"Kinetics of oxidation of tripelennamine hydrochloride by silver (III) periodate complex in presence and absence of ruthenium (III) catalyst"

1 Arunkumar T. Buddanavar

P. G. Department of studies in Chemistry, Karnatak University, Dharwad 580 003, India

2. Sharanappa T. Nandibewoor

P. G. Department of studies in Chemistry, Karnatak University, Dharwad 580 003, India

ABSTRACT

The kinetics of oxidation of Tripelennamine hydrochloride (TPH) drug by silver(III) periodate complex (DPA) have been investigated in presence and absence of ruthenium (III) (Ru(III)) as homogeneous catalyst in aqueous alkaline medium at 298K and at constant ionic strength of 0.2 mol dm^{-3} spectrophotometrically. The reaction between DPA and tripelennamine hydrochloride in alkaline medium exhibits 1:1 stoichiometry in both uncatalyzed and Ru(III) catalyzed reactions (TPH: DPA). The main products was identified and confirmed as ((di-methyl-amino)-methyl)(pyridin-2-yl)-amino (phenyl) methanol by FT-IR and LC-MS spectral studies. Probable mechanisms were proposed and discussed. The activation parameters with respect to slow step of the mechanisms were computed and thermodynamic quantities were also calculated. The catalytic constant was also calculated for catalyzed reaction at different temperatures and activation parameters were computed. The active species of catalyst and oxidant have been identified.

Keywords: Oxidation, Kinetics, Ruthenium (III) catalyst, Tripelennamine hydrochloride, Silver (III) periodate complex.

1. Introduction

Tripelennamine hydrochloride (TPH) is a psychoactive drug and member of the pyridine and ethylenediamine classes that is used as an antipruritic and first-generation antihistamine. It is used in the treatment of asthma, hay fever, rhinitus and urticaria. In addition to its antihistamine

properties, tripelennamine also acts as a weak serotonin reuptake inhibitor (SRI) and dopamine reuptake inhibitor (DRI) [1-3]. Because of its inhibitor properties, tripelennamine is used as the recreational drug.

Diperiodatoargentate(III) (DPA) is a powerful oxidizing agent in alkaline medium with the reduction potential 1.74 V [4]. It is widely used as a volumetric reagent for the determination of various organic and inorganic species [5,6] . Jayaprakash Rao et al. [7,8] have used DPA as an oxidizing agent for the kinetics of oxidation of various substrates. They normally found that order with respect to both oxidant and substrate was unity and OH^- was found to enhance the rate of reaction. It was also observed that they did not arrive at the possible active species of DPA in alkali and on the other hand they proposed mechanisms by generalizing the DPA as $[Ag(HL)L]^{(x+1)-}$. However, Kumar et al.[9–11] put an effort to give an evidence for the reactive form of DPA in the large scale of alkaline pH. When the Ag(III) species are involved, it would be interesting to know which of the species is the active oxidant. In the present investigation, we have obtained the evidence for the reactive species for the DPA in alkaline medium. The DPA is a metal complex with Ag in 3^+ oxidation state like Cu^{3+} in DPC and Fe^{3+} in hemoglobin.

Transition metals are known to catalyze many oxidation-reduction reactions since they involve multiple oxidation states. In recent years, the use of transition metal ions such as osmium, ruthenium, palladium, chromium and iridium either alone or as binary mixtures, as catalysts in various redox processes has attracted considerable interest [12]. The ruthenium (Ru(III)) acts as a catalyst in the oxidation of many organic and inorganic substrates [13,14]. The catalyzed mechanism can be quite complicated due to formation of different intermediate complexes, and different oxidation states of Ru(III). Although the mechanism of catalysis depends on the nature of the substrate, oxidant and on experimental conditions, it has been shown [15] that the metal ions act as catalysts by one of these different paths such as the formation of complexes with reactants or oxidation of the substrate itself or through the formation of free radicals. In earlier reports [16], it has been observed that Ru(III) forms a complex with the substrate, which gets oxidized by the oxidant to form Ru(IV)-substrate complex followed by the rapid redox decomposition to regenerate Ru(III). In another report [17], it has been observed that there involves the formation of a Ru(III)-substrate complex with further cleavage in a concerted manner giving rise to a Ru(I) species, which gets rapidly oxidized by the oxidant to regenerate the catalyst. In some other reports [18], it is observed that Ru(III) forms a

complex with substrate and is oxidized by the oxidant with the regeneration of the catalyst. Hence, understanding the role of Ru(III) in catalyzed reaction is important.

Literature survey reveals that there is no report on the uncatalyzed and catalyzed oxidative mechanism of tripelennamine hydrochloride by diperiodatoargentate(III) in alkaline medium. Such oxidation studies may throw some light on the mechanism of conversions of the compounds in biological systems. In earlier reports of DPA oxidation [18], the order in [OH^-] was found to be less than unity and periodate had a retarding effect in most of the reactions and monoperiodatoargentate(III) (MPA) was considered to be active species. However, in the present study, we have observed entirely different kinetic observations and diperiodatoargentate(III) (DPA) itself is found to be active form of oxidant. In order to understand the active species of oxidant and catalyst, to compute the activity of the catalyst and to propose the appropriate mechanisms, the title reaction is investigated in detail in this present work. An understanding of the mechanism allows the chemistry to be interpreted, understood and predicted.

2. Experimental

2.1. Materials and Reagents

All reagents and chemicals used were of analytical reagent grade and Millipore water was used throughout the work. A solution of TPH (HiMedia Laboratories) was prepared by dissolving an appropriate amount of recrystallized sample in Millipore water. The required concentration of TPH was obtained from its stock solution. A standard stock solution of Ru(III) was prepared by dissolving $RuCl_3$ (S D Fine-Chem.) in 0.20 mol dm^{-3} HCl. The concentration was determined by EDTA titration [19].

A stock standard solution of IO_4^- was prepared by dissolving a known weight of KIO_4 (S.D. Fine - Chem.) in hot water and used after keeping for 24 h to complete the equilibrium. Its concentration was ascertained iodometrically [20] at neutral pH maintained using phosphate buffer. KNO_3 (AR) and KOH (BDH) were used to maintain ionic strength and alkalinity of the reaction, respectively. Aqueous solution of $AgNO_3$ was used to study the product effect, Ag(I). t-Butyl alcohol (S.D. Fine-Chem.) was used to study the dielectric constant of the reaction medium.

2.2. Preparation of DPA

DPA was prepared by oxidizing Ag(I) in presence of KIO_4 as described elsewhere [21]. The mixture of 28 g of KOH and 23 g of KIO_4 in 100 cm^3 of water along with 8.5 g $AgNO_3$ was heated just to boiling and 20 g of $K_2S_2O_8$ was added in several lots with stirring and then allowed to cool. It was filtered through a medium porosity fritted glass filter and 40 g of NaOH was added slowly to the filtrate, whereupon a voluminous orange precipitate agglomerates. The precipitate was filtered and washed three to four times with cold water. The pure crystals were dissolved in 50 cm^3 water and heated to 80 ^{0}C with constant stirring thereby some solid was dissolved to give a red solution. The resulting solution was filtered when it was hot and on cooling at room temperature, the orange crystals separated out and were recrystallized from water.

The DPA complex was characterized from its UV spectrum, which exhibited three peaks at 211, 253 and 362 nm (Fig 1). These spectral features were identical to those reported earlier for DPA [20]. The magnetic moment study revealed that the complex is diamagnetic. The compound prepared was analyzed [21] for silver and periodate by acidifying a solution of the material with HCl, recovering and weighing the AgCl for Ag and titrating the iodine liberated when excess of KI was added to the filtrate for IO_4^-. The stock solution of DPA was used for the required [DPA] in the reaction mixture.

2.3. Instrumentation

All kinetic measurements were performed on a Varian CARY 50 Bio UV- visible spectrophotometer (Varian, Victoria-3170, Australia) and a Peltier Accessory (temperature control) attached. For pH measurements ELICO pH meter model LI 120 was used. The product analysis were carried out by QP-2010S Shimadzu gas chromatograph mass spectrometer and Nicolet 5700-FT-IR spectrometer.

2.4. Kinetic measurements

Kinetic measurements were performed on a Varian CARY 50 Bio UV−visible spectrophotometer. The kinetics was followed under pseudo-first order conditions where [TPH] > [DPA] in both uncatalyzed and catalyzed reactions at 298 ± 0.1 K, unless otherwise specified. In the absence of catalyst the reaction was initiated by mixing the DPA to TPH solution, which

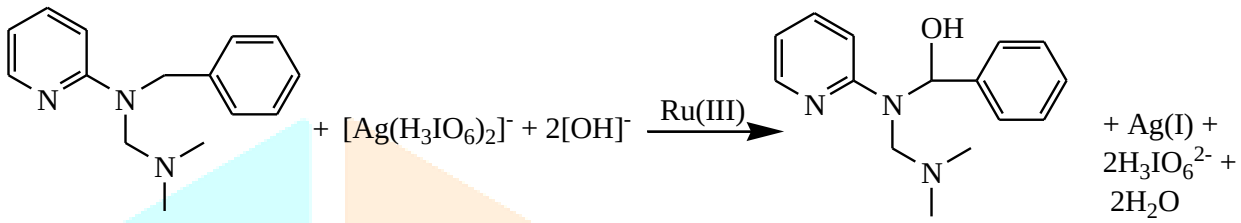
also contained required concentrations of KNO_3, KIO_4 and KOH. The reaction in the presence of Ru(III) catalyst was initiated by mixing the DPA to TPH solution which also contained required concentrations of KNO_3, KOH, KIO_4 and Ru(III) catalyst. Since the initial rate was too fast to be monitored by usual methods in the catalyzed reaction, the kinetic measurements were performed on a spectrophotometer attached to a rapid kinetic accessory. The progress of the reaction was followed spectrophotometrically at 362 nm. The application of Beer's law to DPA at 362 nm was verified and molar absorbency index was found to be 13900 ± 100 dm^3 mol^{-1} cm^{-1}. It was verified that there was almost no interference from other species present in the reaction mixture at this wavelength.

The reaction was followed to more than 85% completion of the reaction. Plots of log(absorbance) versus time lead to the first-order rate constants ('k_U or k_C'). The plots were linear up to 80% completion of reaction. The orders for various species were determined from the slopes of plots of log(k_U or k_C) versus respective concentration of species except for [DPA] in which non-variation of 'k_U and k_C' was observed as expected to the reaction condition. The rate constants were reproducible within ±5%. During the kinetics, a constant concentration viz. 1.0×10^5 mol dm^{-3} of KIO_4 was used throughout the study. The total concentration of OH^- and IO_4^- was calculated by considering the amount present in the DPA solution and that additionally added. Kinetics runs were also carried out in N_2 atmosphere in order to understand the effect of dissolved oxygen on the rate of reaction. No significant difference in the results was obtained under a N_2 atmosphere and in the presence of air. In view of the ubiquitous contamination of carbonate in the basic medium, the effect of carbonate was also studied. The added carbonate had no effect on the reaction rates. In view of the modest concentration of alkali used in the reaction medium, attention was also directed to the effect of the reaction vessel surface on the kinetics. Use of polythene/acrylic wares and quartz or polyacrylate cells gave the same results, indicating that the surface did not have any significant effect on the reaction rates. The spectral changes during the reaction for the standard conditions at 298 K are shown in figure 2. It is evident in the figure that concentration of DPA decreases by observing the absorbance at 362 nm. Regression analysis of experimental data to obtain regression coefficient 'r' and the standard deviation 'S', of points from the regression line, was performed with the Microsoft office Excel-2003 program.

3. Results

3.1. Stoichiometry and product analysis

Different sets of reaction mixtures containing varying ratios of DPA to TPH in presence of constant amount of OH^- and KNO_3 in uncatalyzed reaction and a constant amount of Ru(III) in catalyzed reaction were kept for 2 h in a closed vessel under nitrogen atmosphere. The remaining concentration of DPA was estimated spectrophotometrically at 362 nm. The results indicated 1:1 stoichiometry (TPH: DPA) for both the reactions as given in Scheme 1.



Scheme 1. **Stoichiometry of uncatalyzed and Ruthenium(III) catalyzed Tripelennamine hydrochloride and DPA reaction in alkaline meadium**

The stoichiometric ratio in both the cases suggests the main product as ((di-methyl-amino)-methyl)(pyridin-2-yl)-amino (phenyl) methanol. The product was extracted with ether and recrystallized from aqueous alcohol. It was characterized by FT−IR and GC−MS spectral studies. The nature of the alcoholic –OH was confirmed by the IR spectrum, which shows peaks at 3383 cm^{-1}, 1618 cm^{-1} and 1293 cm^{-1}, for alcoholic –OH stretching, –NH and –CN stretching respectively[22]. Further, the product was subjected to GC−MS spectral analysis. The mass spectrum showed molecular ion peak at 257 amu, confirming ((di-methyl-amino)-methyl)(pyridin-2-yl)-amino (phenyl) methanol (Figure 3). All other peaks observed in GC−MS can be interpreted in accordance with the observed structure of product.

The formation of free Ag^+ in solution was detected by adding KCl solution to the reaction mixture, which produced white turbidity due to the formation of AgCl. It was observed that ((di-methyl-amino)-methyl)(pyridin-2-yl)-amino (phenyl) methanol does not undergo further oxidation under the present kinetic conditions.

3.2. Reaction orders

As the diperiodatoargentate(III) oxidation of tripelennamine hydrochloride in alkaline medium proceeds with a measurable rate in the absence of Ru(III), the catalyzed reaction is understood to occur in parallel paths with contributions from both the catalyzed and uncatalyzed paths. Thus,

the total rate constant (k_T) is equal to the sum of the rate constants of the catalyzed (k_C) and uncatalyzed (k_U) reactions, so $k_C = k_T - k_U$. Hence, the reaction orders have been determined from the slopes of log (k_U or k_C) versus log (concentration) plots by varying the concentrations of TPH, OH^-, $IO_4^-$and catalyst Ru(III), in turn while keeping others constant.

3.3. Effect of varying [DPA]

The oxidant [DPA] was varied in the range of 2.0 x 10^{-5} to 2.0 x 10^{-4} mol dm^{-3} at fixed [TPH], [OH^-], and [IO_4^-] and at constant ionic strength of 0.20 mol dm^{-3} in uncatalyzed and with constant [Ru(III)] in catalyzed reaction and the linearity of the plots of log (absorbance) versus time up to 80% completion of the reaction indicates a reaction order of unity in [DPA] . This is also confirmed by varying of [DPA], which did not result in any change in the pseudo-first-order rate constants, k_U (Table 1 uncatalyzed), k_C (Table 2 Ru(III) catalyzed).

3.4. Effect of varying [TPH]

The effect of TPH was studied for both the cases in the range of 2.0 x 10^{-5} to 2.0 x 10^{-4} mol dm^{-3} at constant concentrations of [DPA], [OH^-],[IO_4^-] and at constant ionic strength of 0.20 mol dm^{-3} in uncatalyzed and with constant concentration of Ru(III) in catalyzed reaction. The k_U and k_C values increased with the increase in concentration of TPH indicating an apparent less than unit order dependence on [TPH] under the conditions of experiment (Table 1 uncatalyzed and Table 2 Ru(III) catalyzed). This was also confirmed by the plots of k_U versus $[TPH]^{0.88}$ and k_C versus $[TPH]^{0.79}$ which were linear rather than the direct plot of k_U versus [TPH] and k_C versus [TPH] (Fig. 4; $r > 0.986$, $S < 0.005$ for uncatalyzed; $r > 0.982$, $S < 0.003$ for Ru(III) catalyzed).

3.5. Effect of varying [alkali]

The effect of alkali concentration was studied for both the uncatalyzed and Ru(III) catalyzed reactions in the range of 0.02 to 0.20 mol dm^{-3} at constant concentrations of [TPH], [DPA], [IO_4^-] and ionic strength of 0.20 mol dm^{-3} in uncatalyzed and with constant concentration of Ru(III) in catalyzed reaction. The rate constants decreased with increase in [alkali] the order was found to be negative fraction in uncatalyzed (Table 1) and in Ru(III) catalyzed reaction (Table 2)

3.6. Effect of varying [periodate]

The effect of periodate concentration was studied for both the uncatalyzed and Ru(III) catalyzed reactions in the range of 0.2 x 10^{-5} to 2.0 x 10^{-5} mol dm^{-3} at constant concentrations of [DPA], [TPH], [OH^-] and ionic strength in uncatalyzed and with constant concentration Ru(III) in catalyzed reaction. It was observed that the added periodate had no effect on the reaction (Tables 1 and Table 2).

3.7. Effect of varying [Ru(III)]

The Ru(III) concentration was varied from 0.2 x 10^{-6} to 2.0 x 10^{-6} mol dm^{-3} range, at constant concentrations of [DPA], [TPH], [OH^-] and ionic strength. The rate constants increased with increase in [Ru(III)] (Table 2) The order in [Ru(III)] was found to be unity from the linearity of the plot of k_C versus [Ru(III)] .

3.8. Effect of varying ionic strength and dielectric constant

The effect of ionic strength (I) was studied for both the uncatalyzed and Ru(III) catalyzed reactions by varying [KNO_3] at constant [DPA], [TPH], [OH^-], [IO_4^-] and [Ru(III)]. It was found that there was no significant effect of ionic strength on the rates of both the uncatalyzed and catalyzed reactions.

The effect of dielectric constant of the medium was studied by varying the t-butyl alcohol and water percentage in the reaction mixture with all the other conditions maintained constant. There was no effect of dielectric constant on the rate of uncatalyzed reaction and Ru(III) catalyzed reaction.

Thus, from the observed experimental results, the rate law for uncatalyzed reaction is given as:

$$\text{Rate} = k_U[\text{DPA}]^{1.0}\,[\text{TPH}]^{0.88}\,[\text{OH}^-]^{-0.66}$$

and the rate law for ruthenium (III) catalyzed reaction is given as:

$$\text{Rate} = k_C[\text{DPA}]^{1.0}\,[\text{TPH}]^{0.79}\,[\text{OH}^-]^{-0.51}\,[\text{Ru(III)}]^{1.0}$$

3.9. Effect of initially added products

In both the cases initially added products, ((di-methyl-amino)-methyl)(pyridin-2-yl)-amino (phenyl) methanol and Ag(I) did not have any significant effect on the rate of reaction.

3.10. Free radical study

For both uncatalyzed and catalyzed reactions, the intervention of free radicals was tested as follows: to the reaction mixture, a known quantity of acrylonitrile (scavenger) had been added initially, was kept for 2 h in an inert atmosphere. On diluting the reaction mixture with methanol, a white precipitate was formed, indicating the intervention of free radicals in the reactions. The blank experiments of either DPA or TPH alone with acrylonitrile did not induce any polymerization under the same condition as those induced for the reaction mixture. Also, initially added acrylonitrile decreases the rate of reaction indicating free radical intervention[23].

3.11. Effect of temperature

The influence of temperature on the rate of reaction was studied for both uncatalyzed and catalyzed reaction at four different temperatures (288, 298, 308 and 318 ^{0}C) under varying concentrations of [TPH] and [alkali] keeping other conditions constant. The rate constant was found to increase with increase in temperature. The rate constant (k_1) of the slow step of the uncatalyzed reaction mechanism was obtained from the slopes and intercepts of plots of $1/k_U$ versus 1/[TPH] and $1/k_U$ versus $[OH^-]$ plots at different temperatures and were used to calculate the activation parameters. The energy of activation corresponding to these constants was evaluated from the Arrhenius plot of $\log k_1$ versus 1/T ($r \geq 0.995$, $S \leq 0.002$) and other activation parameters obtained are tabulated in Table 3.

Similarly, the rate constant (k_2) of the slow step of catalyzed reaction mechanism was obtained from the slopes and the intercept of the plots of $[Ru(III)]/k_C$ versus 1/[TPH] and $[Ru(III)]/k_C$ versus $[OH^-]$ at four different temperatures. The values are given in Table 4 The energy of activation for the rate determining step was obtained by the least square method of plot of log k_2 versus 1/T and other activation parameters calculated for the reaction are presented in Table 4.

3.12. Catalytic activity

It has been pointed out by Moelwyn-Hughes[24] that in presence of the catalyst, the uncatalyzed and catalyzed reactions proceed simultaneously, so that,

$$k_T = k_U + K_C [Catalyst]^x \qquad (1)$$

Here 'k_T' is the total rate constant, 'k_U' the pseudo-first-order rate constant for the uncatalyzed reaction, 'K_C' the catalytic constant and 'x' the order of the reaction with respect to [Ru(III)]. In

the present investigation, x value was found to be unity. Then the value of K_C is calculated using the equation,

$$K_C = \frac{k_T - k_U}{[\text{Catalyst}]^x} = \frac{k_C}{[\text{Catalyst}]^x} \quad (\text{where } k_T - k_U = k_C) \qquad (2)$$

The values of K_C were evaluated for Ru(III) catalyst at different temperatures and were found to vary at different temperatures. Further, plots of log K_C versus 1/T were linear and the values of energy of activation and other activation parameters with reference to catalytic constant were computed. These results are summarized in Table 5.

4. Discussion

In the later period of 20th century the kinetics of oxidation of some organic and inorganic substrates have been studied by Ag(III) species which may be due to its strong versatile nature of two electrons oxidant. Among the various species of Ag(III), $Ag(OH)_4^-$, diperiodatoargentate(III) and ethylenebis (biguanide) (EBS), silver(III) are of maximum attention to the researchers due to their relative stability [25]. The stability of $Ag(OH)_4^-$ is very sensitive towards traces of dissolved oxygen and other impurities in the reaction medium whereupon it had not drawn much attention. However, the other two forms of Ag(III) [26[are considerably stable; the DPA is used in highly alkaline medium and EBS is used in highly acidic medium.

The literature survey [21] reveals that the water soluble diperiodatoargentate(III) has a formula $[Ag(IO_6)_2]^{7-}$ with dsp^2 configuration of square planar structure, similar to diperiodatocopper(III) complex with two bidentate ligands, periodate to form a planar molecule. When the same molecule is used in alkaline medium, it is unlikely to exist as $[Ag(IO_6)_2]^{7-}$, since periodate is known to be in various protonated forms [27] depending on pH of the solution as given in following multiple equilibria (3) – (5).

$$H_5IO_6 \rightleftharpoons H_4IO_6^- + H^+ \qquad (3)$$

$$H_4IO_6^- \rightleftharpoons H_3IO_6^{2-} + H^+ \qquad (4)$$

$$H_3IO_6^{2-} \rightleftharpoons H_2IO_6^{3-} + H^+ \qquad (5)$$

Periodic acid exists as H_5IO_6 in acid medium and as $H_4IO_6^-$ near pH 7. Hence, under alkaline conditions as employed in this study, the main species are expected to be $H_3IO_6^{2-}$and

$H_2IO_6^{3-}$. At higher concentrations, periodate also tends to dimerise. However, formation of this species is negligible under conditions employed for kinetic study. The recent studies have proposed the DPA species as $[Ag(HL)_2]^{x-}$ in which 'L' is a periodate with uncertain number of protons and 'HL' is a protonated periodate of uncertain number of protons. This can be ruled out by considering the alternative form [27] of IO_4^- at pH > 7 which is in the form $H_3IO_6^{2-}$ or $H_2IO_6^{3-}$. Hence, DPA could be as $[Ag(H_3IO_6)_2]^-$ or $[Ag(H_2IO_6)_2]^{3-}$ in alkaline medium. Therefore, under the present condition, diperiodatoargentate(III), may be depicted as $[Ag(H_3IO_6)_2]^-$. The similar speciation of periodate in alkali was proposed [28] for diperiodatonickelate(IV).

4.1. Mechanism for uncatalyzed reaction

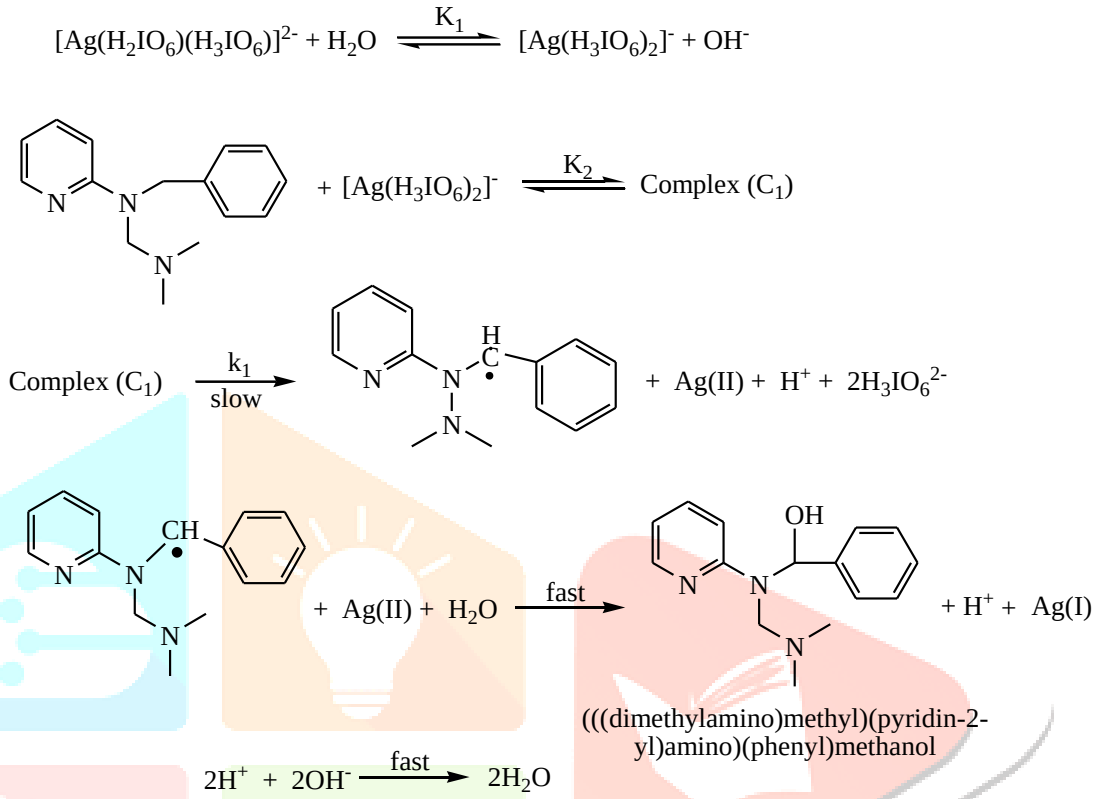
The reaction between DPA and TPH in alkaline medium has the stoichiometry 1:1 (TPH: DPA) with a first order dependence on [DPA] and an apparent order of less than unit order in [substrate], a negative fractional order dependence on [alkali]. No effect of added products was observed. Based on the experimental results, a mechanism is proposed for which all the observed orders in each constituent such as [DPA], [TPH], $[OH^-]$ and $[IO_4^-]$ may be well accommodated.

In the DPA oxidation mechanism of earlier work [18], OH^- had a increasing effect on the rate of the reaction, while periodate has retarding effect on the rate of reaction and DPA itself was considered as active species. However, in the present kinetic study, different kinetic results have been obtained. The result of decrease in rate of reaction with increase in alkalinity can be explained in terms of prevailing equilibrium of formation of $[Ag(H_3IO_6)_2]^-$ from $[Ag(H_2IO_6)(H_3IO_6)]^{2-}$ hydrolysis as given in the following equation(6).

$$[Ag(H_2IO_6)(H_3IO_6)]^{2-} + H_2O \underset{}{\overset{K_1}{\rightleftharpoons}} [Ag(H_3IO_6)_2]^{3-} + OH^- \qquad (6)$$

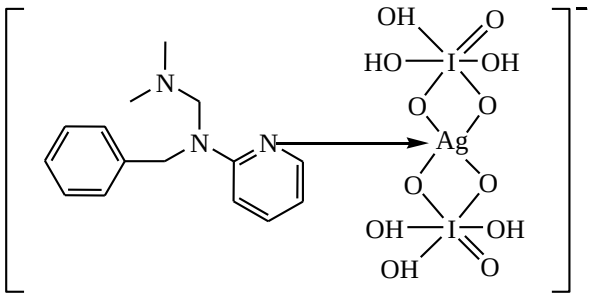
Such type of equilibrium (6) has been well noticed in literature [29]. Because of this reaction and fact that k_U values are inverse function of hydroxyl ion concentration with fractional order in OH^- concentration, the main oxidant species is likely to be $[Ag(H_3IO_6)_2]^-$ and its formation by the above equilibrium is important in the present study. The less than unit order in [TPH] presumably results from formation of a complex (C_1) between the DPA species and TPH prior to the formation of the products. This complex (C_1) decomposes in a slow step to form a free radical derived from TPH. This free radical species further reacts with Ag(II) in a fast step to

form products such as ((di-methyl-amino)-methyl)(pyridin-2-yl)-amino (phenyl) methanol and Ag(I) as given in Scheme 2.



Scheme 2. Detailed mechanism of tripelennamine hydrochloride by diperiodatoargentate(III) with alkaline medium.

The direct plot of k_U versus [TPH] was drawn to know the parallel reaction if any along with interaction of oxidant and reductant. However, the plot of k_U versus [TPH] was not linear. Thus, in Scheme 2, the parallel reaction and involvement of one molecule of TPH in the complex are excluded. The probable structure of the complex (C_1) is given as,



Spectroscopic evidence for the complex formation between oxidant and substrate was obtained from UV–vis spectra of TPH (5.0×10^{-4}), DPA ((5.0×10^{-5}), (OH^- = 0.1 mol dm^{-3}) and a mixture of both. A bathochromic shift of 5 nm from 362 to 367 nm in the spectra of DPA to mixture of DPA and TPH was observed (Figure 5).

The Michaelis-Menten plot proved the complex formation between DPA and TPH, which explains the less than unit order dependence on [TPH]. Such a complex between an oxidant and substrate has also been observed in other studies [18].

Scheme 2 leads to rate law,

$$\text{rate} = \frac{-d[DPA]}{dt} = \frac{k_1 K_1 K_2 [DPA]\ [TPH]}{[OH^-] + K_1 + K_1 K_2 [TPH]} \qquad (7)$$

$$k_U = \frac{\text{rate}}{[DPA]} = \frac{k_1 K_1 K_2 [TPH]}{[OH^-] + K_1 + K_1 K_2 [TPH]} \qquad (8)$$

This explains the all the observed kinetic orders of different species. The rate law can be rearranged into the following equation (9), which is suitable for verification.

$$\frac{1}{k_U} = \frac{[OH^-]}{k_1 K_1 K_2 [TPH]} + \frac{1}{k_1 K_2 [TPH]} + \frac{1}{k_1} \qquad (9)$$

According to above equation other reaction conditions are being constant, the plots of $1/k_U$ versus 1/[TPH] and $1/k_U$ versus $[OH^-]$ should be linear and are found to be so as in Figure 5.

From the slopes and intercepts, the values of k_1, K_1 and K_2 (Table 3), The values of K_1 and K_2 are in good agreement with literature [18]. Using these constants, the rate constants were calculated over different experimental conditions, and there is reasonable agreement between the calculated and the experimental values, which fortifies the proposed mechanism (Scheme 2) and these values are listed in Table 3. A van't Hoff plots were made for variation of K_1 and K_2 with temperature (log K_1 versus 1/T ($r \geq 0.995$, $S \leq 0.001$) and log K_2 versus 1/T ($r \geq 0.986$, $S \leq 0.004$). 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. These values are given in Table 3. A comparison of the ΔH value of second step (11.26 kJ mol^{-1}) of Scheme 2 with that of $\Delta H^{\#}$ (47.60 kJ mol^{-1}) obtained for the slow step of the reaction shows that these values mainly refer to

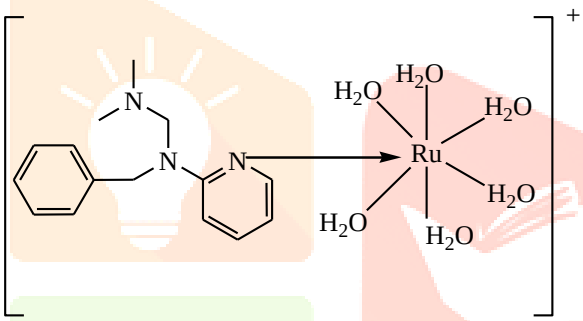
the rate limiting step, supporting the fact that the reaction before rate determining step is fairly fast and involves low activation energy [30].The negligible effect of ionic strength and dielectric constant of medium on the rate might be due to the presence of neutral species as shown in Scheme 2. The high negative value of $\Delta S^{\#}$ (-103.5 JK^{-1} mol^{-1}) suggests the intermediate complex (C_1) is more ordered than the reactants [31].

4.2. Mechanism for Ru(III) catalyzed reaction

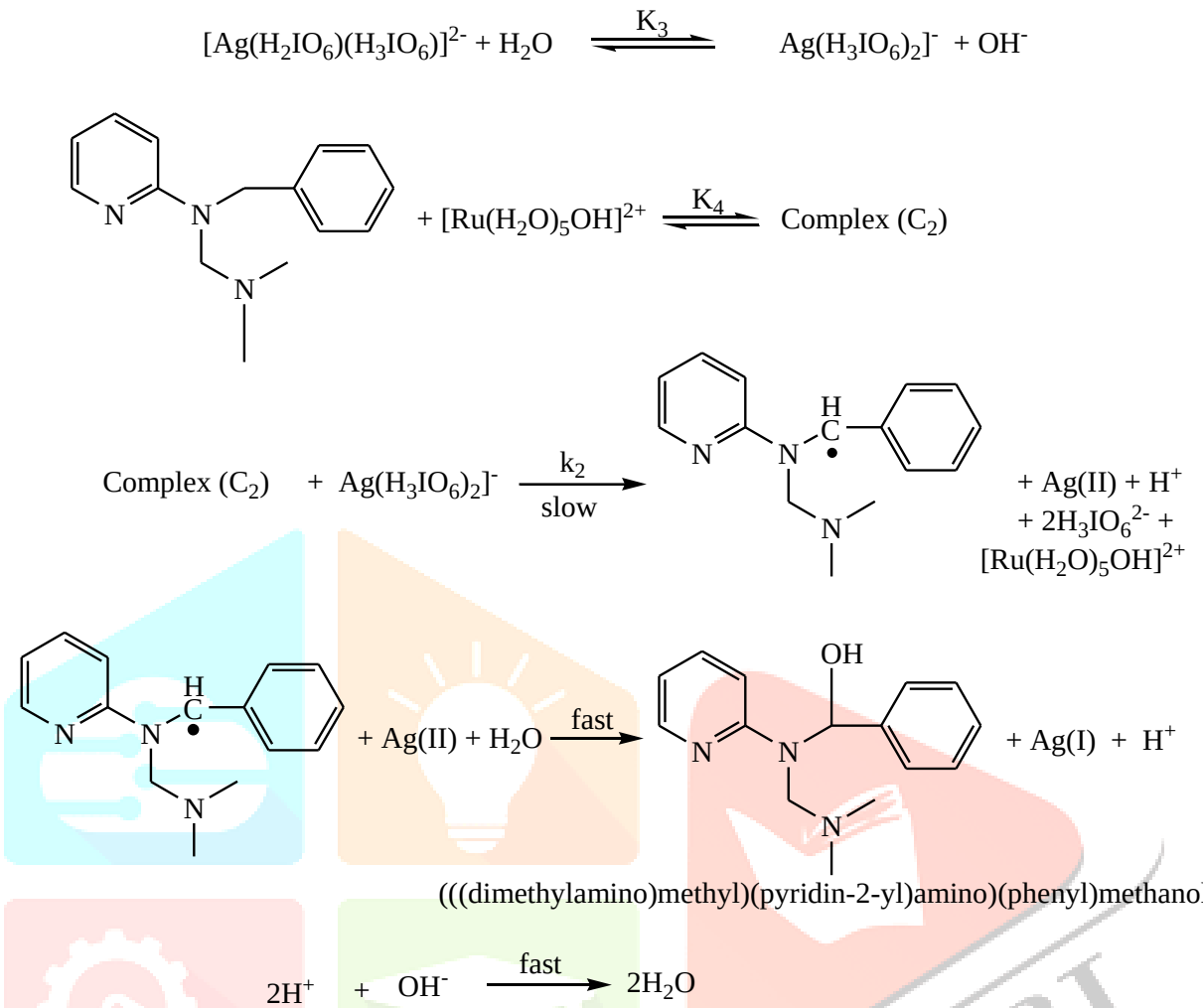
Ruthenium (III) chloride acts as an efficient catalyst in many redox reactions, particularly in an alkaline medium [23]. It is interesting to identify the probable ruthenium (III) chloride species in alkaline media. In the present study it is quite probable that the $[Ru(H_2O)_5OH]^{2+}$ species might assume the general form $[Ru(III)(OH)_x]^{3-x}$. The 'x' value would always be less than six because there are no definite reports of any hexahydroxy ruthenium species. The remainder of the coordination sphere would be filled by water molecules. At higher pH, the electronic spectra studies have confirmed [32] that the ruthenium (III) chloride exists in the hydrated form as $[Ru(H_2O)_6]^{3+}$. Metal ions of the form $[Ru(H_2O)_6]^{3+}$ are also known to exist as $[Ru(H_2O)_5OH]^{2+}$ in an alkaline medium and are most likely mononuclear species. Hence, under the conditions employed, e.g. $[OH^-]$ >> [Ru(III)], ruthenium(III) is mostly present as the hydroxylated species, $[Ru(H_2O)_5OH]^{2+}$. Similar species have been reported between Ru(III) catalyzed oxidation of several other substrates with various oxidants in alkaline medium [33]. In earlier reports of Ru(III) catalyzed oxidation [16,17,18], it has been observed that, if there is a fractional order dependence with respect to [substrate] and Ru(III) and unit order with respect to [oxidant], Ru(III) forms a complex with the substrate. It gets oxidized by the oxidant to form Ru(IV)-substrate complex followed by the rapid redox decomposition to regenerate Ru(III). If the process shows a zeroth order dependence with respect to [oxidant], first order with respect to [Ru(III)] and a fractional order with respect to [substrate], there involves the formation of a Ru(III)-substrate complex. It undergoes further cleavage in a concerted manner giving rise to a Ru(I) species, which is rapidly oxidized by the oxidant to regenerate the catalyst. In some other reports [34, 30] it is observed that Ru(III) forms a complex with substrate and is oxidized by the oxidant with the regeneration of the catalyst. Hence, the study of behavior of Ru(III) in catalyzed reaction becomes significant. The equilibrium step 1 and the stoichiometry were same as in the case of uncatalyzed reaction. In the Ru(III) catalyzed reaction, [DPA] was first order dependence, an apparent order of less than unit order in [TPH], a negative fractional order dependence on [alkali] and order with respect to Ru(III) was found to be unity. No effect of

added products was observed. Based on the experimental results, a mechanism is proposed for which all the observed orders in each constituent such as [DPA], [TPH], [Ru(III)], [OH^-] and [IO_4^-] may be well accommodated.

Spectroscopic evidence for the complex formation between Ru(III) and TPH was obtained from UV–vis spectra of TPH (5.0×10^{-4} mol dm^{-3}), Ru(III) (1.0×10^{-6} mol dm^{-3}, OH^- = 0.1 mol dm^{-3}) and a mixture of both. A hypsochromic shift of 8 nm from 269 nm to 264 nm-in the spectra of Ru(III) to the mixture of Ru(III) and TPH was observed. Attempts to separate and isolate the complex were not successful. The Michaelis-Menten plot proved the complex formation between catalyst and substrate, which explains less than unit order in [TPH]. The possible structure of the complex(C_2) is given as



In the prior equilibrium step 1, the hydroxyl ion concentration with negative fractional order in OH^- concentration, the main oxidant species is likely to be $[Ag(H_3IO_6)_2]^-$ and its formation by the above equilibrium is important in the present study. The less than unit order in [TPH] presumably results from formation of a complex (C_2) between the Ru(III) species and TPH. This complex (C_2) reacts with one mole of DPA in a slow step to give the free radical species of TPH, Ag(II) with the regeneration of catalyst, Ru(III). Further this free radical species of TPH reacts with Ag(II) in a fast step to form the products such as ((di-methyl-amino)-methyl)(pyridin-2-yl)-amino (phenyl) methanol (phenyl) methanol and Ag(I) as given in Scheme 3. The reduction of Ru(III) to lower oxidation state and then regeneration of Ru(III) by oxidant was not possible under the experimental conditions due to observed orders in different constituents of reaction.



Scheme 3. Detailed mechanism for Ru(III) catalyzed oxidation of TPH by diperiodatoargentate(III) with aqueous alkaline medium.

The Michaelis-Menten plot proved the complex formation between catalyst and substrate, which explains less than unit order in [TPH]. Such a complex between a catalyst and substrate has also been observed in earlier studies [35]. From Scheme 3, the rate law (10) is obtained as,

$$\text{rate} = \frac{-d[DPA]}{dt} = \frac{k_2K_3K_4[TPH][Ru(III)][DPA]}{K_3 + [OH]^- + K_3K_4[TPH]^+K_4[TPH][OH]^-} \quad (10)$$

$$\frac{\text{rate}}{[DPA]} = k_C = k_T - k_U = \frac{k_2K_3K_4[TPH][Ru(III)][DPA]}{K_3 + [OH]^- + K_3K_4[TPH]^+K_4[TPH][OH]^-} \quad (11)$$

This explains all the observed kinetic orders of different species. The above equation can be written as below which is suitable for verification.

$$\frac{[Ru(III)]}{k_C} = \frac{[OH]^-}{k_2K_3K_4[TPH]} + \frac{[OH]^-}{k_2K_3} + \frac{1}{k_2K_3[TPH]} + \frac{1}{k_2} \qquad (12)$$

According to equation (12), other conditions being constant, the plots of $[Ru(III)]/k_C$ versus $1/[TPH]$ ($r \geq 0.998$, $S \leq 0.003$) and $[Ru(III)]/k_C$ versus $[OH^-]$ ($r \geq 0.992$, $S \leq 0.005$) should be linear and found to be so (Figure 7). The intercepts and slopes of such plots lead to the values of k_2, K_3 and K_4 (Table 4).

The thermodynamic quantities for the different equilibrium steps, in Scheme 3 can be evaluated as follows. The slopes and intercepts, the values of k_2, K_3 and K_4 were calculated at four different temperatures and are in good agreement with literature [18]. Using these constants, the rate constants were calculated over different experimental conditions, and there is reasonable agreement between the calculated and the experimental values, which fortifies the proposed mechanism (Scheme 3) and these values are listed in Table 4. A van't Hoff plots were made for the variation of K_3 and K_4 with temperature (log K_3 versus $1/T$ and log K_4 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. These values are also given in (Table 4). A comparison of the ΔH value of second step (16.1 kJ mol^{-1}) of Scheme 3 with that of $\Delta H^{\#}$ (12.9 kJ mol^{-1}) obtained for the slow step of the reaction shows that these values mainly refer to the rate limiting step, supporting the fact that the reaction before rate determining step is fairly slow and involves high activation energy [18]. The negative value of $\Delta S^{\#}$ suggests that the intermediate complex is more ordered than the reactants [32] involving distribution of charges as given in Scheme 3.

The negligible effect of ionic strength and dielectric constant might be due to the presence of neutral species in both catalyzed and uncatalyzed reactions (Scheme 2 and 3). The moderate $\Delta H^{\#}$ and $\Delta S^{\#}$ values are favorable for electron transfer reaction. The value of $\Delta H^{\#}$ was due to energy of solution changes in the transition state. The observed modest enthalpy of activation and a higher rate constant for the slow step indicates that the oxidation presumably occurs via an inner-sphere mechanism. This conclusion is supported by earlier observations [36]. The activation parameters evaluated for the catalyzed and uncatalyzed reactions explain the

catalytic effect on the reaction. The catalyst Ru(III) forms the complex (C_2) with substrate which enhances the reducing property of the substrate than that without catalyst. Further, the catalyst Ru(III) modifies the reaction path by lowering the energy of activation.

Conclusion

The comparative study of uncatalyzed and ruthenium (III) catalyzed oxidation of tripelennamine hydrochloride by diperiodatoargentate(III) was studied. Oxidation products were identified and were same in both cases. Among the various species of Ag(III) in alkaline medium, DPA itself, i.e., $[Ag(H_3IO_6)_2]^-$ is considered as active species for the title reaction. Active species of Ru(III) is found to be $[Ru(H_2O)_5OH]^{2+}$. The reaction constants of individual steps in the mechanisms were evaluated for uncatalyzed and Ru(III) catalyzed reactions at different temperatures. The catalytic constants and the activation parameters with reference to catalyst were also computed.

Reference

1 L. R. Goldfrank, N. Flomenbaum, Goldfrank's Toxicologic Emergencies. Mc Graw-Hill, Professional, 2006, pp. 782-787

2 R. Oishi, S. Shishido, M. Yamori, K. Saeki, N. S. Arch, Pharmacol. 349 (1994) 140-144.

3 T. Sato, K. Suemaru, K. Matsunaga, S. Hamaoka, Y. Gomita, R. Oishi, Japan. J. Pharmacol., 71 (1996) 81-84.

4 B. Sethuram, "Some Aspects of Electron Transfer Reactions Involving Organic Molecules", Allied Publishers P. Ltd, New Delhi, 2003.

5 P. K. Jaiswal, K. L. Yadava, Talanta, 17 (1970) 236-238.

6 P. K. Jaiswal, Analyst, 1 (1972) 503-506.

7 P. Jayaprakash Rao, B. Sethuram, T. Navneeth Rao, React. Kinet. Catal. Lett., 29 (1985) 289-296.

8 K. Venkata Krishna, P. Jayaprakash Rao, Indian J. Chem., 37A (1998) 1106-1110.

9 A. Kumar, P. Kumar, P. Ramamurthy, Polyhedron, 18 (1999) 773-782.

10 A. Kumar & P. Kumar, J. Phys. Org. Chem., 12 (1999) 79-88.

11 A. Kumar, P. Vaishali, P. Ramamurthy, Int. J. Chem. Kinet., 32 (2000) 286-293.

12 A. K. Das, Coord. Chem. Rev., 213 (2001) 307-325.

13 K. N. Shivananda, B. Lakshmi, R. V. Jagdeesh, Puttaswamy, K. N. Mahendra, Appl. Catal., A General, 326 (2007) 202-212.

14 P. K. Tandon, A. Mehrotra, M. Srivastava, M. Dhusia, S. B. Singh, Transition Met. Chem., 32 (2007) 991-999.

15 A. K. Singh, S. Srivastava, J. Srivastava, R. Srivastava, P. Singh, J. Mol. Catal. A: Chem., 278 (2007) 72-81.

16 S. Sandu, B. Sethuram, T. N. Rao, J. Indian Chem. Soc., 60 (1983) 198-200.

17 H. P. Panda, B. D. Sahu, Indian J. Chem., 28A (1989) 323-234.

18 S. J. Malode, J. C. Abbar, S. T. Nandibewoor, Inorganic Chimica Acta., 363 (2010) 2430-2442.

19 C. S. Reddy, T. Vijaykumar, Indian J. Chem., 34A (1995) 615-620.

20 G. P. Panigrahi, P. K. Misro, Indian J. Chem., 15A (1977) 1066-1067.

21 G. L. Cohen, G. Atkinson, Inorg. Chem., 3 (1964) 1741-1743.

22 L. J. Bellamy, "The Infrared Spectra of Complex Molecules", (Methuen and Co. Ltd. London), (1958) pp.162-164.

23 R. V. Jagadeesh, Puttaswamy, J. Phys. Org. Chem., 21 (2008) 844-849.

24 E. A. Moelwyn-Hughes, "Kinetics of Reactions in Solutions", (Oxford University Press), London, (1947) p.297-299.

25 L. J. Krishenbaum, L. Mrozowski, Inorg. Chem., 17 (1978) 3718-3719.

26 R. Banerjee, R. Das, S. Mukhopadhyay, J. Chem. Soc., Dalton Trans., 7 (1992) 1317-1321.

27 C. E. Crouthamel, A. M. Hayes, D. S. Martin, J. Am. Chem. Soc., 73 (1951) 82-87.

28 S. Bhattacharya, B. Saha, A. Datta, P. Banerjee, Coord. Chem. Rev., 170 (1998) 47-74.

29 S. J. Malode, N. P. Shetti & S. T. Nandibewoor, Acta Chim. Slov., 56 (2009) 936-945.

30 K. S. Rangappa, M. P. Raghavendra, D. S. Mahadevappa, D. Channegouda, J. Org. Chem., 63 (1998) 531-536.

31 E.S. Lewis"In Investigation of Rates and Mechanism of Reactions in Techniques of Chemistry", Wiley: New York, 1974, pp. 421-427.

32 R. E. Connick & D. A. Fine, J. Amer. Chem. Soc., 82 (1960) 4187-4191.

33 F. A. Cotton, G. Wilkinson, C. A. Murillo, M. Bochmann, "Advanced Inorganic Chemistry", 6th Ed, John Wiley and Sons Inc, New York, 1999.

34 Chanabasayya V. Hiremath, T.S. Kiran, Sharanappa T. Nandibewoor, J. Mol. Catal. A: Chem., 248 (2006) 163-168.

35 K. N. Vinod, Puttaswamy, N. Gowda, J. Mol. Catal. A: Chem., 298 (2009) 60-68.

$[DPA]\times10^5$	$[TPH]\times10^4$	$[OH^-]$	$[IO_4^-]\times10^{-5}$	$k_U\times10^3$ (S^{-1})

36 S. A. Farokhi, S. T. Nandibewoor, Tetrahedron, 59 (2003) 7595-7598.

Table 1.

Effect of variation of [DPA], [TPH], $[OH^-]$ and $[IO_4^-]$ on the oxidation of tripeleammine hydrochloride by diperiodatoargentate (III) in aqueous alkaline medium at 25 ^{0}C and ionic strength *I*=0.20 (mol dm^{-3}).

					Found	Calculated
	2	5	0.1	1.0	2.4	2.5
	5	5	0.1	1.0	2.1	2.5
	8	5	0.1	1.0	2.0	2.5
	10	5	0.1	1.0	1.9	2.5
	15	5	0.1	1.0	2.1	2.5
	20	5	0.1	1.0	2.0	2.5
	5	2	0.1	1.0	0.8	0.9
	5	5	0.1	1.0	2.1	2.5
	5	8	0.1	1.0	2.7	2.9
	5	10	0.1	1.0	3.8	3.9
	5	15	0.1	1.0	4.8	5.1
	5	20	0.1	1.0	6.4	6.7
	5	5	0.02	1.0	5.9	6.2
	5	5	0.05	1.0	3.0	3.5
	5	5	0.08	1.0	2.4	2.8
	5	5	0.1	1.0	2.1	2.5
	5	5	0.15	1.0	1.6	1.9
	5	5	0.2	1.0	1.2	1.4
	5	5	0.1	0.2	2.7	2.9
	5	5	0.1	0.5	2.0	2.3
	5	5	0.1	0.8	2.1	2.6
	5	5	0.1	1.0	2.1	2.5
	5	5	0.1	1.5	1.8	1.9
	5	5	0.1	2.0	1.7	1.8

$[DPA]\times10^5$ (mol dm^{-3})	$[TPH]\times10^4$ (mol dm^{-3})	$[OH]^-$ (mol dm^{-3})	$[IO_4]^-\times10^5$ (mol dm^{-3})	$[Ru(III)]\times10^6$ (mol dm^{-3})	$k_T\times10^3$ (S^{-1})	$k_U\times10^3$ (S^{-1})	$k_2=k_T-k_U\times10^3$ (S^{-1})	
							Found	calculated

Table 2.

Effect of variation of [DPA], [TPH], [OH^-], [IO_4^-] and [Ru(III)] on the ruthenium(III) catalyzed oxidation of tripeleammine hydrochloride by diperiodatoargentate (III) in aqueous alkaline medium at 25 ^{0}C and ionic strength *I*=0.20 (mol dm^{-3}).

2	5	0.1	1.0	1.0	8.8	2.4	6.4	7.9
5	5	0.1	1.0	1.0	9.5	2.1	7.4	7.9
8	5	0.1	1.0	1.0	8.9	2.0	6.9	7.9
10	5	0.1	1.0	1.0	9.2	1.9	7.3	7.9
15	5	0.1	1.0	1.0	9.3	2.1	7.2	7.9
20	5	0.1	1.0	1.0	9.1	2.0	7.1	7.9
5	2	0.1	1.0	1.0	4.3	0.8	3.4	3.7
5	5	0.1	1.0	1.0	9.5	2.1	7.4	7.9
5	8	0.1	1.0	1.0	14.6	2.7	11.8	12.2
5	10	0.1	1.0	1.0	17.2	3.8	13.4	13.8
5	15	0.1	1.0	1.0	22.7	4.8	17.8	18.3
5	20	0.1	1.0	1.0	27.8	6.4	21.3	21.6
5	5	0.02	1.0	1.0	22.2	5.9	16.3	17.2
5	5	0.05	1.0	1.0	14.0	3.0	11.0	11.3
5	5	0.08	1.0	1.0	10.7	2.4	8.3	8.8
5	5	0.1	1.0	1.0	9.5	2.1	7.4	7.9
5	5	0.15	1.0	1.0	7.6	1.6	6.0	6.5
5	5	0.2	1.0	1.0	6.1	1.2	4.9	5.1
5	5	0.1	0.2	1.0	9.7	2.7	7.0	7.4
5	5	0.1	0.5	1.0	9.5	2.0	7.5	7.8
5	5	0.1	0.8	1.0	8.6	2.1	6.5	7.1
5	5	0.1	1.0	1.0	9.5	2.1	7.4	7.9
5	5	0.1	1.5	1.0	8.5	1.8	6.7	7.3
5	5	0.1	2.0	1.0	8.8	1.7	7.1	7.8
5	5	0.1	1.0	0.2	3.7	2.1	1.6	1.9
5	5	0.1	1.0	0.5	5.8	2.1	3.7	4.3
5	5	0.1	1.0	0.8	7.6	2.1	5.5	6.2
5	5	0.1	1.0	1.0	9.5	2.1	7.4	7.9
5	5	0.1	1.0	1.5	12.6	2.1	10.5	11.2
5	5	0.1	1.0	2.0	21.4	2.1	19.3	19.8

Table 3.

Thermodynamic quantities and activation parameters for the oxidation of tripelennamine hydrochloride by diperiodatoargentate(III) in aqueous alkaline medium with respect to slow step Scheme 1.

(A). Effect of temperature on k_1

Temperature (K)	$k_1 \times 10^1$ (s^{-1})
288	0.11

298	0.25
308	0.43
318	0.83

(B). Activation parameter

(B). Parameters	values
Ea(kJ mol^{-1})	50.0
$\Delta H^{\#}$(kJ mol^{-1})	47.6
$\Delta S^{\#}$(J K^{-1} mol^{-1})	-115.6
$\Delta G^{\#}$(kJ mol^{-1})	37.2
logA	7.1

(C). Effect of temperature to calculate K_1 and K_2 for the oxidation of tripelennamine hydrochloride by diperiodatoargentate (III) with aqueous alkaline medium.

Temperature (K)	$K_1 \times 10^1$ (mol dm^{-3})	$K_2 \times 10^{-4}$ (dm^3 mol^{-1})
288	0.16	0.08
298	0.22	0.10
308	0.28	0.11
318	0.39	0.13

(D). Thermodynamic quantities

Thermodynamic quantities	Values from K_1	Values from K_2
ΔH(kJmol^{-1})	22.1	11.2
ΔS (J $K^{-1}mol^{-1}$)	62.2	-79.7
ΔG_{298} (kJmol^{-1})	-18.8	24.1

Table 4.

Thermodynamic quantities and activation parameters for the ruthenium (III) catalyzed oxidation of tripelennamine hydrochloride by diperiodatoargentate(III) in aqueous alkaline medium with respect to slow step scheme 2.

(A). Effect of temperature on k_2

Temperature (K)	$k_2 \times 10^{-5}$ ($dm^3\ mol^{-1}\ s^{-1}$)
288	1.06
298	1.28
308	1.63
318	1.92

(B). Activation parameters

Parameters	values
Ea (kJ mol^{-1})	15.4
$\Delta H^{\#}$(kJ mol^{-1})	12.9
$\Delta S^{\#}$ (JK^{-1} mol^{-1})	-103.5
$\Delta G^{\#}$ (kJ mol^{-1})	31.3
logA	7.8

(C). Effect of temperature to calculate K_1 and K_2 for the oxidation of tripelennamine hydrochloride by diperiodatoargentate (III) with aqueous alkaline medium.

Temperature (K)	$K_3 \times 10^1$ ($dm^3 mol^{-1}$)	$K_4 \times 10^{-5}$ ($dm^3\ mol^{-1}$)
288	10.4	0.28
298	8.3	0.35
308	6.8	0.44
318	4.9	0.54

(D). Thermodynamic quantities

(D). Thermodynamic quantities	Values from K_3	Values from K_4
ΔH (kJ mol^{-1})	-20.5	16.1
ΔS (J $K^{-1}mol^{-1}$)	-60.1	48.4
ΔG_{298} (kJ mol^{-1})	18.2	-14.6

Table 5.

Values of catalytic constants at different temperatures and activation parameters

Tempareture (K)	$K_C \times 10^{-4}$
288	0.41
298	0.74
308	0.98
318	1.5
Ea(kJ mol^{-1})	32.3
$\Delta H^{\#}$(kJ mol^{-1})	29.6
$\Delta S^{\#}$(J K^{-1} mol^{-1})	-185.9
$\Delta G^{\#}$(kJ mol^{-1})	55.7
logA	3.5