



## Copper (III) Periodate Complex-A Portable Oxidant for the Free Radical Induced Oxidation of Thiamine Hydrochloride

Shreekant M. Patil, Atmanand M. Bagoji, Santosh B. Konnur  
and Sharanappa T. Nandibewoor\*

P. G. Department of Studies in Chemistry, Karnatak University, Dharwad-580003, INDIA  
Email: [snandibewoor@yahoo.com](mailto:snandibewoor@yahoo.com)

Accepted on 4<sup>th</sup> March, 2020

### ABSTRACT

The oxidation of thiamine hydrochloride by diperiodatocuprate (III) (DPC) in aqueous alkaline medium at a constant ionic strength of  $0.18 \text{ mol dm}^{-3}$  was investigated spectrophotometrically. 1:3 stoichiometry (thiamine:DPC) was exhibited between the reaction of thiamine and DPC in aqueous alkaline medium. The orders of the reaction with respect to [DPC] and [thiamine] were unity and less than unity respectively in the concentration ranges studied. The rate of the reaction increased as the concentration of alkali increased and periodate had retarding effect on the rate of reaction. Ionic strength and dielectric constant had a negligible effect on the reaction rate. The main reaction products were identified by spot test and spectroscopic analysis. A mechanism involving free radical was proposed. The activation parameters for the slow step of the mechanism and also the thermodynamic quantities for different steps of mechanism were determined and discussed.

### Highlights

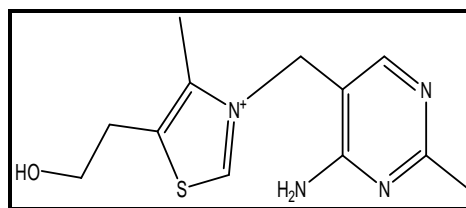
- A mechanism of oxidation of Thiamine by Diperiodatocuprate(III) is proposed on kinetics results.
- The  $[\text{Cu}(\text{H}_2\text{IO}_6)(\text{H}_2\text{O})_2]$  was considered as active species for the title reaction.
- In carrying the reaction, the role of pH is crucial.
- Activation parameters were computed and discussed
- The overall sequences described are consistent with the present kinetics studies.

**Keywords:** Thiamine (vitaminB<sub>1</sub>), Diperiodatocuprate(III), Kinetics, Mechanism, Oxidation.

### INTRODUCTION

Thiamine (TA), thio-vitamin (Scheme 1) is a colourless organosulfur, soluble in water and its structure consists of an aminopyrimidine and thiazole ring linked by a methylene bridge. All living organisms use TA and it is synthesized only in bacteria, fungi, protozoans and plants [1, 2]. Diabetes, beriberi, optic neuropathy and polyneuritics are the results of thiamine deficiency [3, 4].

An important characteristic of transition metals is that they exhibit multiple oxidation states and at higher oxidation states they can form stable complex with suitable polydentate ligands namely,



**Scheme 1.** Chemical structure of Thiamine

diperiodatocuprate(III) (DPC) [5], diperiodatoargentate(III) (DPA) [6] and diperiodatonickelate (IV) (DPN) [7], which are well known oxidizing agents in a certain buffer medium with a suitable pH value. Diperiodatocuprate (III) (DPC) is a flexible one-electron oxidant [8] and due to its poor solubility and stability in aqueous medium, the involvement of DPC in oxidation reactions is inadequate or scanty. Its use as an analytical reagent is now well recognized [9].

An extraordinary role of copper complexes in biological system is explained by several studies. Ongoing fascination in copper complexes is due to their uses as antimicrobial, antiviral, anti-inflammatory, antitumor agents [10], etc. There are multiple equilibria between different copper (III) species when the copper (III) periodate complex is the oxidant and it would be interesting to know which of the species is the active oxidant.

As per the literature survey, the oxidation of thiamine with alkaline copper(III) complex has not been reported so far from kinetic and mechanistic point of view. Such studies are of much importance in understanding the mechanism of oxidation of TA and also in getting the information of copper metal ions interaction with the biologically active compounds. Hence, the present investigation is aimed to unveil the oxidation of TA by DPC and to arrive at plausible mechanism and to understand the reactive species of DPC.

## MATERIALS AND METHODS

**Chemicals and solutions:** Thiamine was purchased from Sigma Aldrich, India. The analytical grade reagents were used in the experiment and Millipore water was used throughout the work. A stock solution was prepared by dissolving a known amount of the TA in Millipore water. The required concentration of TA was obtained from its stock solution. A stock solution of copper sulfate (BDH) was prepared by dissolving appropriate amount of the copper sulfate in Millipore water. A stock standard solution of  $\text{IO}_4^-$  was prepared by dissolving a known weight of  $\text{KIO}_4$  (Riedel-de Haen) in hot water; the stock solution used after keeping for 24 h and its concentration was deduced iodometrically [11] at neutral pH maintained using a phosphate buffer. The temperature was maintained constant to within  $\pm 0.10^\circ\text{C}$ .

The diperiodatocuprate(III) was prepared by standard procedure [5, 12, 13] and standardized by a standard procedure [14]. Copper sulphate (3.54 g), potassium periodate (6.80 g), potassium persulphate (2.20 g) and potassium hydroxide (9.0 g) were added to 250 mL of water. The mixture was shaken thoroughly and heated on a hot plate. The mixture was turned intense red after 3 h and boiling was continued for 20 min. more to complete the reaction. The mixture was filtered through sintered crucible (G4) cooled and diluted to 250 mL. The UV-Vis spectrum of copper (III) complex exhibited three absorption bands at 211, 263 and 419 nm which are characteristic of the DPC. The ionic strength was maintained by adding  $\text{KNO}_3$  (AR) solution and the pH value of the medium was maintained with  $\text{KOH}$  (BDH) solution.

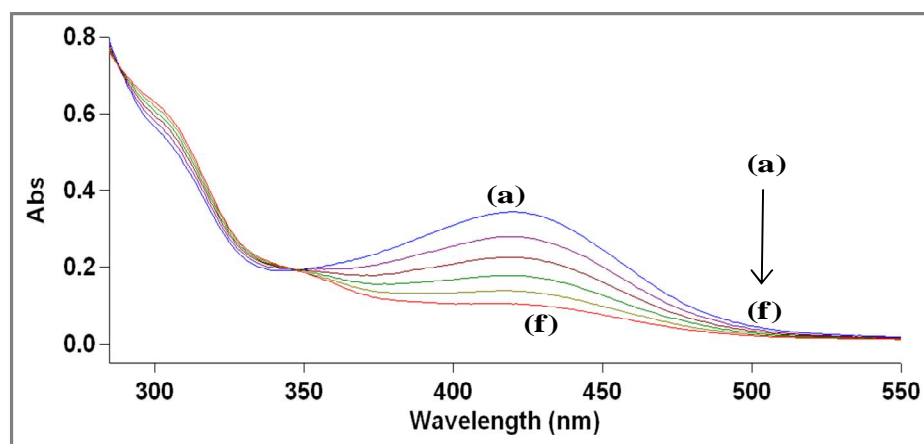
**Instrumentation and kinetic measurements:** The kinetic measurements were carried out on Varian CARY 50 Bio UV-Vis spectrophotometer (Varian, Victoria-3170, Australia) attached with a Peltier Accessory (temperature control). The product analysis was carried out using ESI-MS. ESI-MS data

was obtained on a 17A Shimadzu gas chromatograph with a QP-5050A Shimadzu mass spectrometer using the EI ionisation technique.

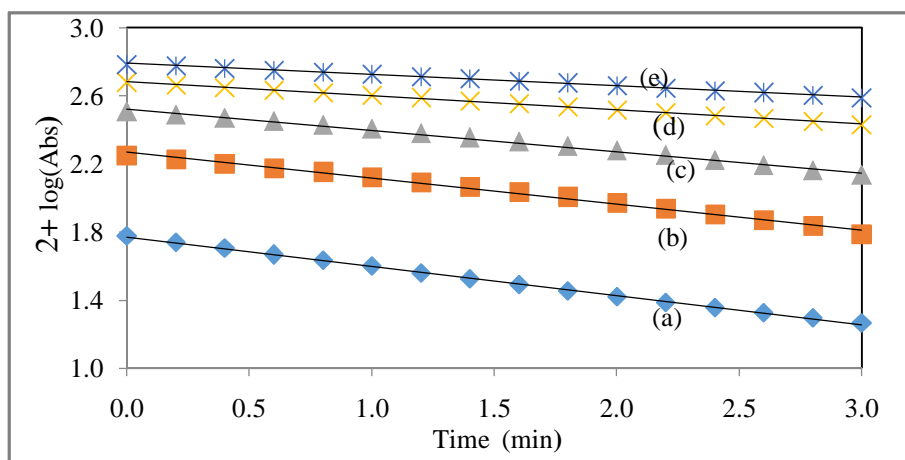
For pH measurement an Elico pH meter model LI 120 was used. The kinetics of oxidation of thiamine was followed under pseudo-first order condition where,  $[TA] > [DPC]$  at  $298 \pm 0.1$  K. The reaction was initiated by mixing thermally equilibrated DPC with TA solution, with required concentrations of KOH,  $KNO_3$  and  $KIO_4$  and progress of the reaction was followed spectrophotometrically at 419 nm by monitoring the decrease in the absorbance due to DPC with molar absorption index,  $\epsilon = 6231 \pm 100 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ . It was also verified that interference from other species in the reaction mixture at the wavelength 419 nm was negligible.

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 2007 programmer.

The rate constants,  $k_{\text{obs}}$  were obtained from the plot of  $\log(\text{absorbance})$  versus time plots and were reproducible within  $\pm 5\%$  error. All the kinetic runs were followed more than 80% reaction completion. During the kinetics, a constant concentration, viz.,  $1.0 \times 10^{-4} \text{ mol dm}^{-3}$  of  $KIO_4$  was used



**Figure 1.** Spectroscopic changes occurring in the oxidation of thiamine by diperiodatocuprate(III) at 298 K,  $[DPC] = 5.0 \times 10^{-4} \text{ mol dm}^{-3}$ ,  $[TA] = 5.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $[OH^-] = 0.08$ ,  $[IO_4^-] = 1.0 \times 10^{-4} \text{ mol dm}^{-3}$  and  $I = 0.18 \text{ mol dm}^{-3}$  with time interval of 1 min (curves a-f).

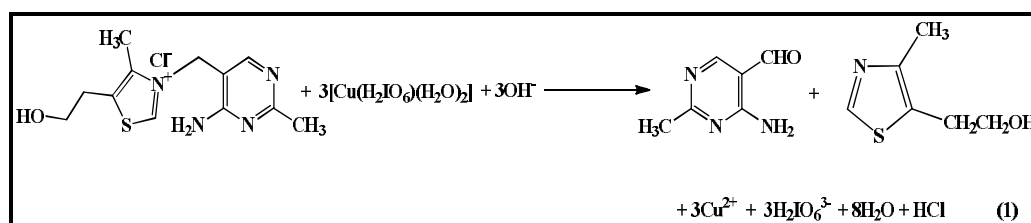


**Figure 2.** First order plots for the oxidation of thiamine by diperiodatocuprate(III) in aqueous alkaline medium at 298 K.  $[DPC] \times 10^{-5} \text{ (mol dm}^{-3}\text{)}$ : (a) 1.0, (b) 3.0; (c) 5.0, (d) 8.0 and (e) 10.

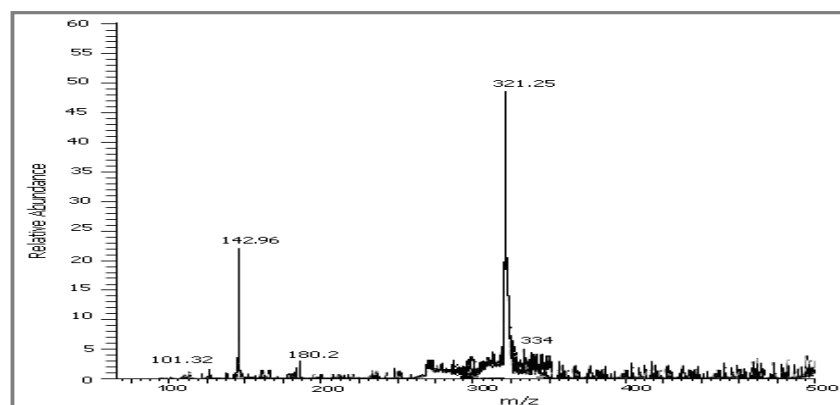
throughout the experiment. Since periodate is present in the excess in DPC, the possibility of oxidation of TA by periodate in alkaline medium at 298 K was tested. The progress of the reaction was followed iodometrically. However, it was found that there was no significant reaction under the experimental conditions employed compared to the DPC oxidation of TA. The total concentration of periodate and  $\text{OH}^-$  was calculated by considering the amount present in the DPC solution and that additionally added. The spectral changes during the reaction are shown in figure 1. It is evident from the Figure that the concentration of DPC decreases at 419 nm. The pseudo-first order rate constants, ' $k_{\text{obs}}$ ', were determined from the log (absorbance) versus time plots (Figure 2). The plots were linear up to 80% completion of reaction.

## RESULTS AND DISCUSSION

**Stoichiometry and product analysis:** Different sets of reaction mixtures containing different ratios of DPC to thiamine at constant ionic strength and  $[\text{KOH}]$ , reaction was kept for 4 h at 298 K in closed vessel under inert atmosphere. The remaining concentration of DPC was estimated by spectrophotometrically at 419 nm. The results indicated 1:3 stoichiometry as given in equation (1). After completion of reaction, the reaction mixture was acidified, concentrated and extracted with ether. The reaction product was further recrystallized from aqueous alcohol.



The main reaction product was identified as 2-(4-methylthiazol-5-yl)ethanol, which was confirmed by ESI-mass spectral analysis (Figure 3). The mass spectrum showed a molecular ion peak at 142.96 amu confirming the presence of 2-(4-methylthiazol-5-yl)ethanol.



**Figure 3.** ESI-Mass spectrum of 2-(4-methylthiazol-5-yl)ethanol with its molecular ion peak at  $m/z = 142.96$ .

**Reaction order:** As the diperiodatocuprate(III) oxidation of thiamine in alkaline medium proceeds with a measurable rate in the absence of catalyst, the reaction is understood to occur in parallel path. The reaction orders have been determined from the slopes of  $\log k_{\text{obs}}$  versus  $\log(\text{concentration})$  plots by varying the concentrations of thiamine, alkali and periodate in turn while keeping the others constant. The reaction was followed under the conditions  $[\text{TA}] = 5.0 \times 10^{-3}$ ,  $[\text{DPC}] = 5.0 \times 10^{-4}$ ,  $[\text{OH}^-] = 0.08$ ;  $I = 0.18/\text{mol dm}^{-3}$ . The rate constant of reaction ( $k_{\text{obs}}$ ) was obtained by the plot of  $\log(\text{absorbance})$  versus time by following the progress of the reaction spectrophotometrically at 419 nm.

**Effect of [diperiodatocuprate(III)]:** The DPC concentration was varied in the range of  $1.0 \times 10^{-5}$  to  $1.0 \times 10^{-4}$  mol dm<sup>-3</sup>. The linearity of the plots of log absorbance versus time up to 80% completion of the reaction indicates a reaction order of unity in [DPC]. This was also confirmed by varying [DPC], which did not result in any change in the pseudo-first-order rate constants,  $k_{\text{obs}}$  (Table 1).

**Effect of [thiamine]:** The thiamine concentration was varied in the range  $1.0 \times 10^{-3}$ - $1.0 \times 10^{-2}$  mol dm<sup>3</sup> at 298 K while keeping other reactant concentrations and conditions constant. The  $k_{\text{obs}}$  value was increased with the increase in concentration of thiamine, indicating an apparent less than unit order dependence on [TA]. This was also confirmed by the plot of  $k_{\text{obs}}$  versus [TA]<sup>0.7777</sup> which is linear rather than the direct plot of  $k_{\text{obs}}$  versus [TA] (Figure 4) ( $r=0.9798$ ,  $S < 0.004$ ) (Table 1).

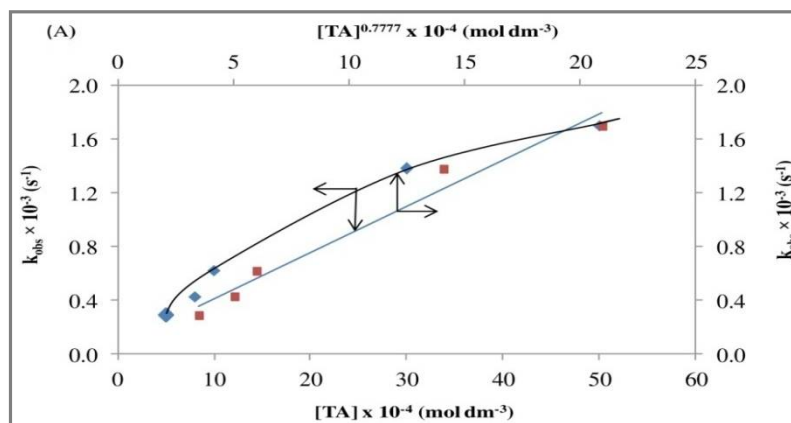


Figure 4. Plots of (A)  $k_{\text{obs}}$  vs [TA]<sup>0.7777</sup> and  $k_{\text{obs}}$  vs [TA] (conditions as in table 1).

**Effect of [alkali] and [periodate]:** The effect of alkali on the reaction was studied at constant concentrations of thiamine and DPC and at a constant ionic strength of 0.18 mol dm<sup>-3</sup> at 298 K. The rate constant increased with increase in [alkali] and less than unit order dependence on [alkali] as given in table 1. The effect of [IO<sub>4</sub><sup>-</sup>] was observed by varying the concentration from  $5.0 \times 10^{-5}$  to  $5.0 \times 10^{-4}$  mol dm<sup>-3</sup> while keeping all other reactants concentrations constant. It was observed that the rate constants decreased by increasing [IO<sub>4</sub><sup>-</sup>] (Table 1).

**Effect of dielectric constant of the medium (D):** The dielectric constant of the medium, D, was varied by varying the t-butyl alcohol-water percentage. The dielectric constants of the reaction medium at various composition of t-butyl alcohol and water (v/v) were calculated from the equation,  $D = V_1D_1 + V_2D_2$ , where  $D_1$  and  $D_2$  are dielectric constants of pure water and t-butyl alcohol, i.e., 78.5 and 10.9 at 298 K respectively, and,  $V_1$  and  $V_2$  are the volume fractions of the components, water and t-butyl alcohol respectively, in the total volume of mixture. It was found that the decreasing polarity had no effect on the rate of reactions.

**Effect of ionic strength (I):** The addition of KNO<sub>3</sub> at constant [DPC], [TA], [OH<sup>-</sup>] and [IO<sub>4</sub><sup>-</sup>] was found that increasing ionic strength had no significant effect on the rate of the reaction.

**Effect of initially added products:** The initially added products, Cu(II) and 2-(4-methylthiazol-5-yl) ethanol did not have any significant effect on the rate of reaction reactions.

**Test for free radicals:** The involvement of free radicals in the reaction was examined as follows. A known quantity of acrylonitrile monomer was initially added to the reaction mixture and was kept for 2 hr in an inert atmosphere. A white precipitate was formed on diluting the reaction mixture with methanol, indicating the involvement of free radicals in the reaction [15]. The blank experiments of either DPC or thiamine alone with acrylonitrile did not induce any polymerization under the same conditions.

**Table 1.** Effect of variation of [DPC], [TA], [OH<sup>-</sup>], and [IO<sub>4</sub><sup>-</sup>] concentrations the oxidation of thiamine by DPC in aqueous alkaline medium at 298 K [I = 0.18 mol dm<sup>-3</sup>]

[DPC] × 10 <sup>4</sup> (mol dm <sup>-3</sup> )	[TA] × 10 <sup>3</sup> (mol dm <sup>-3</sup> )	[KIO <sub>4</sub> ] × 10 <sup>4</sup> (mol dm <sup>-3</sup> )	[OH <sup>-</sup> ] × 10 <sup>2</sup> (mol dm <sup>-3</sup> )	K <sub>obs</sub> × 10 <sup>2</sup> (s <sup>-1</sup> )
1	5	1	8	0.66
3	5	1	8	0.69
5	5	1	8	0.62
8	5	1	8	0.61
10	5	1	8	0.58
5	1	1	8	0.29
5	3	1	8	0.43
5	5	1	8	0.62
5	8	1	8	1.38
5	10	1	8	1.7
5	5	0.5	8	1.02
5	5	0.8	8	0.81
5	5	1	8	0.62
5	5	3	8	0.36
5	5	5	8	0.25
5	5	1	3	0.35
5	5	1	5	0.52
5	5	1	8	0.62
5	5	1	10	0.82
5	5	1	30	1.31

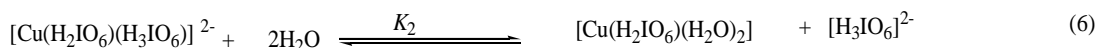
**Effect of temperature:** The influence of temperature on the rate of reaction were studied for at four different temperatures (288, 298, 308 and 318 K) under varying concentrations of thiamine, alkali and periodate keeping other conditions constant. The rate constant increased with increase in temperature. The rate constant ( $k_1$ ) of the slow step and equilibrium constants of [scheme 2](#) for the reaction were obtained from the slopes and intercepts of plots of  $1/k_{obs}$  versus  $1/[TA]$ ,  $1/k_{obs}$  versus  $[OH^-]$  and  $1/k_{obs}$  versus  $[IO_4^-]$  at four 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  $1/T$  ( $r=0.9824$ ,  $S \leq 0.011$ ) and other activation parameters obtained are tabulated in [table 2](#). The thermodynamic quantities with respect to  $K_1$ ,  $K_2$  and  $K_3$  were calculated from van't Hoff's equation and are presented in [table 2](#).

**Mechanism of the reaction:** Due to versatile behavior of one-electron oxidant, the oxidation of many organic and inorganic compounds by Cu(III) species had been carried out. The literature survey reveals that the water soluble copper(III) periodate complex is reported [[16](#)] to be  $[Cu(HIO_6)_2(OH)_2]^{7-}$ . However, in aqueous alkaline medium and at the high pH range as employed in the study, periodate is unlikely to exist as  $HIO_6^{4-}$  (as present in the complex) as is evident from its involvement in the multiple equilibria, (2) to (4) [[17](#)] depending on the pH of the solution, as given below.

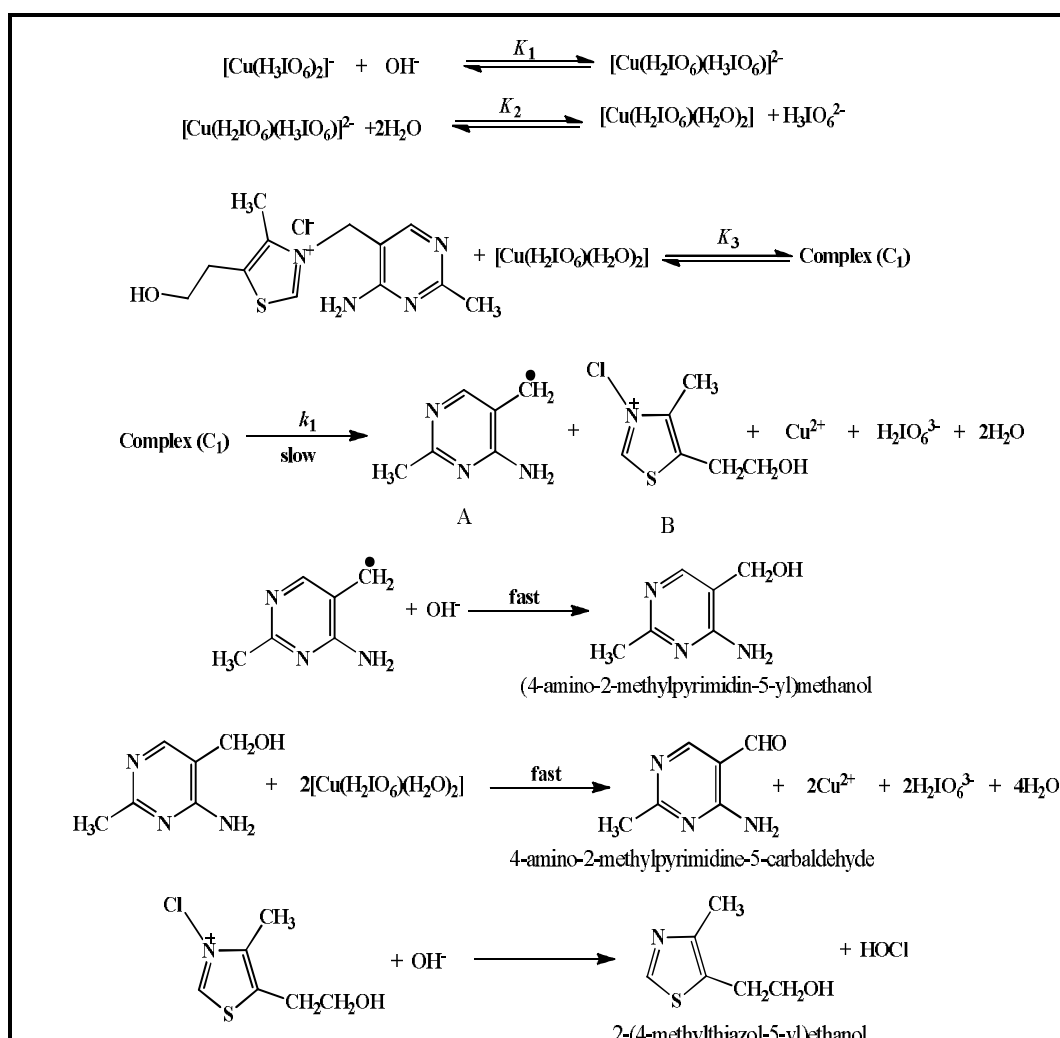


Periodic acid exists in the acid medium as  $H_5IO_6$  and as  $H_4IO_6^-$  at around pH 7. Thus under the conditions employed, in alkaline medium the main species are expected to be  $H_3IO_6^{2-}$  and  $H_2IO_6^{3-}$ . At higher concentrations, periodate also tends to dimerise [[18](#)]. However, formation of this species is negligible under conditions employed for kinetic study. Hence, at the pH employed in this study, the soluble copper(III) periodate complex exists as diperiodatocuprate(III),  $[Cu(H_3IO_6)(H_2IO_6)]^{2-}$ , a conclusion also supported by earlier work [[18](#)].

Lister [19] proposed three forms of copper(III) periodate in alkaline medium, viz., diperiodatocuprate(III) (DPC), monoperoxidatocuprate(III) (MPC), and tetrahydroxocuprate(III). The last one is ruled out, as its equilibrium constant is  $8.0 \times 10^{-11}$  at 313 K. Hence, in the present study, DPC and MPC are considered as the active forms of copper(III) periodate complex. It may be expected that a lower periodate complex such as MPC is more important in the reaction than DPC. The results of increase in the rate with increase in alkali concentration and decrease in rate with increase in periodate concentration (Table 1) suggest an equilibrium of the copper(III) periodate complex to form a monoperoxidatocuprate(III) (MPC) species as shown in equations (5) and (6). Similar results have been well reported in literature [20].



The reaction between the diperiodatocuprate(III) complex and thiamine in alkaline medium has a 1:3 stoichiometry (TA:DPC) with a first order dependence on [DPC], less than unit order in [substrate] and [alkali] and a negative fractional order in [periodate]. No effect of the added products was observed. Based on the experimental results, a mechanism as in scheme 2 was proposed in which all the observed orders in each constituent such as [oxidant], [reductant],  $[\text{OH}^-]$ , and  $[\text{IO}_4^-]$  are well accommodated.



Scheme 2. Detailed scheme for the oxidation of thiamine by DPC.

The less than unit order in [TA] is due to the formation of a complex ( $C_1$ ) between the oxidant and TA prior to the formation of the products.  $K_3$  is the composite equilibrium constant comprising the equilibrium between active species of thiamine and MPC species. Then, this complex ( $C_1$ ) decomposes in a slow step to form a free radical species (A) and intermediate species (B). The free-radical species (A) formed further reacts with one mole OH to give (4-amino-2-methylpyrimidin-5-yl)methanol, which is converted into byproduct of the reaction i.e., 4-amino-2-methylpyrimidine-5-carbaldehyde upon reacting with two molecules of MPC. The intermediate species (B) reacts with one mole of OH to give main product 2-(4-methylthiazol-5-yl) ethanol, which was identified by its ESI-MS (Figure 4). The detailed mechanism for the oxidation of thiamine by diperiodatocuprate(III) is represented as given in scheme 2.

Since scheme 2 is in accordance with generally well accepted principle of non-complementary oxidations taking place in sequence of one-electron steps, the reaction between the substrate and oxidant would afford a radical intermediate. A free radical scavenging experiment revealed such a possibility. This type of radical intermediate has also been observed in earlier work [12, 22]. Spectroscopic evidence for the complex formation between oxidant and substrate was obtained from UV-Vis spectra of thiamine ( $5.0 \times 10^{-3}$  mol dm<sup>-3</sup>), DPC ( $5.0 \times 10^{-4}$  mol dm<sup>-3</sup>), [OH<sup>-</sup>] = 0.08 mol dm<sup>-3</sup> and a mixture of both. A bathochromic shift of about 6 nm from 419 to 425 nm in the spectra of DPC was observed.

According to Scheme 2, the rate law Eq. (7) is derived as,

$$k_{\text{obs}} = \frac{\text{Rate}}{[\text{DPC}]} = \frac{k_1 K_1 K_2 K_3 [\text{TA}] [\text{OH}^-]}{[\text{H}_2\text{IO}_6^{3-}] + K_1 [\text{OH}^-] [\text{H}_2\text{IO}_6^{3-}] + K_1 K_2 [\text{OH}^-]^2 + K_1 K_2 K_3 [\text{TA}] [\text{OH}^-]} \quad (7)$$

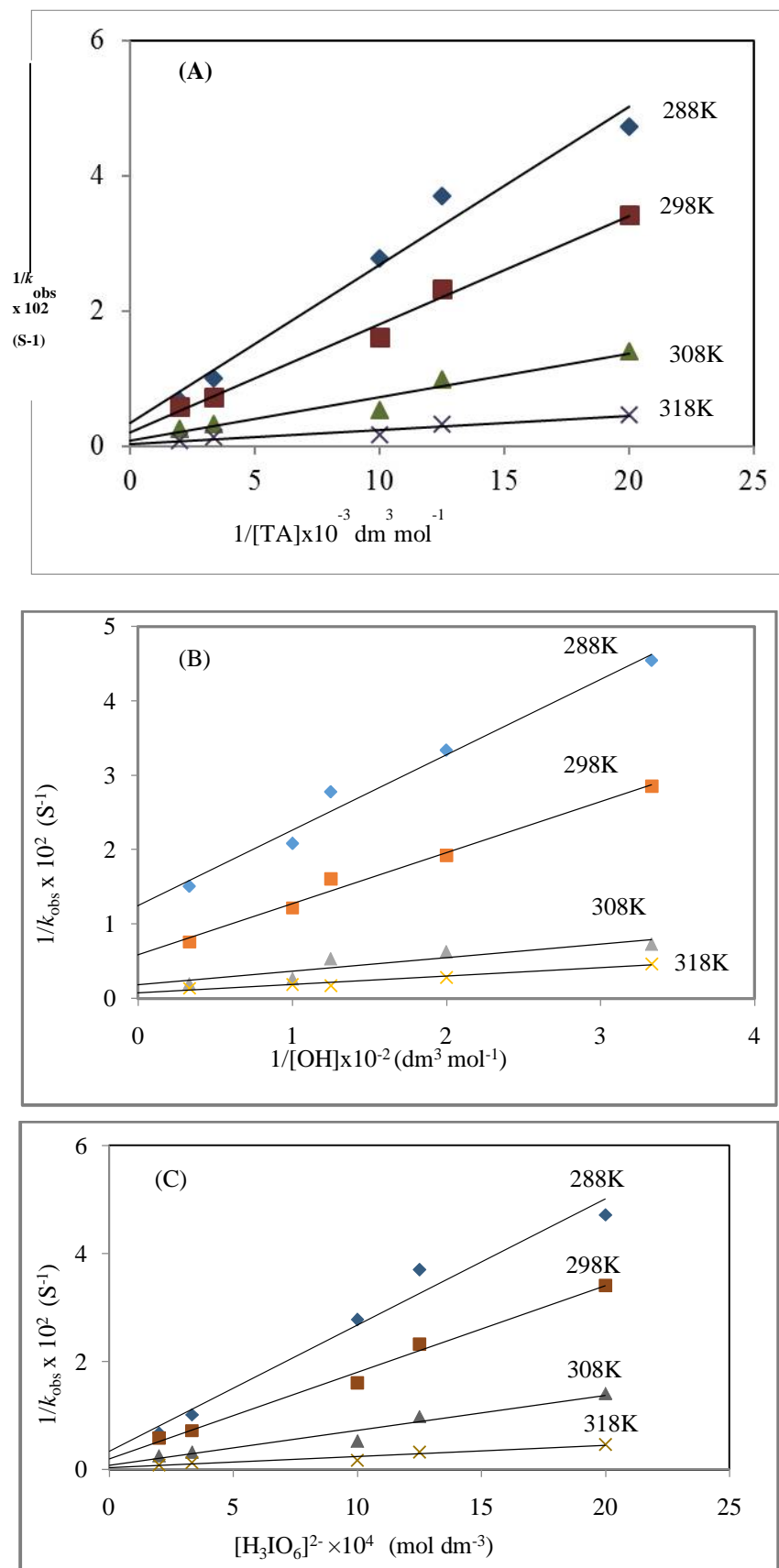
By rearranging the above Eq. (7), Eq. (8) was obtained which is suitable for verification.

$$\frac{1}{k_{\text{obs}}} = \frac{[\text{H}_2\text{IO}_6^{3-}]}{k_1 K_1 K_2 K_3 [\text{TA}] [\text{OH}^-]} + \frac{[\text{H}_2\text{IO}_6^{3-}]}{k_1 K_2 K_3 [\text{TA}]} + \frac{1}{k_1 K_3 [\text{TA}]} + \frac{1}{k_1} \quad (8)$$

According to Eq. (8), other conditions being constant, plots of  $1/k_{\text{obs}}$  v/s  $1/[\text{OH}^-]$  ( $r \geq 0.9961$ ,  $S \leq 0.001$ ),  $1/k_{\text{obs}}$  v/s  $1/[\text{TA}]$  ( $r \geq 0.9874$ ,  $S \leq 0.004$ ),  $1/k_{\text{obs}}$  v/s  $[\text{H}_3\text{IO}_6^{2-}]$  ( $r \geq 0.9909$ ,  $S \leq 0.005$ ) are linear at different temperatures (Figure 5). The slopes and intercepts of such a plots lead to the values of  $k_1$ ,  $K_1$ ,  $K_2$  and  $K_3$  as  $4.905 \times 10^{-2}$  s<sup>-1</sup>,  $9.24 \times 10^{-1}$  dm<sup>3</sup> mol<sup>-1</sup>,  $0.599 \times 10^{-3}$  mol dm<sup>-3</sup> and  $5.36 \times 10^3$  dm<sup>3</sup> mol<sup>-1</sup> respectively. The values of  $K_1$  and  $K_2$  are in good agreement with the literature [23]. The equilibrium constant  $K_1$  is far greater than  $K_2$  which may be attributed to the greater tendency of DPC to undergo hydrolysis as compared to the dissociation of hydrolyzed species in alkaline medium. All these results are interpreted satisfactorily in scheme 2. In the same manner the values of  $k_1$ ,  $K_1$ ,  $K_2$  and  $K_3$  were calculated at different temperatures and tabulated in table 2.

The thermodynamic quantities for the different equilibrium steps in Scheme 2 can be evaluated as follows. The thiamine, periodate and hydroxide ion concentrations (Table 1) were varied at different temperatures. A van't Hoff's plot was made for variation of  $K_1$  with temperature ( $\log_{10} K_1$  vs.  $1/T$  ( $r \geq 0.9512$ ,  $S \leq 0.004$ )) and the values of enthalpy of reaction  $\Delta H$ , entropy of reaction  $\Delta S$ , and free energy of reaction  $\Delta G$  were calculated for the first equilibrium step. These values are given in table 2. A comparison of the later values ( $\Delta H = 41.5$  kJ mol<sup>-1</sup>) with those obtained for the slow step of the reaction ( $\Delta H^\ddagger = 54.7$  kJ mol<sup>-1</sup>) shows that these values mainly refer to the rate-limiting step, supporting the fact that the reaction before rate-determining step is fairly fast since it involves low-activation energy [24]. In the same manner,  $K_2$  and  $K_3$  values were calculated at different temperatures and their corresponding values of the thermodynamic quantities are given in the table 2.





**Figure 5.** Verification of rate law (5) for the oxidation of TA by doperiodatocuprate (III). Plots of (A)  $1/k_{\text{obs}}$  v/s  $1/[\text{TA}]$ , (B)  $1/k_{\text{obs}}$  v/s  $1/[\text{OH}]$ , (C)  $1/k_{\text{obs}}$  v/s  $[\text{H}_3\text{IO}_6]^{2-}$ , at four different temperatures (conditions as in Table 1).

**Table 2(A).** Activation parameters with respect to the slow step of Scheme 2 and thermodynamic quantities for the oxidation of thiamine by diperiodatocuprate(III) in aqueous alkaline medium. {[DPC] =  $1.0 \times 10^{-4}$  mol dm<sup>-3</sup>; [TA] =  $5.0 \times 10^{-3}$  mol dm<sup>-3</sup>; [OH<sup>-</sup>] = 0.08 mol dm<sup>-3</sup>; [IO<sub>4</sub><sup>-</sup>] =  $1 \times 10^{-4}$  mol dm<sup>-3</sup>; I = 0.18 mol dm<sup>-3</sup>}

Temperature (K)		$k_1$ ( $\times 10^2$ ) (s <sup>-1</sup> )	
(A) Effect of temperature			
288		2.948	
298		4.905	
308		12.08	
318		26.91	
Activation of parameters			
Ea(kJ mol <sup>-1</sup> )		57.1±1.4	
$\Delta H^\ddagger$ (kJ mol <sup>-1</sup> )		54.6±0.3	
$\Delta S^\ddagger$ (J K <sup>-1</sup> mol <sup>-1</sup> )		-86±3.0	
$\Delta G^\ddagger$ (kJ mol <sup>-1</sup> )		80.4±0.2	
(B) Effect of temperature to calculate $K_1$ , $K_2$ and $K_3$ for the oxidation of thiamine by diperiodatocuprate(III) in alkaline medium.			
Temperature(K)	$K_1 \times 10^1$ (dm <sup>3</sup> mol <sup>-1</sup> )	$K_2 \times 10^3$ (mol dm <sup>-3</sup> )	$K_3 \times 10^{-3}$ (dm <sup>3</sup> mol <sup>-1</sup> )
288	6.03	1.475	3.77
298	9.24	0.599	5.36
308	2.27	0.233	8.59
318	2.75	0.105	11.4
(C) Thermodynamic quantities using $K_1$ , $K_2$ , and $K_4$			
Thermodynamic quantities	Values from $K_1$	Values from $K_2$	Values from $K_3$
$\Delta H$ (kJ mol <sup>-1</sup> )	41.5	-67.5	28.9
$\Delta S$ (J K <sup>-1</sup> mol <sup>-1</sup> )	141	-288	169
$\Delta G_{298}$ (kJ mol <sup>-1</sup> )	-0.499	19.82	-21.28

The negligible effect of ionic strength and solvent on the rate of reaction reveals the involvement of neutral species in reaction as seen in scheme 2. A high negative value of  $\Delta S^\ddagger$  ( $-86 \text{ JK}^{-1} \text{ mol}^{-1}$ ) suggests that intermediate complex ( $C_1$ ) is more ordered than the reactants [25]. The observed modest activation energy and sizeable entropy of activation supports a complex transition state in the reaction [26].

## APPLICATION

The applied chemist uses kinetics to devise new and/or better ways of achieving desired chemical reactions. The mathematical models that describe chemical reaction kinetics provide chemists and chemical engineers with tools to better understand and describe chemical processes such as food decomposition, microorganism growth, stratospheric ozone decomposition, and the complex chemistry of biological systems. Hence understanding the mechanism of title work is of great importance to explore new derivatives.

## CONCLUSION

The oxidation of thiamine by diperiodatocuprate(III) was studied. Oxidation products were identified. Among the various species of Cu(III) in alkaline medium,  $[\text{Cu}(\text{H}_2\text{IO}_6)(\text{H}_2\text{O})_2]$  was considered as active species for the title reaction. Based experimental results the probable mechanisms was proposed for the reaction. Thermodynamic quantities and activation parameters of individual steps in the mechanisms was evaluated for reactions at different temperatures. The descriptions of the mechanisms are consistent with all the experimental evidences including kinetic, spectral and product studies.

## ACKNOWLEDGEMENT

The corresponding author thanks the UGC, New Dehli for the award of UGC-BSR faculty fellowship to Dr. S.T. Nandibewoor and BSR fellowship to Mr. S.B. Konnur. Thanks to University Scientific

Instruments Center (USIC) and Department of Chemistry Karnatak University, Dharwad, for providing necessary laboratory facilities.

### Appendix- Rate law for oxidation of TA by DPC

From Scheme 2, rate law can be derived as follows,

$$\text{Rate} = \frac{-d[\text{DPC}]}{dt} = k_1 [\text{Complex}] = k_1 [C_1] \quad (\text{i})$$

From the law of mass action, the third equilibrium constant is given by

$$K_3 = \frac{[C_1]}{[\text{Cu}(\text{H}_2\text{IO}_6)(\text{H}_2\text{O})_2] [\text{TA}]}$$

This can be rearranged to give

$$[C_1] = K_3 [\text{Cu}(\text{H}_2\text{IO}_6)(\text{H}_2\text{O})_2] [\text{TA}] \quad (\text{ii})$$

Equation (i) takes the form upon substituting the  $[C_1]$  from equation (ii)

$$\text{Rate} = \frac{-d[\text{DPC}]}{dt} = k_1 K_3 [\text{Cu}(\text{H}_2\text{IO}_6)(\text{H}_2\text{O})_2] [\text{TA}] \quad (\text{iii})$$

The second equilibrium constant is given by

$$K_2 = \frac{[\text{Cu}(\text{H}_2\text{IO}_6)(\text{H}_2\text{O})_2] [\text{H}_3\text{IO}_6^{2-}]}{[\text{Cu}(\text{H}_2\text{IO}_6) (\text{H}_3\text{IO}_6)^{2-}]}$$

### REFERENCES

- [1]. T. P. Begley, A. Chatterjee, J. W. Hanes, A. Hazra, S. E. Ealick, Cofactor biosynthesis-still yielding fascinating new biological chemistry, *Curr. Opin. Chem. Bio.*, **2008**, 12,118-125.
- [2]. M. E. Webb, A. Marquet, R. R. Mendel, F. Rebeill, A. G. Smith, Elucidating biosynthetic pathways for vitamins and cofactors, *Nat. Prod. Rep.*, **2007**, 24,988-1008.
- [3]. L. Kathleen Mahan, S. Escott-Stump, *Krause's Food, Nutrition, & Diet Therapy*. The University of Michigan, Michigan, USA, Saunders, **2004**.
- [4]. J. B. Wyngaarden, L. H. Smith, *Cecil's Textbook of Medicine* (18th edition). W B Saunders, Philadelphia, **1988**.
- [5]. H. Yao, M. Zhang, W. Zeng, X. Zeng, Z. Zhang, A novel chemiluminescence assay of mitoxantrone based on diperiodatocuprate(III) oxidation. *Spectrochimica Acta Part A*, **2014**, 117, 645-650.
- [6]. J. H. Shan, H. Y. Wang, C. Y. Song, F. Wang, Kinetics and mechanism of oxidation of 2-amino-1-butanol by diperiodatoargentate(III) in alkaline medium, *Bull. Chem. Soc. Ethiop.*, **2009**, 23, 297-302.
- [7]. R. S. Shettar, S. T. Nandibewoor, Mechanistic and spectral investigations of ruthenium(III)-catalysed oxidation of 4-hydroxycoumarin by alkaline diperiodatonickelate(IV) (stopped flow technique), *J. Mol. Catal. A. Chem.*, **2005**, 234, 137-143.

- [8]. V. P. Pattar, P. A. Magdum, D. G. Patil, S. T. Nandibewoor, Thermodynamic, kinetic and mechanistic investigations of piperazine oxidation by diperiodatocuprate(III) complex in aqueous alkaline medium, *J. Chem. Sci.*, **2016**, 128, 477-485.
- [9]. Y. Hu, G. Li, Z. Zhang, A flow injection chemiluminescence method for the determination of lincomycin in serum using a diperiodato-cuprate (III)-luminol system, *Luminescence*, **2011**, 26, 313-318.
- [10]. J. E. Weder, C. T. Dillon T. W. Hambley, B. J. Kennedy, P. A. Lay, J. R. Biffin, H. L. Regtop, N. M. Davies, Copper complexes of nonsteroidal anti-inflammatory drugs: An Opportunity yet to be realized, *Coord. Chem. Rev.*, **2002**, 232, 95-126.
- [11]. G. P. Panigrahi, P. K. Misro, Kinetics and mechanism of oxidation of Os(VIII) catalysed oxidation of unsaturated acids by sodium periodate, *Indian. J. Chem.*, **1978**, 16A, 201-204.
- [12]. J. Shan, X. Wang, H. Shen, Kinetics and mechanism of oxidation of N,N-dimethyl ethanolamine by diperiodatocuprate(III) complex in alkaline medium, *Asian J. Chem.*, **2011**, 23, 180-182.
- [13]. J. Shan, Q. Wang, Z. Zhang, J. Han. Oxidation of neopentyl glycol by diperiodatocuprate(III) in alkaline medium-a kinetic and mechanistic study, *Asian J. Chem.*, **2015**, 27, 1537-1539.
- [14]. G. H. Jeffery, J. Bassett, J. Mendham, R.C. Denney, *Vogel's Textbook of Quantitative Chemical Analysis*, 5th edn., ELBS, Longman, Essex, UK, **1996**, 455, 679.
- [15]. R.V. Jagdeesh, Puttaswamy, Ru(III), Os(VIII), Pd(II) and Pt(IV) catalysed oxidation of glycyl-glycine by sodium N-chloro-p-toluenesulfonamide: comparative mechanistic aspects and kinetic modeling, *J. Phys. Org. Chem.*, **2008**, 21, 844-858.
- [16]. Y. Hu, Li Gongke, A novel flow injection chemiluminescence method for the determination of Ractopamine in urine by using trivalent copper, *Anal. Methods*. **2013**, 5, 678-683.
- [17]. J. C. Bailar, H. J. Emeleus, S. R. Nyholm, A. F. Trotman-Dickenson, *Comprehensive Inorganic Chemistry*, Vol 2, Pergamon Press, Oxford, **1975**, 1456.
- [18]. A. M. Bagoji, P. A. Magdum, S. T. Nandibewoor, Oxidation of acebutolol by copper(III) periodate complex in aqueous alkaline medium: a kinetic and mechanistic approach, *J. Sol. Chem.*, **2016**, 45, 1715-1728.
- [19]. M. W. Lister, The stability of some complexes of trivalent copper, *Can. J. Chem.*, **1953**, 31, 638-652.
- [20]. R. R. Hosamani, N. P. Shetti, S. T. Nandibewoor, A kinetic and mechanistic study on the oxidation of L-cystine by alkaline diperiodatocuprate(III): A free radical intervention, *Kinet. Catal.*, **2009**, 50, 530-539.
- [21]. M. Jaky, Z. Szeverenyi, L. I. Simandi, Formation of manganate(V) in oxidations by permanganate ion in strongly alkaline solution, *Inorg. Chim. Acta.*, **1991**, 186, 33-37
- [22]. S. B. Konnur, S. T. Nandibewoor, Autocatalyzed oxidation of amino acid, L-Citrulline by diperiodatocuprate(III) complex in aqueous alkaline medium: a kinetics and mechanistic approach, *J. Chem. Sci.*, **2020**, 132, (In Press)
- [23]. D. C. Hiremath, T. S. Kiran, S. T. Nandibewoor, Oxidation of vanillin by diperiodatocuprate (III) in aqueous alkaline medium: a kinetic and mechanistic study by stopped flow technique, *Int. J. Chem. Kinet.*, **2007**, 39, 236-244.
- [24]. D. C. Bilehal, R. M. Kulkarni, S. T. Nandibewoor, Kinetics and mechanistic study of the ruthenium(III) catalyzed oxidative deamination and decarboxylation of L-valine by alkaline permanganate, *Can. J. Chem.*, **2001**, 79, 1926-1933.
- [25]. A. Weissberger, *Investigations of Rates and Mechanism of Reactions in Techniques of Chemistry*, vol. 4, Wiley, New York, **1974**, 421.
- [26]. S. A. Farokhi, S. T. Nandibewoor, Kinetic, mechanistic and spectral studies for the oxidation of sulfanilic acid by alkaline hexacyanoferrate(III), *Tetrahedron*, **2003**, 59, 7595-7602.