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Oxidation of Threonine by Sodium Metaperiodate in Alkaline Medium using Transition metal complex species $[RhCl_4(H_2O)_2]^-$ as Homogeneous Catalyst in its nano-concentration range: A Kinetic and Mechanistic Study

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Abstract : The kinetics of oxidation of threonine by $[NaIO_4]$ in the presence of Rh(III) as homogeneous catalyst in alkaline medium in its nano-concentration range has been investigated iodometrically at 35^0C. The reaction follows first order kinetics with respect to $[IO_4^-]$ and [threonine]. The order of reaction is first with respect to $[OH^-]$ at its lower concentration tending towards zero order at its higher concentrations The reaction exhibits first order dependence with respect to [Rh (III)]. Positive effect of $[Cl^-]$ on the rate of oxidation of threonine has been noted.Rate of reaction is not influenced by the change in ionic strength (μ) and dielectric constant (D) of the medium. To study the effect of temperature, the reaction has been studied at four different temperatures from 303K – 318K. Various activation parameters such as energy of activation, enthalpy of activation, entropy of activation and free energy of activation have been calculated. $[H_2IO_6^{3-}]$ and $[RhCl_4(H_2O)_2]^-$ have been postulated as the reactive species of periodate and Rh(III)chloride respectively in alkaline medium. A most probable reaction mechanism consistent with the kinetic data,spectral evidences, stiochiometry and product analysis has been proposed for Rh(III)-catalysed oxidation of threonine.

Keywords : Kinetics, Mechanism, Oxidation, Rh(III) chloride, Sodium metaperiodate, Threonine.

Introduction

It is a well known fact that proteins are the most abundant organic molecules of the living systems and protein are the polymer of L-α-amino acids[1].Each protein has a unique sequence of amino acids which is determined by the genes contained in DNA. The primary structure of a protein largely responsible for its function. A vast majority of genetic diseases are due to abnormalities in the amines and sequences of protein. It is reported in literature[2] that threonine is an essential amino acid classified as non-polar and forms active sites of enzymes and helps in maintaining proper conformation by keeping them in proper ionic states. Kinetic studies of uncatalyzed[2,3]and catalyzed oxidation of threonine using Ir(III)[4], copper nanoparticles[5] as catalystby various oxidant has been investigated. The coordination chemistry of Rh(III) has drawn considerable attention due to chemical reactivity and anti-tumor activity, electronic structure and catalytic function of its complexes with potential industrial applications[6]. Periodate has been widely used as an oxidizing agent in aqueous medium[7,8]. Periodate oxidations of uncatalyzed L-arginine[9],Serine and threonine[10] have been already investigated. Earlier it was reported[11] that oxidation with periodate has been shown to cause denaturation of proteins and in activator of enzymes and these finding have been interpreted on the basis of attache of periodate on essential amino acids. Periodate is reported[10] as highly specific with serine and threonine because of its groups contained by these amino acids. In the light of above mentioned facts the reaction for the oxidation of threonine by sodium metaperiodate in alkaline medium using Rh(III) chloride as homogenous catalyst has attracted an attention and prompted us to investigate the same.

Our main objectives are –

(1) to ascertain role of Rh(III) as catalyst in its nano-concentration range in redox process involving threonine as reductant and $NaIO_4$ as oxidant in alkaline medium.

(2) to probe the oxidative capacity of $NaIO_4$ in the oxidation of threonine in the presence of chlorocomplexe of Rh(III) chloride as catalyst.

(3) to determine the relative activities of various chlorocomplexes of Rh(III) in the oxidation of threonine by IO_4^- in alkaline medium.

(4) to ascertain the reactive species of Rh(III), threonine and $NaIO_4$ in alkaline medium and to verify the existence of various complexes formed between reactive species of Rh(III), threonine and reactive species of $NaIO_4$ during the course of a reaction in proposed investigation

(5) to calculate activation parameters like E_a, $\Delta S^\#$, $\Delta H^\#$, $\Delta G^\#$ and A for each redox system.

(6) topropose a suitable reaction path for the oxidation of threonine by sodium metaperiodate in alkaline medium using chlorocomplex of Rh(III) as homogeneous catalyst.

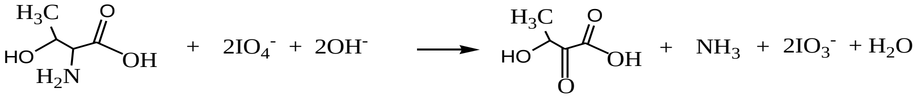
Experimental

All the solutions were prepared in doubly distilled water.The solution of rhodium(III) chloride (Loba) was prepared by dissolving 1 g of sample in hydrochloric acid (HCl) of known strength and the strength of rhodium(III) chloride ($RhCl_3.3H_2O$) was found to be 3.80×10^{-3} M. The solution of sodium metaperiodate (Sigma chemicals) was prepared by dissolving weighed amount of its in double distilled water. Solution of threonine was always freshly prepared before use. An aqueous solution of perchloric acid, sodium perchlorate, potassium chloride, sodium hydroxide, sodium thiosulphate and potassium iodide (all of E.Merck) were prepared in double distilled water.

The reaction mixture containing the desired volume of all reactants i.e. $NaIO_4$, OH^-, Rh(III) chloride and water except threonine was taken in conical flask which kept in the thermostatic bath at constant temperature 35^0C. After 30 min, when the solution has attained the temperature of the bath requiste volume of threonine was added and aliquots of the reaction mixture were withdrawn quickly at known intervals of time and poured into another flask containing a of 4% potassium iodide (Merck) solution to arrest the reaction. The actual progress of reaction was followed by estimating liberated amount of iodine against standard sodium thiosulphate solution using starch as an indicator.

Stoichiometry and products analysis

Different sets of experiments were performed under the conditions [$NaIO_4$] >> [Threonine] at 35ºC for several days. Estimation of unconsumed $NaIO_4$ indicated that two mole of $NaIO_4$ were consumed to oxidize one mole of threonine. Accordingly, the following stoichiometric equation for the oxidation of threonine by IO_4^- in presence of alkali is suggested:



Kinetics Results and Discussion

Kinetics of oxidation of threonine by sodium metaperiodate in alkaline medium in presence of Rh (III) chloride as homogeneous catalyst has been studied at constant temperature 35^{0}C. Order of reaction with respect to each reactant was determined by varying the concentrations of oxidant, threonine, Rh(III) chloride and OH^-, one by one in different sets keeping concentrations of all other reactants constant at constant temperature. The initial rate(-dc/dt) of reaction in each kinetic run was determined by the slope of the tangent of the plot drawn between unconsumed $NaIO_4$and time and pseudo first-order rate constant (k_1) was calculated by dividing the observed initial rate by the [$NaIO_4$].It is clear from the data given in Table 1 that throughout the variation of periodate, the rate of the reaction increases in the same proportion in which the concentration of $NaIO_4$ is increased, which leads to the conclusion that the order of reaction with respect to $[IO_4]^-$is unity.Table-1 also indicates that the first-order rate constant (k_1) increases with increase in concentration of threonine, suggesting first order dependence of the reaction on [threonine].The effect of [OH^-] on the rate of reaction was studied at constant [substrate], [$NaIO_4$], [catalyst]and ionic strength at35ºC. The data presented in table-1shows first order dependence of rate on lower concentration of medium which tends towards zero order at its higher concentration. The rate constants obtained were found to increase with the increase in [catalyst] (Table-1). Further, the plot k_1 versus [Rh(III)] was found to be a straight line passing through origin indicating the order with respect to [Rh(III)] to be unity. The role of KCl and $NaClO_4$ was just to fix the chloride ion concentration.The results indicated negligible effect of μ on the reaction rate. For the effect of dielectric constant of the medium on pseudo first-order rate constant (k_1) the experiments, by varying the concentration of ethanol from 5% to 20% were performed under uniform conditions. It is observed that change in dielectric constant of the medium has no effect on the rate of the oxidation.The rate of reaction increased slightly with the increase in [Cl^-], showing positive effect of [Cl^-] on the rate of reaction (Table-1). The reaction under investigation has been studied at four different temperatures and observed k_1 values were utilized to calculate activation parameters like energy of activation, entropy of activation, enthalpy of activation and free energy of activation and also the Arrhenius frequency factor(A)(Table-2).

Table-1: Observed values of rate constants for the variations of [$NaIO_4$],[Threonine], [Rh(III)], [NaOH] and [KCl] in the Rh(III)-catalysed oxidation of threonine at 35^0 C

[$NaIO_4$] × 10^3 M	[Threonine] × 10^2 M	[NaOH] × 10^2 M	[Rh(III)] × 10^9 M	[KCl]× 10^5 M	k_1 × 10^4 (sec^{-1})
0.50	1.00	10.00	7.56	5.00	4.40
1.00	1.00	10.00	7.56	5.00	4.33
2.00	1.00	10.00	7.56	5.00	4.15
2.50	1.00	10.00	7.56	5.00	4.44
3.00	1.00	10.00	7.56	5.00	4.43
4.00	1.00	10.00	7.56	5.00	4.32
5.00	1.00	10.00	7.56	5.00	4.50
1.00	0.50	10.00	7.56	5.00	1.60
1.00	1.00	10.00	7.56	5.00	3.30
1.00	2.00	10.00	7.56	5.00	6.08
1.00	3.00	10.00	7.56	5.00	9.60
1.00	3.50	10.00	7.56	5.00	11.33
1.00	4.00	10.00	7.56	5.00	12.70
1.00	5.00	10.00	7.56	5.00	16.66
1.00	1.00	5.00	7.56	5.00	2.60
1.00	1.00	10.00	7.56	5.00	4.60
1.00	1.00	20.00	7.56	5.00	6.60
1.00	1.00	30.00	7.56	5.00	10.30
1.00	1.00	40.00	7.56	5.00	13.88
1.00	1.00	50.00	7.56	5.00	13.60
1.00	1.00	60.00	7.56	5.00	14.00
1.00	1.00	70.00	7.56	5.00	13.80
1.00	1.00	10.00	3.78	5.00	1.60
1.00	1.00	10.00	7.56	5.00	3.05

1.00	1.00	10.00	11.34	5.00	4.80
1.00	1.00	10.00	15.12	5.00	6.66
1.00	1.00	10.00	22.68	5.00	11.11
1.00	1.00	10.00	30.24	5.00	12.66
1.00	1.00	10.00	37.80	5.00	16.66
1.00	1.00	10.00	7.56	1.50	1.50
1.00	1.00	10.00	7.56	3.00	2.77
1.00	1.00	10.00	7.56	6.00	5.18
1.00	1.00	10.00	7.56	9.00	7.50
1.00	1.00	10.00	7.56	12.00	9.00
1.00	1.00	10.00	7.56	15.00	10.33

Solution condition:[KCl] = 5.00×10^{-5} M, $\mu = 0.70$M

Table-2:Value of activation parameters of Rh(III)-catalysed oxidation of Threonine by Sodium metaperiodate in alkaline medium at 35^0 C

Compound	**Ea (kJmol^{-1})**	**$k_r\times10^9$ (mol^{-2}L^{2}s^{-1})**	**$\Delta H^\#$ (kJmol^{-1})**	**$\Delta G^\#$ (kJ mol^{-1})**	**$\Delta S^\#$ (JK^{-1}mol^{-1})**	**A (mol^{-1}dm^{3}s^{-1})**
Threonine	85.56	1.73	82.97	20.94	201.39	4.60×10^{23}

Conditions:[$NaIO_4$] = 1.00×10^{-3}M, [Threonine] = 1.00×10^{-2}M, [Rh(III)] = 7.56×10^{-9}M,
[NaOH] = 10.00×10^{-2}M, $\mu = 0.70$ M, [KCl] = 5.00×10^{-5}M

Reactive species of sodium metaperiodate in alkaline medium

It is reported[11] that periodic acid is a strong oxidant. The standard potential for the periodate couple in alkaline solution was found to be lower than acidic solution. The existence of periodic acid as an equilibrium mixture between the free acid (H_5IO_6) and its various ions in aqueous solution (pH = 0-7) is reported.By making a basis for the plots of extinction co-efficientvs. wavelength for periodate, C. R. Wasmuth and co-workers have reported[12]that there are different forms of periodic acids with the change in pH from 1 to 13.6. According to them at pH equal to 1, 75% of periodate remains in the form of $H_5IO_6^-$ and at pH equal to 6.5 it remains 97% in the form of IO_4^- and 3% in the form of $H_4IO_6^-$. At pH equal to 10.2, 100% periodate remains in the form of $H_3IO_6^{2-}$ and at pH equal to 13.6, it remains 100% in the form of $H_2IO_6^{3-}$.In the present paper, the study has been made for Rh(III) catalyzed oxidation of threonine in alkaline medium. Throughout the study, the pH of the solution was maintained either at about 13 or above than that. As per the report available and as per the spectrum for periodate solution alone, where a single peak was observed, it can be concluded that 100% of periodate is present in the form of $H_3IO_6^{2-}$ in the reaction under investigation. The effect of variation of [OH^-] on the rate of oxidation of threonine, it was found that there is a positive effect of [OH^-] on the rate of reaction.

Reactive species of Rh(III) chloride in alkaline medium

The present study has been made for the oxidation of threonine by $NaIO_4$ in presence of chloro-complex of Rh(III) as homogeneous catalyst. A solution of Rh(III) chloride was prepared in 3.00 M HCl, and its concentration was determined as 3.79×10^{-3} M. This stock solution was further diluted, and in each kinetic run the Rh(III) chloride concentration was fixed in the order of 10^{-9} M. In view of the reported literatures[13-16], [$RhCl_3(H_2O)_3$]can be considered as the starting species of Rh(III) chloride in alkaline medium.In view of the literature reported earlier and also in view of the conditions under which experiments where performed to determining the order of reaction with respect to the reactants involved in the reaction, it can be concluded that the starting species of Rh(III) chloride in alkaline medium is the species[$RhCl_3(H_2O)_3$]. In the present study when the positive effect of [Cl^-] on the rate of oxidation is combined with the spectra collected forRh(III)-chloride solution with two different concentration of Cl^-, it can be assumed that the following equilibrium exists in the reaction under investigation(Fig-1 (5),(6) and (7)).

$$\underset{C_1}{[RhCl_3(H_2O)_3]} + Cl^- \overset{K_2}{\rightleftharpoons} \underset{C_2}{[RhCl_4(H_2O)_2]^-} + H_2O \qquad (II)$$

The increase in absorbance from 0.55 to 0.59 and 0.65 with the increase in [Cl$^-$], it can be inferred that out of the species $[RhCl_3(H_2O)_3]$ and $[RhCl_4(H_2O)_2]^-$, the species $[RhCl_4(H_2O)_2]^-$is the reactive species of Rh(III) chloride in alkaline medium because only with this reactive species the positive effect of [Cl$^-$] on the rate of reaction can be very explained and suitable rate law can be derived.

Reactive species of threonine in alkaline medium

On the basis of protolysis data, it has been reported[17] that more than 99.9% of amino acids are existing in the form of $H_2NCH(CH(OH)R)COO^-$ (R= H, Me) in the alkaline medium. From this report, it is clear that threonine in a alkaline medium will exist in the following form

$$CH_3CH(OH)CHNH_2COOH + OH^- \rightleftharpoons CH_3CH(OH)CHNH_2COO^- + H_2O$$

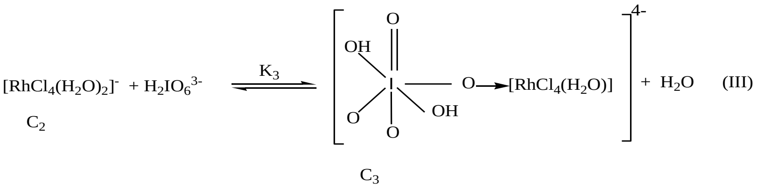
From the observed positive effect of [OH$^-$] on the rate of reaction, it can be concluded that the species $CH_3CH(OH)CHNH_2COO^-$ is the reactive species of threonine in its Rh(III)-catalysed oxidation by IO_4^- in alkaline medium.

Spectroscopic evidence for the formation of complex or complexes in Rh(III)-catalysed oxidation of threonine

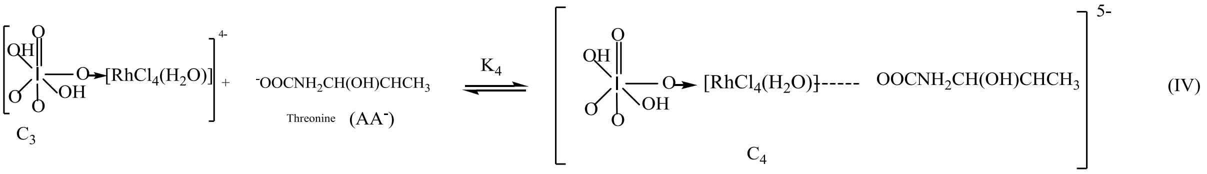
Efforts were made to ascertain possible formation of complexes between different reactive species during the course of reaction with the help of VARIAN CARY WIN UV–VIS spectrophotometer. For this, the spectra for various solutions of IO_4^-, Rh(III), OH$^-$, KCl and amino acid were collected. When spectra for the solutions of IO_4^- alone and for the solutions of IO_4^- with two different concentration of OH$^-$ were collected, it was found that there is substantial increase in absorbance from 0.22 to 0.29 and 0.37 with the increase in [OH$^-$] (Fig-1(1),(2) and(3)). This indicates the existence of following equilibrium in the reaction under investigation.

$$H_3IO_6^{2-} + OH^- \overset{K_1}{\rightleftharpoons} H_2IO_6^{3-} + H_2O \qquad (I)$$

When two different concentrations of Rh(III) were added to the solution of $NaIO_4$ and OH$^-$, it was found that there is an increase in absorbance from 0.37 to 0.46 and 0.55 (Fig-1 (3)-(5) This increase in absorbance with the increase in [Rh(III)] is due to more and more formation of a complex between reactive species of Rh(III) chloride i.e. $[RhCl_4(H_2O)_2)]^-$ and reactive species of $NaIO_4$ i.e. IO_4^-, according to this equilibrium mentioned below,



Whenspectra for the solutions of IO_4^-, OH$^-$, Rh(III) chloride and Cl$^-$ with five different concentrations of amino acid were collected,(Fig-1 ((7)-(12)), increase in absorbance from 0.65 to 1.09 with the increase in amino acid concentration might be assumed as due to more and more formation of a complex formed between C_3 and [AA$^-$].



The formation of 1:1 complex betweenC$_3$ and [AA$^-$] is supported by Job's plot (1/ΔA vs. 1/ [AA]) where a straight line with positive intercept on1/ΔA axis was obtained (Fig-2).

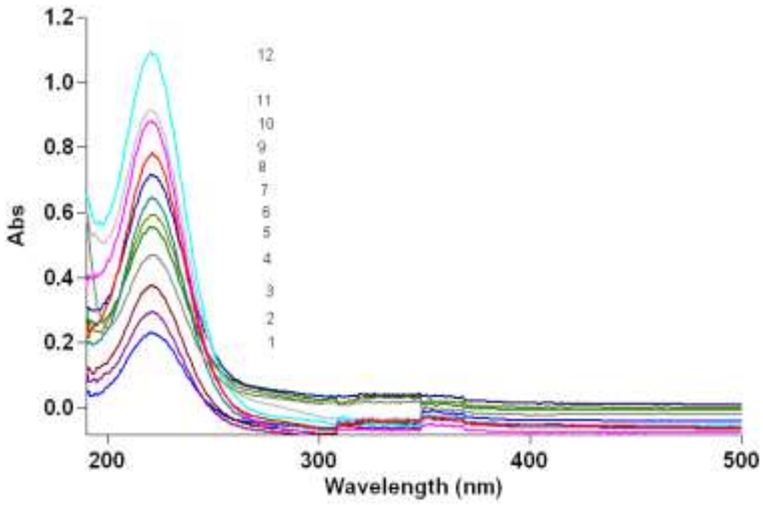


Figure-1:(1) [IO$_4^-$] = 1.00 x 10^{-5} M (2) [IO$_4^-$] = 1.00 x 10^{-5} M, [OH$^-$] = 20.00 x 10^{-4} M(3) [IO$_4^-$] = 1.00 x 10^{-5} M, [OH$^-$] = 50.00 x 10^{-4} M(4) [IO$_4^-$] = 1.00 x 10^{-5} M, [OH$^-$] = 50.00 x 10^{-4} M, [Rh(III)] = 15.12 x 10^{-6} M(5) [IO$_4^-$] = 1.00 x 10^{-5} M, [OH$^-$] = 50.00 x 10^{-4} M, [Rh(III)] = 30.24 x 10^{-6} M(6) [IO$_4^-$] = 1.00 x 10^{-5} M, [OH$^-$] = 50.00 x 10^{-4} M, [Rh(III)] = 30.24 x 10^{-6} M, [KCl] = 1.00 x 10^{-5} M(7) [IO$_4^-$] = 1.00 x 10^{-5} M, [OH$^-$] = 50.00 x 10^{-4} M, [Rh(III)] = 30.24 x 10^{-6} M, [KCl] = 2.00 x 10^{-5} M(8) [IO$_4^-$] = 1.00 x 10^{-5} M, [OH$^-$] = 50.00 x 10^{-4} M, [Rh(III)] = 30.24 x 10^{-6} M, [KCl] = 2.00 x 10^{-5} M, [Threonine] = 1.00 x 10^{-2} M(9) [IO$_4^-$] = 1.00 x 10^{-5} M, [OH$^-$] = 50.0 x 10^{-4} M, [Rh(III)] = 30.24 x 10^{-6} M, [KCl] = 2.00 x 10^{-5} M, [Threonine] = 2.00 x 10^{-2} M(10) [IO$_4^-$] = 1.00 x 10^{-5} M, [OH$^-$] = 50.00 x 10^{-4} M, [Rh(III)] = 30.24 x 10^{-6} M, [KCl] = 2.00 x 10^{-5} M, [Threonine] = 4.00 x 10^{-2} M(11) [IO$_4^-$] = 1.00 x 10^{-5} M, [OH$^-$] = 50.00 x 10^{-4} M, [Rh(III)] = 30.24 x 10^{-6} M, [KCl] = 2.00 x 10^{-5} M, [Threonine] = 5.00 x 10^{-2} M(12) [IO$_4^-$] = 1.00 x 10^{-5} M, [OH$^-$] = 50.00 x 10^{-4} M, [Rh(III)] = 30.24 x 10^{-6} M, [KCl] = 2.00 x 10^{-5} M, [Threonine] = 6.00 x 10^{-2} M.

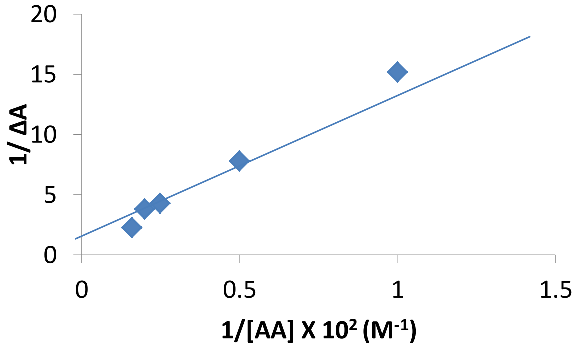
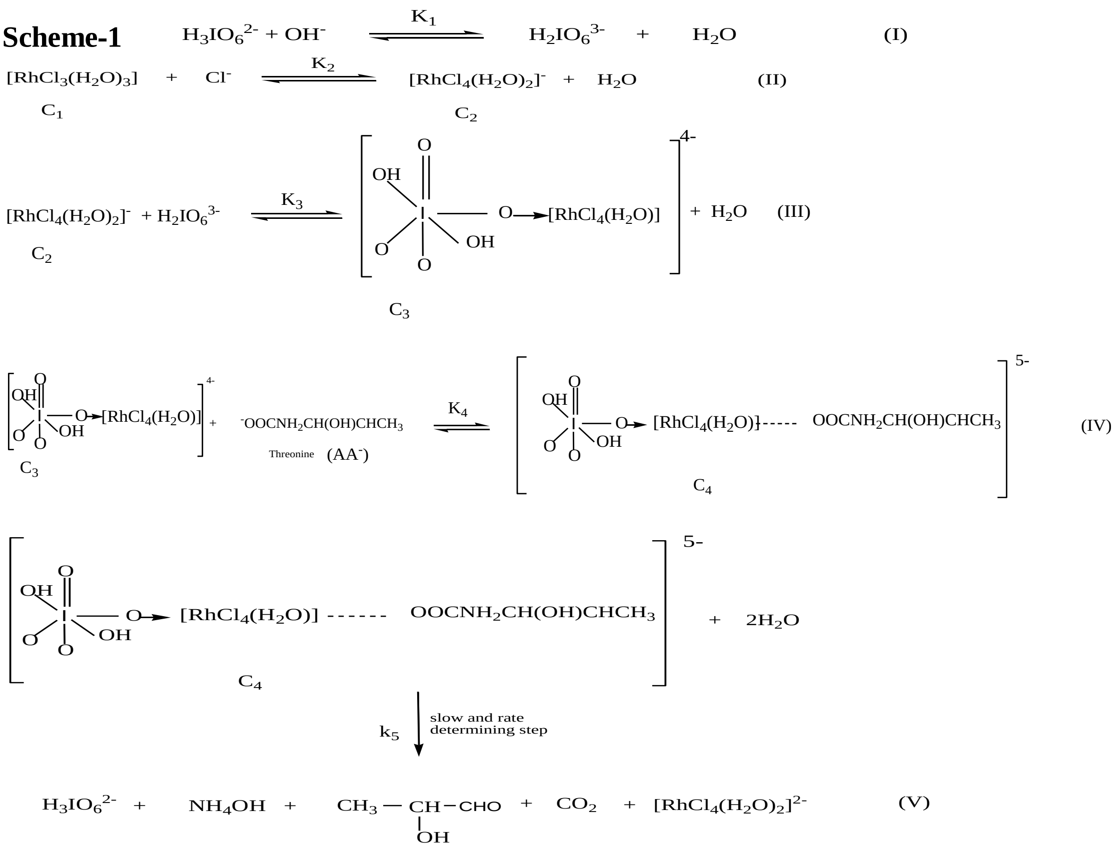


Figure-2:Plot between 1/ΔA and 1/ [AA] at 35 ^{0}C

Reaction mechanism and derivation of rate law

Making basis to the observed kinetic orders with respect to each reactant, spectroscopic evidences collected for the formation of complex or complexes in the reaction and giving due weightage to the effect of [Cl$^-$] on the rate of oxidationas well as the activation parameters,a probable reaction path in the form of scheme-1 can beproposed for the Rh(III)-catalysed oxidation of threonine by IO$_4^-$ in alkaline medium.

Scheme-1



Considering the stoichiometric data and above mechanistic steps, the rate in terms of disappearance of IO_4^- may be expressed as

$$\text{rate} = \frac{-d[IO_4^-]}{dt} = 2k_5[C_4] \qquad (1)$$

On applying the law of chemical equilibrium to steps (I)-(IV) and taking help of the Eq. where total concentration of Rh(III) is expressed as $[Rh(III)]_T = [C_1] + [C_2] + [C_3]$, we have

$$\text{rate} = \frac{2k_5\, K_1K_2K_3K_4\, [H_3IO_6^{2-}]\, [AA^-]\, [Rh\,(III)]_T [OH^-]\, [Cl^-]}{1 + K_2[Cl^-] + K_1K_2K_3[H_3IO_6^{2-}][OH^-]\, [Cl^-]} \qquad (2)$$

Total concentration of periodate ionat any moment in the reaction can be shown as $[IO_4^-]_T = [H_3IO_6^{2-}] + [H_2IO_6^{3-}] = [H_3IO_6^{2-}] + K_1\, [H_3IO_6^{2-}]\, [OH^-]$

$$[H_3IO_6^{2-}] = \frac{[IO_4^-]_T}{1 + K_1\, [OH^-]} \qquad (3)$$

On substituting the value of $[H_3IO_6^{2-}]$ from Eq.(3) to Eq.(2), we get

$$\text{rate} = \frac{2k_5\, K_1K_2K_3K_4\, [IO_4^-]_T\, [AA^-]\, [Rh\,(III)]_T\, [OH^-]\, [Cl^-]}{1 + K_1[OH^-] + K_2[Cl^-] + K_1K_2[OH^-][Cl^-] + K_1K_2K_3\, [IO_4^-]_T [OH^-][Cl^-]} \qquad (4)$$

Under the condition, $1 + K_1K_2[OH^-][Cl^-] >> \{ K_1[OH^-] + K_2[Cl^-]\}$, above Eq. will take the shape of Eq.(5)

$$\text{rate} = \frac{-d[IO_4^-]}{dt} = \frac{2k_5\, K_1K_2K_3K_4\, [IO_4^-]_T\, [AA^-]\, [Rh\,(III)]_T\, [OH^-]\, [Cl^-]}{1 + K_1K_2[OH^-][Cl^-] + K_1K_2K_3\, [IO_4^-]_T [OH^-][Cl^-]} \qquad (5)$$

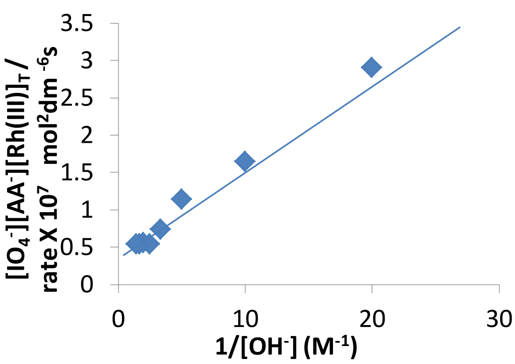
On the basis of observed unity order in $[IO_4^-]$ throughout the variation, the inequality $1+K_1K_2[OH^-][Cl^-] >> K_1K_2K_3[IO_4^-]_T[OH^-][Cl^-]$ can be assumed as valid one and under this condition Eq. (5) will be reduced to Eq. (6).

$$\text{rate} = \frac{-d[IO_4^-]}{dt} = \frac{2\,k_5\;K_1K_2K_3K_4\;[IO_4^-]_T\;[AA^-]\;[Rh\,(III)]_T\;[OH^-]\,[Cl^-]}{1\;+\;K_1K_2[OH^-][Cl^-]} \qquad (6)$$

Eq. (6) is the final rate law which clearly explains our experimental findings, i.e., the unityorder in $[IO_4^-]$, [Threonine] and [Rh(III)] throughout their variation and first-order kinetics with respect to $[OH^-]$, at itslow concentration which tends to zero order at its high concentration.Observed positive effect of $[Cl^-]$ on the rate of reaction is also in accordance with rate law(6). Eq.(6) can also be written as

$$\frac{[IO_4^-]_T\,[AA^-][Rh(III)]_T}{\text{rate}} = \frac{1}{2\,k_5\;K_1K_2K_3K_4\,[Cl^-]\,[OH^-]} + \frac{1}{2k_5\,K_3K_4} \qquad (7)$$

According to Eq.(7), when $[IO_4^-]_T[AA^-][Rh(III)]_T$ / rate values are plotted against 1/ $[OH^-]$ and 1/ $[Cl^-]$ straight lines with positive intercepts on Y-axis will be obtained (Fig-3,4). From the slopes and intercepts of straight lines, the value of $2k_5K_1K_2K_3K_4$ and K_1K_2were calculatedand found as 1.43×10^{12} $mol^{-4}dm^2s^{-1}$and $0.37\times 10^5 mol^{-2}dm^6$ respectively. On substituting the values of $k_5K_1K_2K_3K_4$ and K_1K_2 in Eq. (6) for the variations of $[OH^-]$ and $[Cl^-]$ at constant concentrations of all other reactants, the rate of reaction for each kinetic run has been calculated and found as very close to experimental rates of reaction. This clearly proves the validity of rate law (6) and hence the proposed mechanism. Observed positive entropy of activation is due to most reactive activated complex C_4, becomes less polar than the initial state because of being dispersedover a greater volumewhere interaction is being made between a charge species $C_3$and a neutral water molecule. This further supports the rate determining step and hence the proposed mechanism



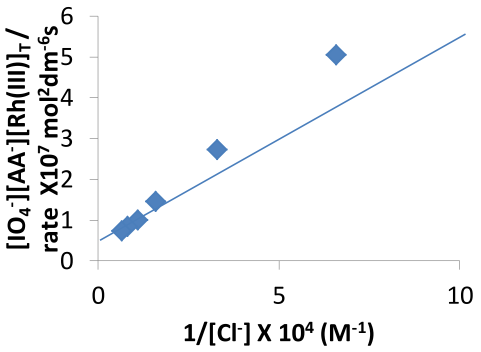


Fig-3: Plot between $[IO_4^-][AA^-][Rh(III)]_T$/ Fig-4: Plot between $[IO_4^-][AA^-][Rh(III)]_T$/raterate and 1/$[OH^-]$ at 35 ^{0}Cand 1/$[Cl^-]$ at 35 ^{0}C

Table-3: Calculated and Experimental values of the rate for the variations of $[OH^-]$ and $[Cl^-]$ in Rh(III)-catalysed oxidation of threonine by IO_4^- at 35^0C

$[OH^-]x10^2$(M)	$[Cl^-]\times10^5$ (M)	$-dc/dt \times 10^7$ (M sec^{-1})	$-dc/dt \times 10^7$ (M sec^{-1})	$-dc/dt \times 10^7$ (M sec^{-1})
		Rate calculated on the basis of rate law(6)	Experimental rates	Rate calculated on the basis of multiple regression analysis
5.00	5.00	2.47	2.60	2.23
10.00	5.00	4.58	4.60	3.78
20.00	5.00	7.89	6.60	6.44
30.00	5.00	10.46	10.30	8.78
40.00	5.00	12.42	13.88	10.94
50.00	5.00	14.07	13.60	12.97
60.00	5.00	15.37	14.00	14.91
70.00	5.00	16.52	13.80	16.77
10.00	1.50	1.54	1.50	1.31
10.00	3.00	2.92	2.77	2.41
10.00	6.00	5.31	5.18	4.45
10.00	9.00	7.31	7.50	6.36
10.00	12.00	9.00	9.00	8.22
10.00	15.00	10.46	10.33	10.01

Multiple regression analysis

Multiple regression analysis has also been used to calculate orders for the variation of each [Rh(III)], $[OH^-]$ and [Threonine] and in each case it has been found that the reaction rates calculated on the basis of equations of fitted model for threonine are in close agreement with observed rates and the rates calculated on the basis of the rate law (6)(Table-3). This also proves the validity of rate law (6) and hence the proposed mechanism. The equation of the fitted model is,

Col_1 = 10.4164 +0.893477* Col_2 + 0.764723* Col_3+ 0.921254* Col_4 + 0.884501* Col_5

Where Col_1 = ln k_1,Col_2 = ln$[AA^-]$, Col_3 = ln$[OH^-]$, Col_4 = ln[Rh(III)] and Col_5 = ln $[Cl^-]$

Applications

Based on the observed kinetic data and spectroscopic evidence, a most probable reaction path for Rh(III)- catalyzed oxidation of threonine by sodium metaperiodate in alkaline medium has been proposed.

Conclusion

Making basis to the observed kinetic data and spectrophotometric information, the following conclusions for the oxidation of threonine by sodium metaperiodate using Rh(III) as catalyst in alkaline medium were derived

1. $[H_2IO_6]^{3-}$and anionic form of threonine have been assumed as the reactive species of periodate and threonine respectively in alkaline medium.
2. The positive effect of $[Cl^-]$ on the rate of reaction indicates that $[RhCl_4(H_2O)_2]^-$ is the reactive species of Rh(III) chloride in alkaline medium.
3. The observed kinetic and spectral data is well supported by the formation of a reactive complex, C_3, between reactive species of Rh(III)chloride and IO_4^- in alkaline medium.
4. The observed spectroscopic data supports the interaction between charged species, C_3 and anionic form of threonine, in Eq. (IV) of reaction scheme 1.

5. Threonine keto acid is formed by the decomposition of most reactive activated complex, C_4.

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