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Kinetic studies of Rh(III)-catalysed oxidation of pentoxifylline by potassium iodate in alkaline medium

Ashok Kumar Singh*, Ritu Swamini Bala, Jaya Srivastava, Ranju Pradhan, Rupam Yadav, Shahla Rahmani

Department of Chemistry, University of Allahabad, Allahabad, 211002, India

Abstract : The kinetic and mechanistic investigation of pentoxifylline by potassium iodate in alkaline medium using Rh(III) as homogeneous catalyst has been carried out at 35^0C. The reaction shows first-order dependence on Rh(III) and pentoxifylline concentration. The order of reaction was found to be fractional positive with respect to $[IO_3^-]$. Variation of $[OH^-]$ and $[Cl^-]$ showed no effect on the rate of the reaction. The reaction remains unaffected by the change in ionic strength and dielectric constant of the medium. Various activation parameters (E_a, $\Delta H^\#$, $\Delta S^\#$, $\Delta G^\#$, and A)were calculated with the help of rate constants obtained at four different temperatures. $[RhCl_3(H_2O)_3]$ was postulated as the reactive species of Rh(III) chloride in alkaline medium. 1-(5-carboxy-pentyl)-3,7-dimethyl-3,7-dihydro-purine-2,6-dione and formaldehyde were identified as the main oxidation products. A suitable mechanism consistent with kinetic observations and spectroscopic information has been proposed which is supported by the observed positive entropy of activation.

Keywords : Pentoxifylline, Rh(III)-catalysis, Spectroscopic information, Multiple regression analysis, Alkaline medium.

Introduction

Rosenberg et al.[1] introduced an interest in the study of biological properties of transition metal complexes. It is reported[2,3] that rhodium complexes are versatile catalysts. Though rhodium is not a bio-essential element, its compounds have useful applications in the biological field. Rh(III) complexes are also reported[4,5,1] to have outstanding anticancer properties, chemical reactivity, antibacterial and antitumor activity, electronic structure and catalytic functions with potential industrial applications. A number of Rh(III)-catalyzed[6-9] kinetic studies for the oxidation of various organic compounds like sugars, alcohols, ketones, amino acids and antibiotics etc. in acidic and alkaline medium have been reported. Pentoxifylline (3,7-dimethyl-1-(5-oxo-hexyl)-3,7-dihydro-purine-2,6-dione) (PTX), a tri-substituted purine and xanthine derivative with many anti-inflammatory effects[10]. It is a hemorheologic agent used to treat intermittent claudication resulting from peripheral arterial disease[11]. Apart from its well-known hemorheological properties[12] and medicinal value, it exhibits a wide range of immunological activities[13]. Reports are available in literature on the oxidation of pentoxifylline by copper(III) periodate complex[14,15]. Potassium iodate has been used as an oxidant in catalysed oxidation of many organic compounds[16-18]. Though few studies are available on the catalysed oxidation of pentoxifylline but no information is available where Rh(III)chloride has been used as catalyst in the oxidation of pentoxifylline by KIO_3 in alkaline medium, the present study has been undertaken. The aim of the present study is to propose the most probable reaction path for the kinetics of oxidation of biologically important pentoxifylline by KIO_3 using chloro complex of Rh(III) as homogeneous catalyst in alkaline medium and to check the possibility of the formation of a complex between the reactive species of Rh(III) chloride and the reactive species of KIO_3 in alkaline medium.

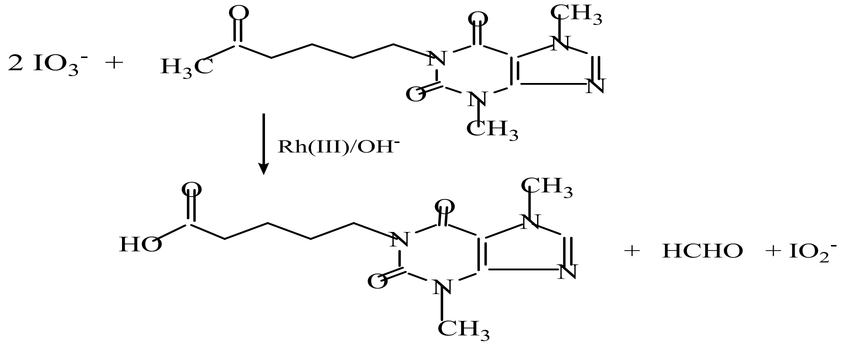
Experimental

All chemicals used were of reagent grade and double distilled water was used throughout the work. Aqueous solution of PTX (Sigma Aldrich) was prepared fresh each day. A solution of Rh(III) chloride (Loba) was prepared in HCl of known strength. A stock solution of KIO_3 (E. Merck) was prepared by dissolving a weighed amount in double-distilled water, and its concentration was ascertained iodometrically. All other standardized solutions of NaOH(Qualigens),KCl, $NaClO_4$, $HClO_4$ (E Merck), KI (Qualigens) and sodium thiosulphate were prepared with double distilled water.

All the kinetic measurements were carried out at constant temperature 35^0Con a thermostatic water bath. The reaction mixture containing the desired volume of all reactants except PTX was taken in conical flask in the thermostatic bath for thermal equilibrium. The required volume of PTX solution, also equilibrated at the same temperature, was poured immediately into reaction mixture to initiate the reaction. Reaction rates were measured by following the decrease of iodate concentration with time iodometrically.

Stoichiometry and product analysis

To probe the reaction stoichiometry, a set of solutions of varying $[IO_3^-]$:[PTX] ratios were equilibrated at room temperature for 72 h under the conditions of $[IO_3^-]$ >> [PTX]. Determination of unconsumed IO_3^- indicated that two moles of IO_3^- were required to oxidise one mole of PTX. Accordingly, the following stoichiometric equation isproposed:



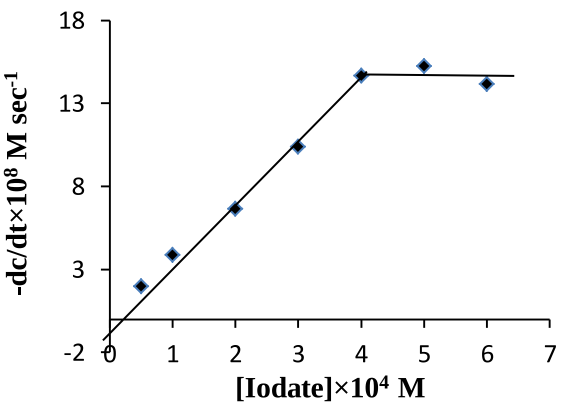
1-(5-carboxy-pentyl)-3,7-dimethyl-3,7-dihydro-purine-2,6-dione and formaldehyde were identified as the main oxidation products by the help of equivalence and kinetic studies.

Results and Discussion

For the determination of the order of reaction with respect to each reactant, the help of Ostwald's isolation method in conjunction with van't Hoff's differential method has been taken. The rate of reaction (−d*c*/d*t*) was determined by the slope of the tangent drawn at a fixed $[IO_3^-]$ in each kinetic run.The first-order rate constant (k_1) was calculated from

$$k_1 = (-dc/dt) / [IO_3^-]$$

Figure 1 where –dc/dt values are plotted against varying concentration of IO_3^-, clearly shows that the first-order kinetics observed at low concentration of IO_3^- tends towards zero-order kinetics at its higher concentration.The direct proportionality observed between k_1 and [PTX] clearly shows first-order kineticswith respect to PTX concentration throughout its variation (Figure 2). Unity order in [Rh(III)](Table 1) and nil effects of $[OH^-]$ and $[Cl^-]$ on the rate of oxidation havealso been observed. Variations in ionic strength and dielectric constant of the medium did not show any effect on the rate of reaction. On the basis of observed rate constant at 35,40,45 and 50 ^{0}C, the activation parameters like energy of activation (E_a),enthalpy of activation ($\Delta H^\#$), entropy of activation ($\Delta S^\#$), Gibbs free energy of activation ($\Delta G^\#$) and Arrhenius frequency factor (A) were calculated and found as 16.53×10^3 $KJmol^{-1}$ 66.54 $KJmol^{-1}$,81.30J/Kmol, 41.49$KJmol^{-1}$and $2.51\times10^{17}M^{-2}s^{-1}$respectively.



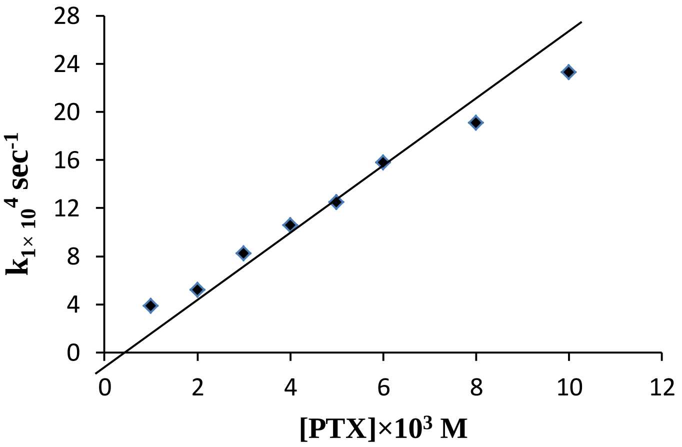


Figure 1.Plot between –dc/dt and $[IO_3^-]$at 35 °CFigure 2.Plot between k_1 and [PTX]at 35 °C
[Rh(III)] = 3.00 ×10^{-8} M,[PTX] = 1.00× 10^{-3} M, [Rh(III)] = 3.00 ×10^{-8} M,$[IO_3^-]$ = 1.00× 10^{-4} M,
[NaOH] = 40.00 × 10^{-2} M, μ = 0.42 M [NaOH] = 40.00 × 10^{-2} M, μ =0.42 M

Reactive species of potassium iodate in alkaline medium

Reports are available where kinetic studies for Ru(III)-[19,20] and Os(VIII)-catalysed[19] oxidation of organic substrates by potassium iodate in acidic medium have been made. In these reports either HIO_3 or IO_3^- has been taken as the reactive species of potassium iodate in acidic medium. Reports are also available where using $NaIO_4$ as an oxidant the kinetic studies for Ru(III)-[21] and ruthenate ion-catalysed[22] oxidation of redusing sugars in alkaline medium have been made. In these studies, it is concluded that IO_4^- is converted into IO_3^- which indicates that IO_3^- is the stable species of potassium iodate in alkaline medium.In this case,when an effort was made to find support for the reactive species of KIO_3 in alkaline medium on the basis of spectral information, it was found that there is a single peak at 192 nm for KIO_3 in alkaline medium which does not change when the change in concentration of hydroxyl ions was made. The spectra of various alkaline solutions of KIO_3 showing single peak provides further support for the assumption that IO_3^- is the reactive species of KIO_3 in alkaline medium. In view of the reported kinetic data and spectral evidence, it can very easily be concluded that the species IO_3^- is the reactive species of KIO_3 in the oxidation of PTX in alkaline medium.

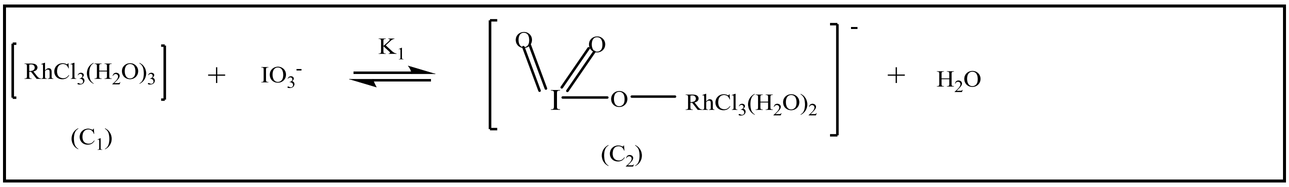
Reactive species of Rh(III) chloride in alkaline medium

In the present study of the oxidation of PTX by KIO_3, Rh(III) chloride has been used as homogeneous catalyst. The solution of Rh(III) chloride was prepared in 3M HCl solution and its strength was determined as 3.79 x 10^{-3}M. This stock solution was further diluted and in each kinetic run, the Rh(III) chloride concentration was in the order of 10^{-8} M. James and Remple[23] have found that $RhCl_3$ in 3-5 M HCl solutions exists mainly in the form of $[Rh(H_2O)Cl_5]^{2-}$. Their findings are contrary to the results reported by Harrod and Halpern[24], who had observed that $[RhCl_6]^{3-}$ is the predominant species of $RhCl_3$ in 3-5 M HCl solutions. In the study regarding hydration of acetylenes catalyzed by Rh(III) chloride complexes, James and Remple[25]have observed that the activity of the $[Rh(H_2O)Cl_5]^{2-}$ species in 0.2 M HCl-5.80 M $HClO_4$ is about twice that in the 3 M HCl media and this is likely due to an increase in the C_2H_2 solubility by about 2. According to them, the cationic species show no reactivity and neutral $[RhCl_3(H_2O)_3]$ species shows reactivity and this reactivity increases to a maximum for a solution containing 5:1chloro species. They have further observed that the hexachloro complex is very much less active. On the basis of reported[23,24,26,27]literature, it can be inferred that at 3M HCl, the lone species $[RhCl_6]^{3-}$ is present in the solution of Rh(III) chloride at the time of its preparation, which can very easily be converted into $[RhCl_5(H_2O)]^{2-}$, $[RhCl_4(H_2O)_2]^{1-}$ and $RhCl_3(H_2O)_3$ with the dilution. In view of earlier reports[28] and observed order with respect to[Rh(III)] and $[OH^-]$ and also in view of the spectrum collected for Rh(III) chloride solution, $[RhCl_3(H_2O)_3]$ can be considered as the starting species of Rh(III) chloride in alkaline medium. This assumption is supported by the nil effect of $[Cl^-]$ on the rate of oxidation.

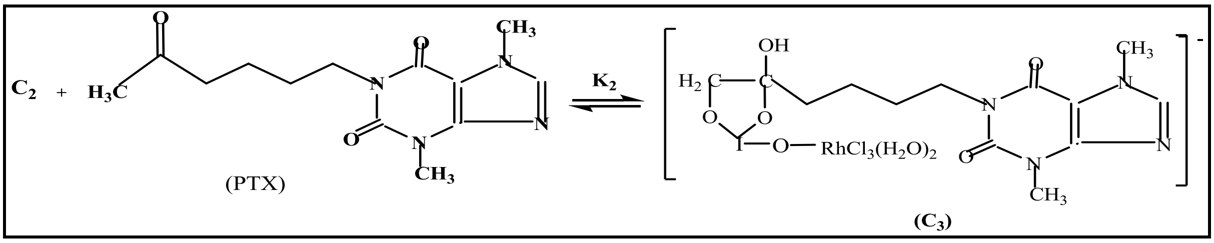
Spectroscopic evidence for the formation of complexes during the course of reaction

Efforts have been made to verify the possible formation of complexes in the reaction by obtaining spectra with the help of VARIAN CARY WIN UV–VIS spectrophotometer (Figure 3). Initially, the spectra for

$RhCl_3(H_2O)_3$and $RhCl_3(H_2O)_3$ and OH^- solutions were recorded. When two different concentrations of KIO_3 were added to the solution of Rh(III) and OH^-, it was found that there is an increase in absorbance from 0.201 to 0.377 and 0.539 (Figure 3: (3,4)). This increase in absorbance with the increase in [KIO_3] is due to more and more formation of a complex between reactive species of Rh(III) chloride i.e. [$RhCl_3(H_2O)_3$]and reactive species of KIO_3 i.e. IO_3^- according to the following equilibrium:



Further when five different concentrations of PTX were added to the solution of Rh(III), OH^- and KIO_3, it was found that there is an increase in absorbance from 0.539 to 0.637, 0.861,1.153,1.598 and 1.992with a slight shift in λ_{max} value towards longer wavelength, that is, from 273.47 to 274.30 nm (Figure 3: (5)-(9).This indicates that PTX will combine with the complex, C_3 to form a new complex according to the following equilibrium-



The formation of this 1:1 complex, $C_3$is supported by Job's plot[29] ($1/\Delta A$ vs $1/[S]$) where a straight line with positive intercept on y-axis was obtained (Figure 4). ΔA on y-axis indicates the difference in absorbance of the solution containing Rh(III), OH^-, KIO_3 and PTXand the solution containing Rh(III) and OH^- and KIO_3.

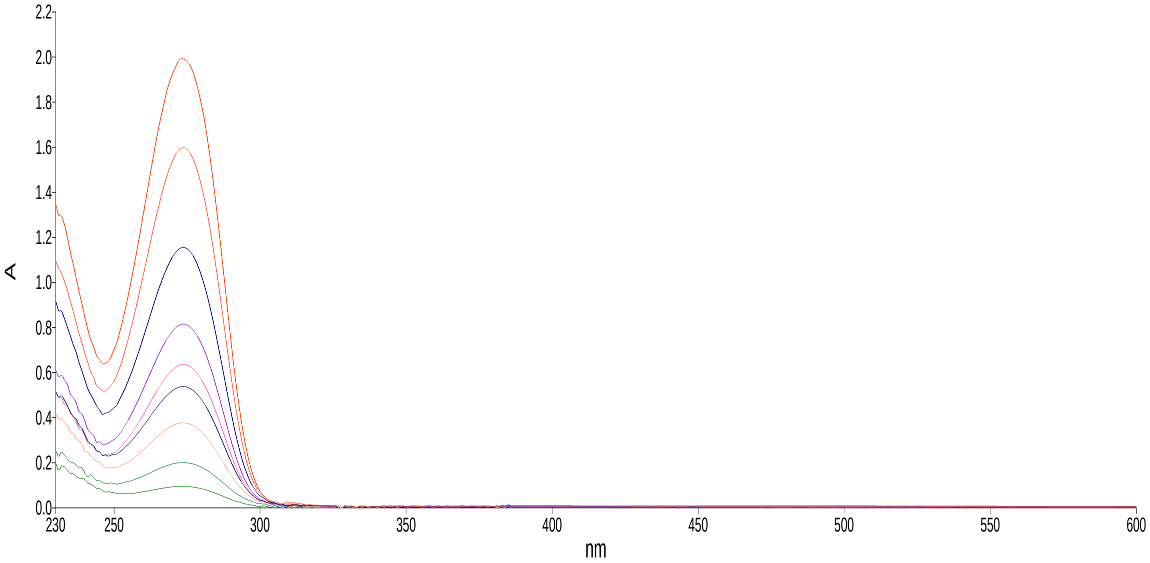


Figure 3: Spectra of various solutions containing Rh(III), OH^-, KIO_3 and PTX at room temperature (1)[Rh(III)] = 3.80×10^{-6} M, (2) [Rh(III)] =3.80×10^{-6} M, [OH^-] = 10.00×10^{-4} M,(3) [Rh(III)] = 3.80×10^{-6} M, [OH^-] = 10.00×10^{-4} M,[IO_3^-] = 1.00×10^{-5} M (4) [Rh(III)] = 3.80×10^{-6} M, [OH^-] = 10.00×10^{-4} M, [IO_3^-] = 3.00×10^{-5} M, (5) [Rh(III)] = 3.80×10^{-6} M, [OH^-] = 10.00×10^{-4} M, [IO_3^-] = 3.00×10^{-5} M,[PTX] = 1.00×10^{-4} M,(6) [Rh(III)] = 3.80×10^{-6} M, [OH^-] = 10.00×10^{-4} M, [IO_3^-] = 3.00×10^{-5} M, [PTX]=2.00×10^{-4} M, (7) [Rh(III)] =3.80×10^{-6}M, [OH^-] = 10.00×10^{-4} M, [IO_3^-] = 3.00×10^{-5} M, [PTX] = 4.00×10^{-4}M,(8)[Rh(III)] =3.80×10^{-6}M, [OH^-] = 10.00×10^{-4} M, [IO_3^-] = 3.00×10^{-5} M,[PTX] = 6.00×10^{-4}M (9)[Rh(III)] =3.80×10^{-6}M, [OH^-] = 10.00×10^{-4} M, [IO_3^-] = 3.00×10^{-5} M,[PTX] = 8.00×10^{-4}M

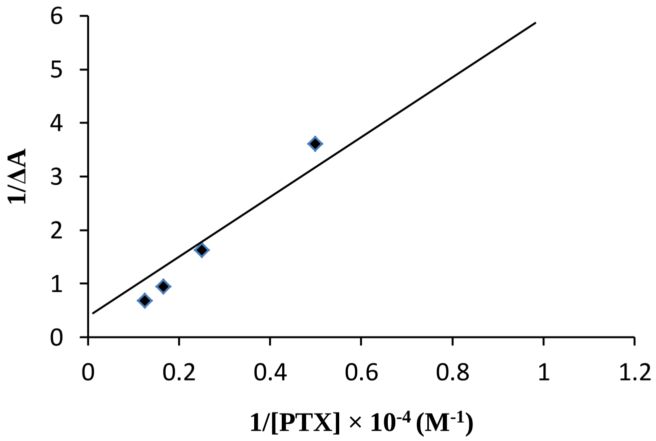
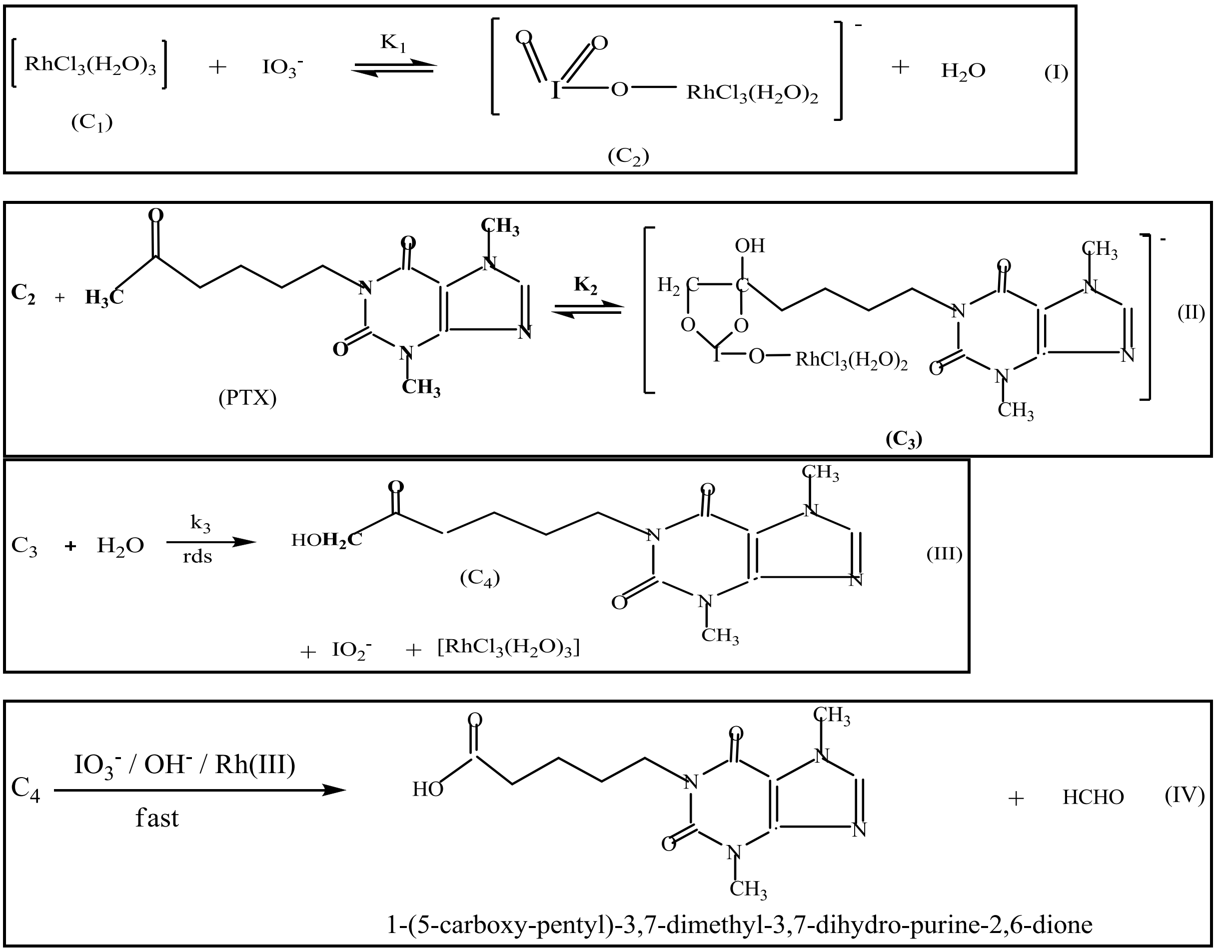


Figure 4:Plot between 1/ΔA and 1/[PTX] [Rh(III)] = 3.80× 10^{-6}M, [OH^-] = 10.00×10^{-4} M, [KIO_3] = 3.00×10^{-5} M

Reaction mechanism and derivation of rate law

On the basis of observed kinetic orders with respect to reactants involved in the reaction, spectroscopic evidence collected for the formation of complexes during the course of reaction and the positive entropy of activation, a most probable reaction scheme 1 in the following form can be proposed-



Scheme 1

On the basis of scheme-1, the rate in terms of disappearance of IO_3^- can be expressed as-

$$\text{rate} = -\frac{d[IO_3^-]}{dt} = 2k_3[C_3] \quad (1)$$

On applying the law of chemical equilibrium to steps (I) and (II), we get equations (2) and (3) respectively,

$$K_1 = \frac{[C_2]}{[C_1][IO_3^-]}, \quad [C_2] = K_1[C_1][IO_3^-] \quad (2)$$

$$\text{and} \quad K_2 = \frac{[C_3]}{[C_2][PTX]}, \quad [C_3] = K_2[C_2][PTX]$$

$$[C_3] = K_1K_2[C_1][PTX][IO_3^-] \quad (3)$$

At any moment in the reaction, the total concentration of Rh(III) i.e. $[Rh(III)]_T$ can be shown as-

$$[Rh(III)]_T = [C_1] + [C_2]$$

$$\text{Or} \quad [Rh(III)]_T = [C_1] + K_1[C_1][IO_3^-]$$

$$\text{Or} \quad [Rh(III)]_T = [C_1]\{1 + K_1[IO_3^-]\}$$

$$\text{Or} \quad [C_1] = \frac{[Rh(III)]_T}{1 + K_1[IO_3^-]} \quad (4)$$

With the help of equations (1), (3) and (4), we can write the expression for the rate of reaction as-

$$\text{rate} = -\frac{d[IO_3^-]}{dt} = \frac{2k_3K_1K_2[Rh(III)]_T[PTX][IO_3^-]}{1 + K_1[IO_3^-]} \quad (5)$$

Equation (5) is the final rate law which is in agreement with the kinetic observations made for the effect of $[IO_3^-]$, $[Rh(III)]_T$, $[OH^-]$ and [PTX] on the rate of oxidation of PTX.

On reversing equation (5), we have equation (6)

$$\frac{[Rh(III)]_T[PTX]}{\text{rate}} = \frac{1}{2k_3K_1K_2[IO_3^-]} + \frac{1}{2k_3K_2} \quad (6)$$

According to equation (6), if a plot is made between $[Rh(III)]_T$ [PTX]/rate and $1/[IO_3^-]$, a straight line having positive intercept on *y*-axis will be obtained. When a plot between $[Rh(III)]_T$ [PTX]/rate and $1/[IO_3^-]$ was made, a straight line having positive intercept on *y*-axis was obtained (Figure 5).This not only proves the validity of rate law (5) butalso gives support to the proposed reaction scheme 1. From the slope and intercept of the straight line, the values of k_3K_2 and K_1were calculated and found as $0.83\times10^4 M^{-1} s^{-1}$ and $7.9\times10^2 M^{-1}$, respectively.Utilizing these values of rate constants, the reaction rates for the variations of $[OH^-]$, $[IO_3^-]$, [Rh(III)] and [PTX] have been calculated according to the rate law (5) and found to be in close agreement with the observed rates (Table 1). This further confirms the validity of rate law (5).

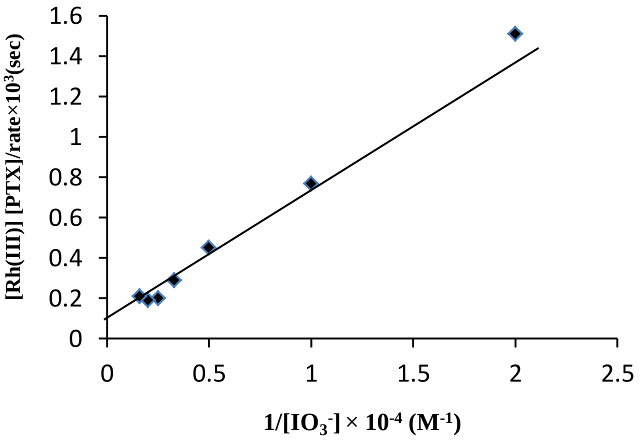


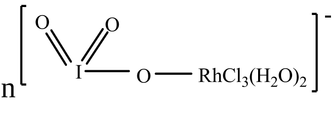
Figure 5: Plot between $[Rh(III)]_T$ [S]/rateand $1/[IO_3^-]$ [Rh(III)] = 3.00 $\times 10^{-8}$ M, $[OH^-]$ = 40.00× 10^{-2} M, [PTX] = 1.00 × 10^{-3} M, μ = 0.42 M

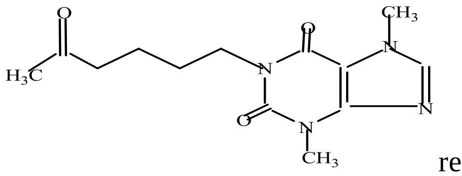
Table 1: Comparison of observed rates with the rates calculated for the variation of [Rh(III)] and [PTX]in the Rh(III)-catalysed oxidationof PTX at 35 °C

[PTX] × 10^3 (M)	**[Rh(III)] $\times 10^8$ (M)**	**− d*c*/d*t* ($\times 10^7$ M s^{-1})**		
		Experimental	**Calculated on the basis of rate law (5)**	**Calculated by Multiple Regression Analysis (Eq. 7)**
1.00	3.00	0.38	0.37	0.43
2.00	3.00	0.52	0.68	0.68
3.00	3.00	0.82	0.95	0.90
4.00	3.00	1.06	1.19	1.10
5.00	3.00	1.25	1.38	1.27
6.00	3.00	1.58	1.61	1.44
8.00	3.00	1.91	1.92	1.74
10.00	3.00	2.33	2.22	2.03
1.00	1.00	0.19	0.12	0.15
1.00	2.00	0.30	0.24	0.29
1.00	3.00	0.38	0.36	0.43
1.00	4.00	0.53	0.50	0.56
1.00	5.00	0.70	0.62	0.70
1.00	6.00	0.84	0.77	0.83
1.00	8.00	1.25	1.11	1.11
1.00	10.00	1.50	1.43	1.35

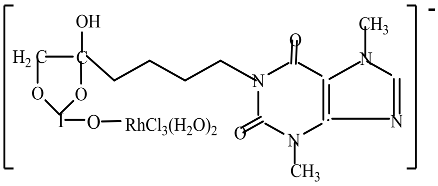
Solution conditions- $[IO_3^-]$ = 1.00×10^{-4} M, $[OH^-]$ = 40.00×10^{-2} M, μ = 0.42 M

Role of entropy of activation

It is a known fact[30] that for reactions between two oppositely charged species there is generally an entropy increase in going from reactant to activated complex whereas for reactions between two similarly charged species there is decrease in the entropy of activation.When reaction takes place with the involvement of an ion and a molecule or dipole the transition state will have the same charge, but it will be dispersed over a greater volume, as a result of which the transition state will be less polar than the reactants. This would lead to an increase in entropy. In the present study of Rh(III)-catalysed oxidation of PTX, the observed positive entropy of activation is due to an interaction between an ion  and a molecule,



resulting in the formation of a complex, C_3, i.e.



in the step before rate determining step. This is also supported by the spectroscopic evidence collected for the formation of complex, C_3, in the step (II) of the proposed mechanism and also by the negligible effect of μ on the rate of oxidation of PTX.

Multiple regression analysis

Multiple regression analysis has also been used to calculate rates for the variation of each [Rh(III)] and [PTX] in the oxidation of PTX. Table 1 shows that the reaction rates calculated on the basis of equation of fitted model (Eq.7) are in close agreement with the observed rates and the rates calculated on the basis of the rate law (5). This further proves the validity of rate law (5) and hence the proposed reaction path. The equation of the fitted model is:

$$\text{Col\_1} = 5.80311 + 0.919799*\text{Col\_2} + 0.827972*\text{Col\_3} \qquad (7)$$

Where, Col_1 = ln k_1, Col_2 = ln[Rh(III)], Col_3 = ln [PTX]

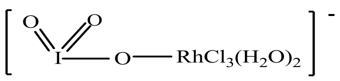
Comparative studies

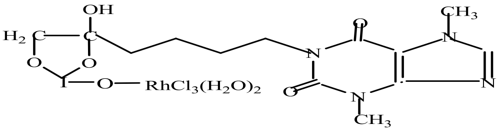
The results of the present study of Rh(III)-catalysed oxidation of PTX by potassium iodate in alkaline medium was compared with the results reported for Os(VIII)-catalysed[14] oxidation of PTX by alkaline copper(III) periodate complexand Ru(III)-catalysed[15] oxidation of PTX by copper(III) periodate complex in alkaline medium. When the present study has been made for the effect of $[IO_3^-]$ on the rate of oxidation, it is found that the first-order kinetics observed at low concentration of IO_3^- tends towards zero-order at its higher concentration. Contrary to this, first-order kinetics with respect to oxidant i.e. diperiodatocuprate(III) was obtained throughout its variation in both the reported studies. The observed direct proportionality between the rate and [PTX] throughout its variation in the present study is different from less than unity order in [PTX] reported for Os(VIII)- and Ru(III)-catalysed oxidation. In the present study as well as in the reported other two studies, the order with respect to catalyst concentration was found to be unity. Observed nil effect of $[OH^-]$ on the rate of oxidation in the present study is entirely different from other two reported studies where the increase in the rate of reaction with the increase in $[OH^-]$ was found. On the basis of observed kinetic data and spectroscopic evidence collected, it is concluded that $[RhCl_3(H_2O)_3]$ is the reactive species of Rh(III) chloride in the present study of oxidation of PTX in alkaline medium. $[OsO_4(OH)_2]^{2-}$and $[Ru(H_2O)_5OH]^{2+}$ were found as the reactive species of Os(VIII) and Ru(III), respectively in other two reported studies. Positive entropy of activation was observed in the present study as well as in the reported Os(VIII)-catalysed oxidation whereas on the basis of negative entropy of activation in the reported Ru(III)-catalysed oxidation, it is suggested that the intermediate complex is more ordered than the reactants. In view of the facts mentioned above, it can very easily be said that the present study is different in many respects from the other two studies reported earlier.

Conclusions

The following conclusions were derived from the observed kinetic data and spectroscopic evidence collected for Rh(III)-catalysed oxidation of PTX by potassium iodate in alkaline medium-

1. IO_3^- and $[RhCl_3(H_2O)_3]$ have been determined as the reactive species of potassium iodate and Rh(III) chloride in alkaline medium, respectively.

2. In step (I) of the proposed reaction scheme1, the formation of complex, C_2, that is  between reactive species of Rh(III) chloride and reactive species of KIO_3 in alkaline medium is well supported by the observed kinetic data and spectral information.

3. An interaction between a charged species, C_2 and a neutral molecule, PTX resulting in the formation of most reactive activated complex, C_3 i.e.  in the step (II) of the proposed reaction scheme 1 is not only supported by the spectroscopic evidence but also by the observed positive entropy of activation and Job's plot.

4. There is no effect of ionic strength of the medium (μ) on the rate of oxidation of PTX.

5. The close similarly between the observed rates and the rates calculated on the basis of multiple regression analysis, eq. (7) clearly proves the validity of rate law (5) and hence the proposed reaction scheme 1.

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