Available online at **www.joac.info**

ISSN: 2278-1862

Journal of Applicable Chemistry

2020, 9 (2): 276-287

(International Peer Reviewed Journal)

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: stnandibewoor@yahoo.com

Accepted on 4th March, 2019

ABSTRACT

The oxidation of thiamine hydrochloride by diperiodatocuprate (III) (DPC) in aqueous alkaline medium at a constant ionic strength of 0.18 mol dm^{3} *was investigated spectrophotometrically. 1:3 stoichiometry (thaimine: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

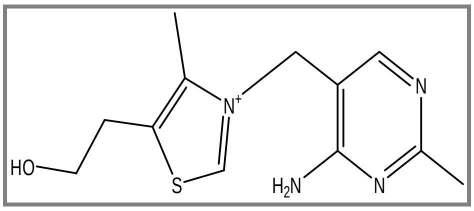
- A mechanism of oxidation of Thaimine by Diperiodatocuprate(III) is proposed on kinetics results.
- The [$Cu(H_2IO_6)(H_2O)_2$] was considered as active species for the title reaction.
- In carrying the reaction, the role of pH is crucial.
- Activation parameters were computed and discussed
- The overall sequences described are consistent with the present kinetics studies.

Keywords: Thiamine (vitaminB_1), 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 polyneutrics 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 IO_4^- was prepared by dissolving a known weight of 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 ±0.10°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 250mL 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 KNO_3 (AR) solution and the pH value of the medium was maintained with 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±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, $\varepsilon = 6231 \pm 100$ $dm^3mol^{-1}cm^{-1}$. 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_{obs} were obtained from the plot of log (absorbance) versus time plots and were reproducible within ± 5% error. All the kinetic runs were followed more than 80% reaction completion. During the kinetics, a constant concentration, viz., 1.0×10^{-4} mol dm^{-3} of KIO_4 was used

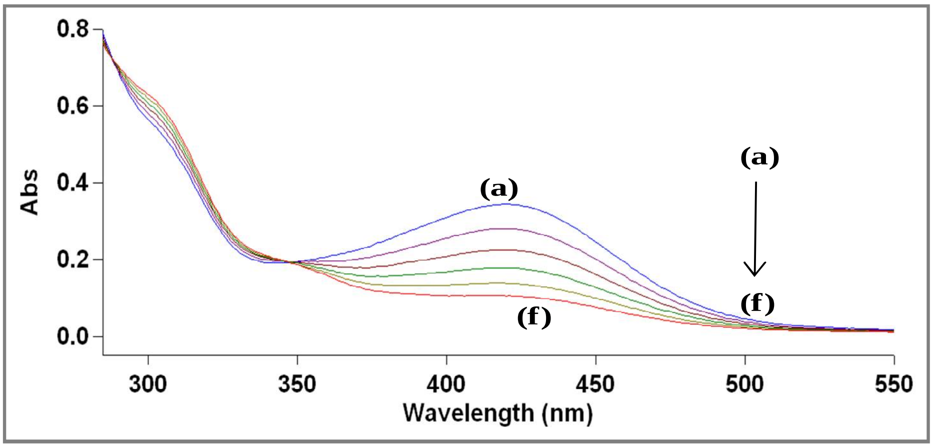


Figure 1. Spectroscopic changes occurring in the oxidation of thiamine by diperiodatocuprate(III) at 298 K, $[DPC]= 5.0 \times 10^{-4}$ mol dm^{-3}, $[TA] = 5.0 \times 10^{-3}$ $moldm^{-3}$, $[OH^-] = 0.08$, $[IO_4^-] = 1.0\times 10^{-4}$ mol dm^{-3} and I = 0.18 mol dm^{-3} with time interval of 1 min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

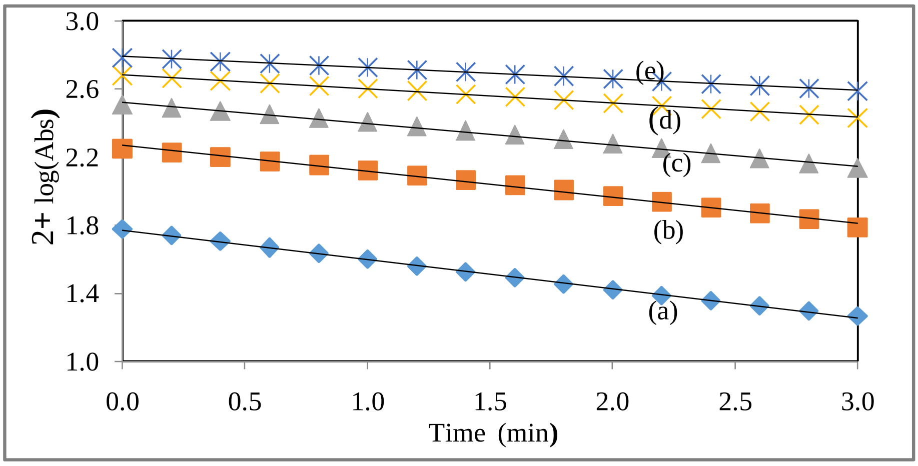
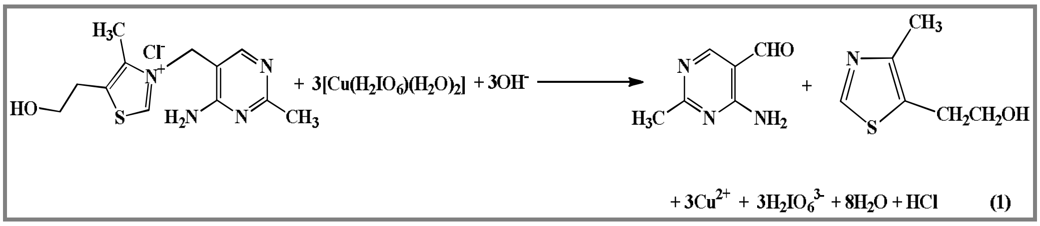


Figure 2. First order plots for the oxidation of thiamine by diperiodatocuprate(III) in aqueous alkaline medium at 298 K. $[DPC]\times10^{-5}$ $(moldm^{-3})$: (a) 1.0, (b) 3.0; (c) 5.0, (d) 8.0 and (e) 10.

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 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_{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 [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 recrystalized 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.

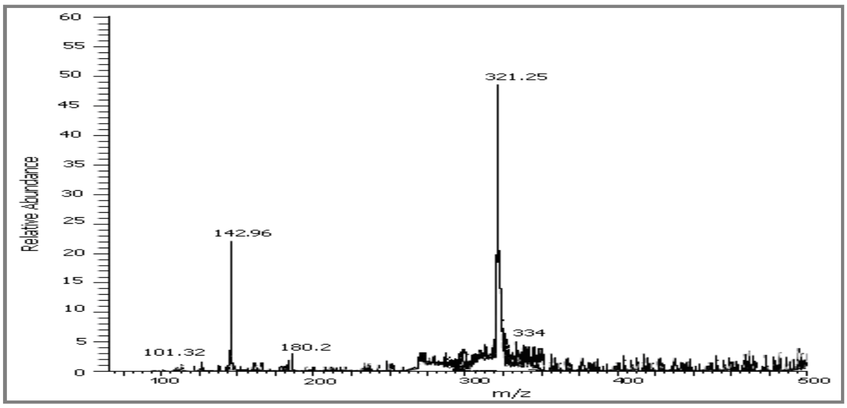


Figure 3. ESI-Mass spectrum of 2-(4-methylthiazol-5-yl)ethanol with its molecular ion peak at m/z = 142.96.

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_{obs} versus log(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 [TA] = 5.0×10^{-3}, [DPC] = 5.0×10^{-4}, $[OH^-]$ =0.08; I=0.18/mol dm^{-3}. The rate constant of reaction (k_{obs}) was obtained by the plot of log (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 1.0×10^{-5} to 1.0×10^{-4}mol dm^{-3}. 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_{obs} (Table 1).

Effect of [thiamine]: The thiamine concentration was varied in the range 1.0×10^{-3}-1.0×10^{-2} mol dm^{3} at 298 K while keeping other reactant concentrations and conditions constant. The k_{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_{obs} versus $[TA]^{0.7777}$ which is linear rather than the direct plot of k_{obs} versus [TA] (Figure 4) (r=0.9798, S < 0.004) (Table 1).

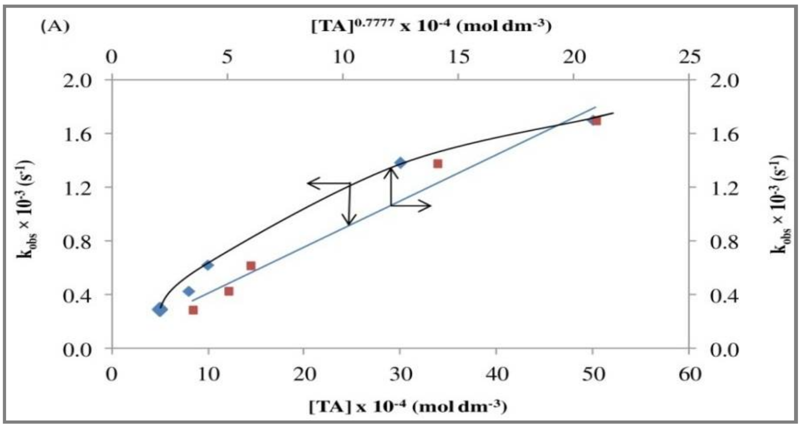


Figure 4. Plots of (A) k_{obs} vs $[TA]^{0.7777}$ and k_{obs} vs [TA] (conditions as in table 1).

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^{-3} 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 $[IO_4^-]$ was observed by varying the concentration from 5.0×10^{-5} to 5.0×10^{-4} mol dm^{-3} while keeping all other reactants concentrations constant. It was observed that the rate constants decreased by increasing $[IO_4^-]$ (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_3 at constant [DPC], [TA], $[OH^-]$ and $[IO_4^-]$ 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 thiaminealone with acrylonitrile did not induce any polymerization under the same conditions.

Table 1. Effect of variation of [DPC], [TA], [OH$^-$], and [IO$_4^-$] concentrations the oxidation of thiamine by DPC in aqueous alkaline medium at 298 K [I = 0.18 mol dm^{-3}]

[DPC] × 10^4 (moldm^{-3})	[TA] × 10^3 (moldm^{-3})	[KIO$_4$] ×10^4 (moldm^{-3})	[OH] ×10^2 (moldm^{-3})	K_{obs} ×10^2 (s^{-1})
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 ≤ 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.

$$H_5IO_6 \rightleftharpoons H_4IO_6^- + H^+ \qquad (2)$$

$$H_4IO_6^- \rightleftharpoons H_3IO_6^{2-} + H^+ \qquad (3)$$

$$H_3IO_6^{2-} \rightleftharpoons H_2IO_6^{3-} + H^+ \qquad (4)$$

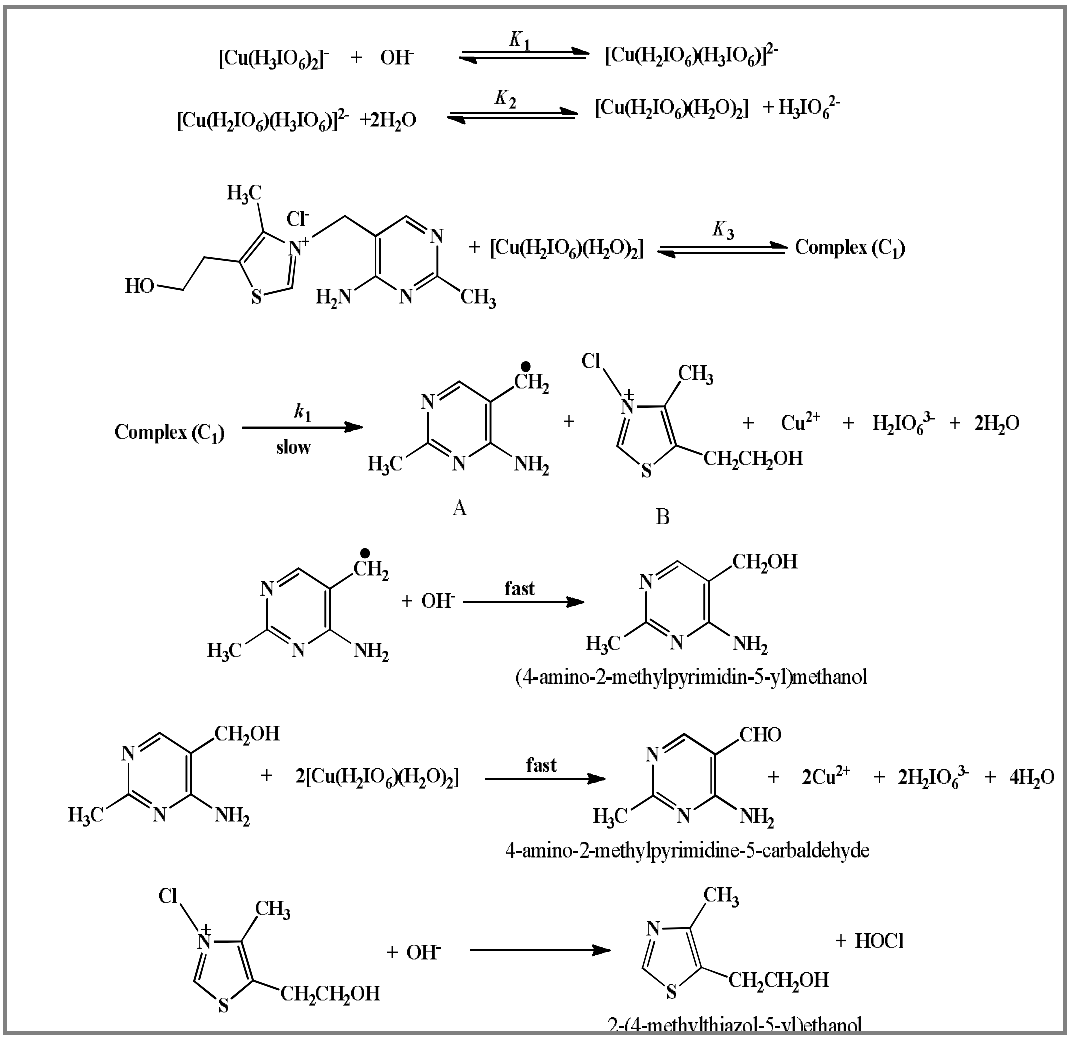
Periodic acid exists in the acid medium as H_5IO_6 and as $H_4IO_6^-$ at around pH 7. Thus under the conditions employed, in alkaline medium the main species are expected to be $H_3IO_6^{2-}$ and $H_2IO_6^{3-}$. At higher concentrations, periodate also tends to dimerise [18]. However, formation of this 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), monoperiodatocuprate(III) (MPC), and tetrahydroxocuprate(III). The last one is ruled out, as its equilibrium constant is 8.0 × 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 monoperiodatocuptrate(III) (MPC) species as shown in equations (5) and (6). Similar results have been well reported in literature [20].

$$[Cu(H_3IO_6)_2]^- + OH^- \overset{K_1}{\rightleftharpoons} [Cu(H_2IO_6)(H_3IO_6)]^{2-} + H_2O \qquad (5)$$

$$[Cu(H_2IO_6)(H_3IO_6)]^{2-} + 2H_2O \overset{K_2}{\rightleftharpoons} [Cu(H_2IO_6)(H_2O)_2] + [H_3IO_6]^{2-} \qquad (6)$$

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], [OH^-], and [IO_4^-] are well accommodated.



Scheme 2. Detailed scheme for the oxidation of thiamineby 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 afree 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 thiamineby 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 (5.0×10^{-3} mol dm^{-3}), DPC (5.0×10^{-4} mol dm^{-3}), $[OH^-] = 0.08$ mol dm^{-3} 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,

$$k_{obs} = \frac{\text{Rate}}{[\text{DPC}]} = \frac{k_1K_1K_2K_3\,[\text{TA}]\,[\text{OH}^-]}{[\text{H}_2\text{IO}_6^{3-}] + K_1[\text{OH}^-]\,[\text{H}_2\text{IO}_6^{3-}] + K_1K_2[\text{OH}^-] + K_1K_2K_3\,[\text{TA}]\,[\text{OH}^-]} \qquad (7)$$

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

$$\frac{1}{k_{obs}} = \frac{[\text{H}_2\text{IO}_6^{3-}]}{k_1K_1K_2K_3\,[\text{TA}]\,[\text{OH}]^-} + \frac{[\text{H}_2\text{IO}_6^{3-}]}{k_1K_2K_3\,[\text{TA}]} + \frac{1}{k_1K_3\,[\text{TA}]} + \frac{1}{k_1} \qquad (8)$$

According to Eq. (8), other conditions being constant, plots of $1/k_{obs}$ v/s $1/[OH^-]$ ($r \geq 0.9961$, $S \leq 0.001$), $1/k_{obs}$ v/s 1/[TA] ($r \geq 0.9874$, $S \leq 0.004$), $1/k_{obs}$ v/s $[H_3IO_6^{2-}]$ ($r \geq 0.9909$, $S \leq 0.005$) 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 4.905×10^{-2} s^{-1},9.24×10^{-1} dm^{3}mol^{-1}, 0.599×10^{-3} mol dm^{-3} and 5.36×10^3 dm^3 mol^{-1} 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, perioadate 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 ΔH, entropy of reaction ΔS, and free energy of reaction ΔG were calculated for the first equilibrium step. These values are given in table 2. A comparison of the later values (ΔH=41.5 kJ mol^{-1}) with those obtained for the slow step of the reaction ($\Delta H^{\#}$=54.7 kJ mol^{-1}) 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.

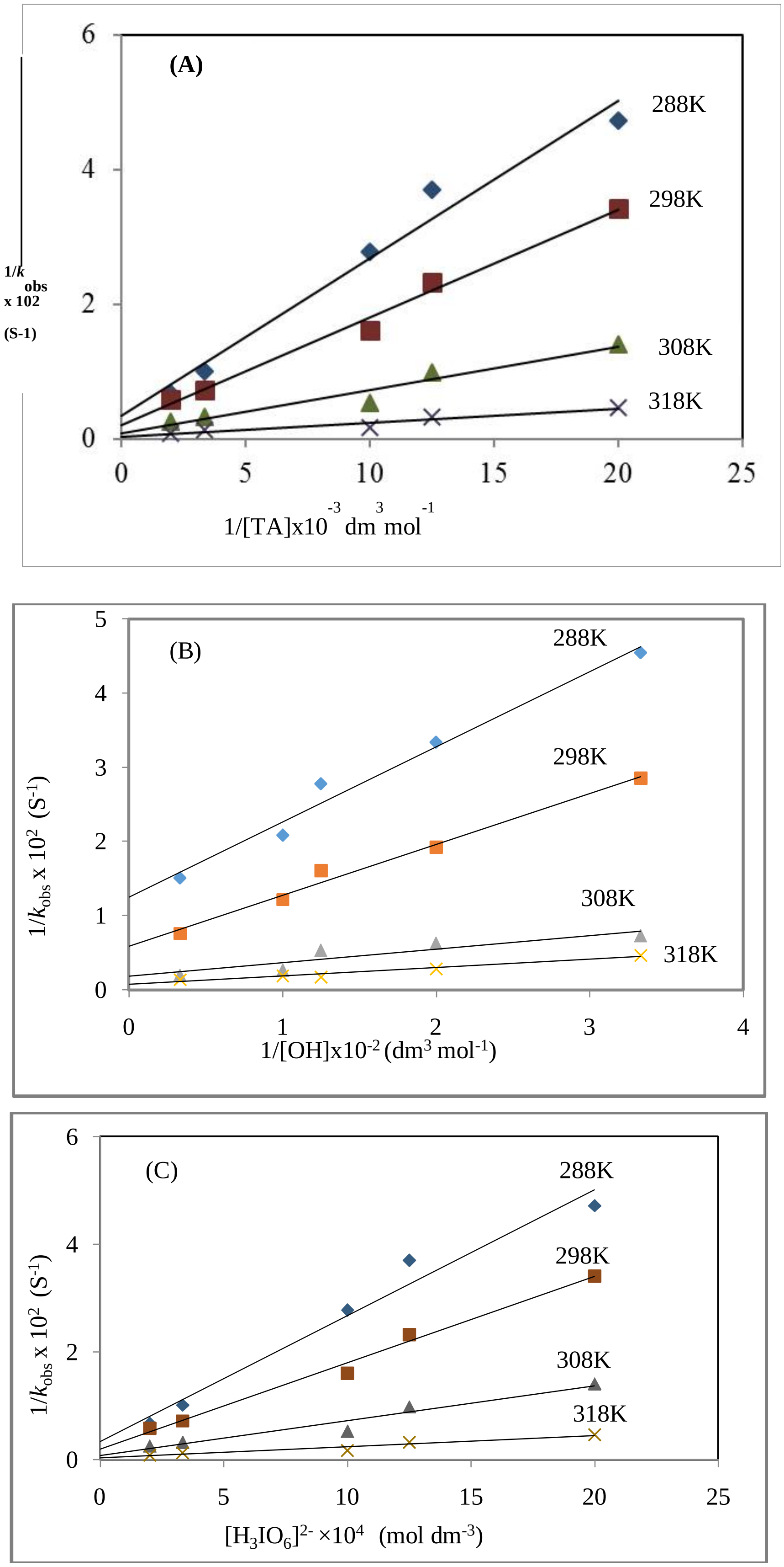


Figure 5. Verification of rate law (5) for the oxidation of TA by diperiodatocuprate (III). Plots of (A) 1/k_{obs} v/s 1/[TA], (B) 1/k_{obs} v/s 1/[OH^-], (C) 1/k_{obs} v/s [$H_3IO_6^{2-}$], at four different temperatures (conditions as in Table 1).

Table 2(A). Activation parameters with respect to the slow step of Scheme 2 and thermodynamic quantities for the oxidation of thiamineby diperiodatocuprate(III) in aqueous alkaline medium. {[DPC] =1.0 ×10^{-4} mol dm^{-3}; [TA] = 5.0 ×10^{-3} mol dm^{-3}; [OH^-] = 0.08 mol dm^{-3}; [IO_4^-] = 1×10^{-4} mol dm^{-3}; I = 0.18 mol dm^{-3}}

Temperature (K)	**k_1 (x10^2) (s^{-1})**		
(A) Effect of temperature			
288	2.948		
298	4.905		
308	12.08		
318	26.91		
Activation of parameters			
Ea(kJ mol^{-1})	57.1±1.4		
$\Delta H^{\#}$(kJ mol^{-1})	54.6±0.3		
$\Delta S^{\#}$($J \cdot K^{-1} mol^{-1}$)	-86±3.0		
$\Delta G^{\#}$(kJmol^{-1})	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_1x10^1 (dm^3 mol^{-1})	K_2x10^3 ($moldm^{-3}$)	K_3x10^{-3}(dm^3mol^{-1})
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
ΔH(kJmol^{-1})	41.5	-67.5	28.9
ΔS($J \cdot K^{-1}$ mol^{-1})	141	-288	169
ΔG_{298}(kJ mol^{-1})	-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 $\Delta S^{\#}$ (-86 $JK^{-1}mol^{-1}$) 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, $[Cu(H_2IO_6)(H_2O)_2]$ 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,

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

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

$$K_3 = \frac{[C_1]}{[\text{Cu}(H_2IO_6)(H_2O)_2]\,[\text{TA}]}$$

This can be rearranged to give

$$[C_1] = K_3\,[\text{Cu}(H_2IO_6)(H_2O)_2]\,[\text{TA}] \qquad \text{(ii)}$$

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

$$\text{Rate} = \frac{-d[\text{DPC}]}{dt} = k_1\,K_3\,[\text{Cu}(H_2IO_6)(H_2O)_2]\,[\text{TA}] \qquad \text{(iii)}$$

The second equilibrium constant is given by

$$K_2 = \frac{[\text{Cu}(H_2IO_6)(H_2O)_2]\,[H_3IO_6^{2-}]}{[\text{Cu}(H_2IO_6)\,(H_3IO_6)]^{2-}}$$

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