–MS and IR spectra. Activation parameters were evaluated for catalyzed reactions. The suitable mechanism is proposed and the corresponding rate law is derived. The description of the mechanism is consistent with all the experimental evidence.

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