Mechanistic investigation of oxidation of tripelennamine hydrochloride by diperidatocuprate (III) in an aqueous alkaline medium

1. Arunkumar T. Buddanavar,

PG. Dept of Chemistry, Karnataka university, Dharwad

2. Atmanand M. Bagoji

PG. Dept of Chemistry, Karnataka university, Dharwad

3. Sharanappa T. Nandibewoor

PG. Dept of Chemistry, Karnataka university, Dharwad

Abstract: Illuminating the complex reactions of molecules in aqueous solution is one of the most important tasks of experimental studies of reaction dynamics. The behavior of the reactant molecules in aqueous solution at different temperatures was analyzed in the present paper. The oxidant diperiodatocuprate(III) (DPC) was used for the oxidation of tripelennamine hydrochloride(TPH) in aqueous alkaline medium,. The order of the reaction with respect to [DPC] was unity when [DPC] << [TPH], while the order with respect to [TPH] and [OH$^-$] were less than unity, whereas negative less than unity in [IO$_4^-$] over the concentration range studied. The accelerating and retarding effect on rate of reaction was observed with an increase in [OH$^-$] and [IO$_4^-$] respectively. The final products of oxidation were identified by GC-MS spectral analysis and plausible mechanism was proposed. The reaction constants involved in the different steps of the reaction mechanism were calculated with respect to slow step. The activation parameters and the thermodynamic quantities were determined. Active species of diperiodatocuprate (III) was found to be MPC i.e. [Cu (H$_2$IO$_6$) (H$_2$O)$_2$].

Introduction:

Tripelennamine hydrochloride (TPH) is the hydrochloride salt form of tripelennamine, and it is a psychoactive drug and member pyridine and ethylenediamine classes that is used as an antipruritic and first generation antihistamine H1 antagonist with low sedative action but frequent gastrointestinal irritation. It is used in the treatment of asthma, hay fever, urticarial and rhinitis; and also veterinary application, tripelennamine also acts as a weak serotonin reuptake(SRI) and dopamine reuptake inhibitor(DRI)[1-3]. Tripelennamine is administered by various routes, including topically.

Diperodatocuprate (III) (DPC) is a powerfull oxidizing agent in alkaline medium and it is widely used as a volumetric reagent for the determination of various organic and inorganic species. It has been used

as oxidizing agent for the kinetics of oxidation 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 DPC in alkaline and on the other hand they proposed mechanism by generalizing the DPC as $[Cu\ (HL)\ L]^{(x+1)-}$. In the present investigation we have obtained the evidence for the reactive species for the DPC in alkaline medium. The DPC is a metal complex with Cu in oxidation state like Ag in DPA and Fe in haemoglobin. Thus, the studies of DPC become important because of their biological significance and selectivity towards the oxidant.

A variety of organic substrates are oxidized by diperiodatocuprate (III) (DPC) in alkaline medium. However, there are no reports on the oxidation of tripelennamine by DPC in alkaline medium. In the present work, redox reaction involving the oxidation of TPH by DPC in alkaline, edium has been studied. This particular work has taken because of lack of literature on the oxidation of TPH by DPC. Reaction was followed conveniently by spectrophotometer in UV- Visible region. The details of such studies are given below. Although the oxidation of TPH by alkaline DPC has been studied recently, the behavior of TPH towards DPC is interest to verify nature of the active species.

EXPERIMENTAL

2.1. Materials and Reagents:

All the chemicals used were of reagent grade, and double distilled water (Milli pore water) was used throughout the work. A solution of tripeleneamine hydrochloride was prepared by dissolving an appropriate amount of recrystallized sample in double distilled water. The copper (III) periodate complex was prepared by standard procedure 3.54g of copper sulphate, 6.80g of potassium periodate, 2.20g of potassium persulphate and 9.0g of potassium hydroxide were added to about 250 cm^3 of water. The order of addition is not important. The mixture was shaken thoroughly and heated on a hot plate. In about 20 minutes the boiling mixture was turned intense red and the boiling was continued for another 20 minutes more for the completion of the reaction. The mixture was then cooled, filtered through sintered crucible (G4) and diluted to 250cm^3

The persulphate used was just sufficient to oxidize copper (II) to copper (III) and was used therefore completely removed during boiling. If an excess of persulphate was used, boiling for a long time was

necessary for its complete decomposition. Existence of copper (III) complex was verified by its UV- vis spectrum, which showed an adsorption band with maximum absorption at 418nm. The aqueous solution of copper (III) was standardized by iodometric titration and gravimetrically by the thiocynate method. The copper (II) solution was prepared by dissolving the known amount of copper sulfate (BDH) in distilled water. Periodate solution was prepared by weighing the required amount of sample in hot water and used after 24 hours. Its concentration was ascertained iodometrically at neutral pH by phosphate buffer. KOH and KNO_3 were employed to maintain the required aikalinity and ionic strength, respectively, in reaction solutions.

2.2. Kinetic measurements

The kinetics measurements were performed on a Varian CARY 50 Bio UV–Visible spectrophotometer (Varian, Victoria-3170, Australia) attached with a Peltier Accessory (temperature control). The product analysis was carried out using GC-MS (Agilent 1100 series-API 2000) mass spectrometer ionization technique. For pH measurement an Elico pH meter model LI 120 was used.The kinetics was followed under pseudo first-order condition, where [TPH] > [DPC] at 298 K unless specified. The reaction was initiated by mixing the DPC with TPH solution, which also contained the required concentration of KNO_3, KOH, KIO_4, and the progress of the reaction was followed spectrophotometrically at 418nm by monitoring the decrease in absorbance due to DPC with the molar absorptionindex to be 6250 dm^3 mol^{-1} cm^{-1}.

The pseudo first-order rate constants, k_{obs} were determined from the log (absorbance) versus time plots and the rate constants were reproducible within 5% error. The plots were linear up to 60% completion of reaction under the range of [0H$^-$] used and an example run is given in Table 1. The spectral changes during the reaction are shown in Figure 1. It is evident from the figure that the concentration of DPC decreases by observing the absorbance at 418nm. During the kinetics, a constant concentration viz.1.0×10^{-4} $moldm^{-3}$ of KIO_4 was used throughout the study unless otherwise stated. Since periodate is present in the excess in DPC, the possibility of oxidation of tripelennamine hydrochloride by periodate in alkaline medium at 298 K was tested. However, it was found that there was no significant reaction under the experimental conditions employed compared to the DPC oxidation of tripeleneamine hydrochloride. The total

concentrations of periodate and OH⁻ was calculated by considering the amount present in the DPC solution and that additionally added.

Table 1 Example run for the oxidation of tripelennamine hydrochloride by DPC in aqueous alkaline medium at 298 K.

$[TPH] = 1.0 \times 10^{-3}$ mol dm⁻³; $[DPC] = 1.0 \times 10^{-4}$ mol dm⁻³; $[OH^-] = 0.2$ mol dm⁻³; $[IO_4^-] = 1.0 \times 10^{-4}$ mol dm⁻³; and $I = 0.3$ mol dm⁻³

Time (min)	Absorbance (418 nm)	$[DPC] \times 10^4$ (mol dm⁻³)
0.0	0.5973	0.955
0.5	0.5623	0.899
1.0	0.5358	0.857
1.5	0.5131	0.820
2.0	0.4955	0.792
2.5	0.4801	0.768
3.0	0.4668	0.746
3.5	0.4550	0.728
4.0	0.4460	0.713
4.5	0.4379	0.700
5.0	0.4318	0.690
5.5	0.4240	0.678
6.0	0.4169	0.667
6.5	0.4101	0.656
7.0	0.4034	0.645
7.5	0.3973	0.635
8.0	0.3915	0.626
8.5	0.3815	0.610
9.0	0.3747	0.599
9.5	0.3719	0.595
10.0	0.3647	0.583

Figure 1 Spectrocopic changes occurring in the oxidation of tripelennamine hydrochloride by diperiodatocuprate(III) at 298 K.

$[DPC] = 1.0 \times 10^{-4}$ mol dm⁻³; $[TPH] = 1.0 \times 10^{-4}$ mol dm⁻³;

$[OH^-] = 0.2$ mol dm⁻³ and $I = 0.3$ mol dm⁻³ with scanning time interval of 0.5 min.
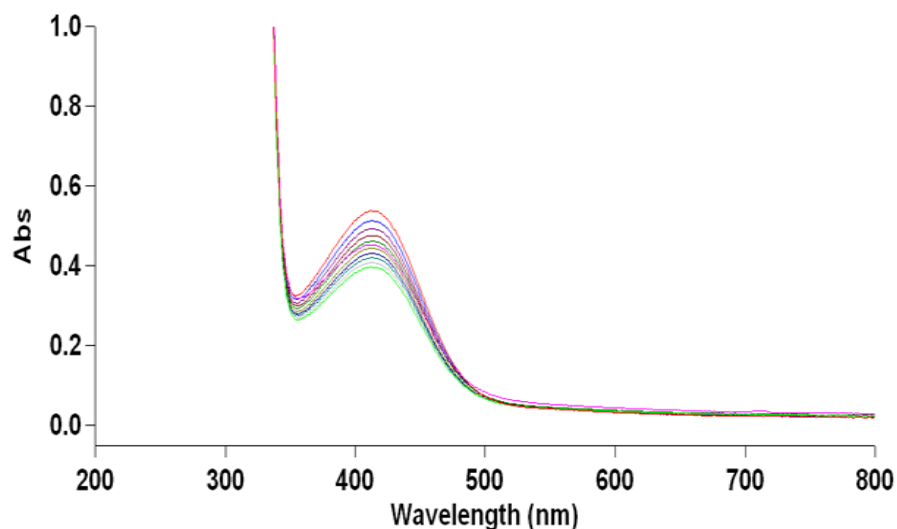
RESULTS

3.1. Stoichiometry and Product analysis

In order to find the exact number of DPC molecules required to oxidize one molecule of TPH, the stoichiometry study has been carried spectrophotometrically with excess DPC in 2.0×10^{-1} mol dm^{-3} KOH and at constant ionic strength of 0.30 mol dm^{-3}. Reaction mixtures containing different initial concentrations of the reactants were equilibrated for about 3 hours under nitrogen atmosphere at 298 K. The unreacted DPC was estimated spectrophotometrically. The experimental results indicated that one mole of trippleamine hydrochloride consumed two moles of diperiodatocuprate(III).
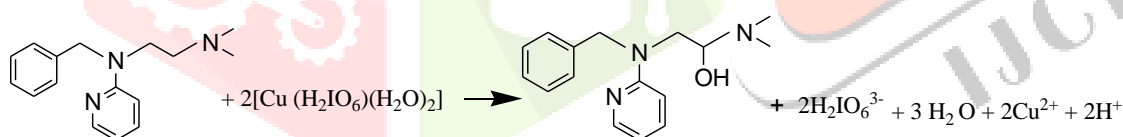

The main oxidation product was identified as 2-(benzyl(pyridin-2-yl)amino)-1-(dimethylamino)ethanol by its GC-MS spectra(Figure 2). The mass spectrum showed the molecular ion peak at 197 amu, which is the molecular weight of fragmented daughter molecule of the product. It was observed that 2-(benzyl(pyridin-2-yl)amino)-1-(dimethylamino)ethanol did not undergo further oxidation under the present kinetic condition.

3.2. Reaction order

The reaction orders with respect to TPH, alkali, periodate, concentrations were determined from the slopes of log k_{obs} versus log (concentration) plots by varying the concentration of TPH, alkali, periodate in turn while keeping all other concentrations and conditions constant.

Figure 2 GC-MS of oxidation product with its molecular ion peak at 197 amu.
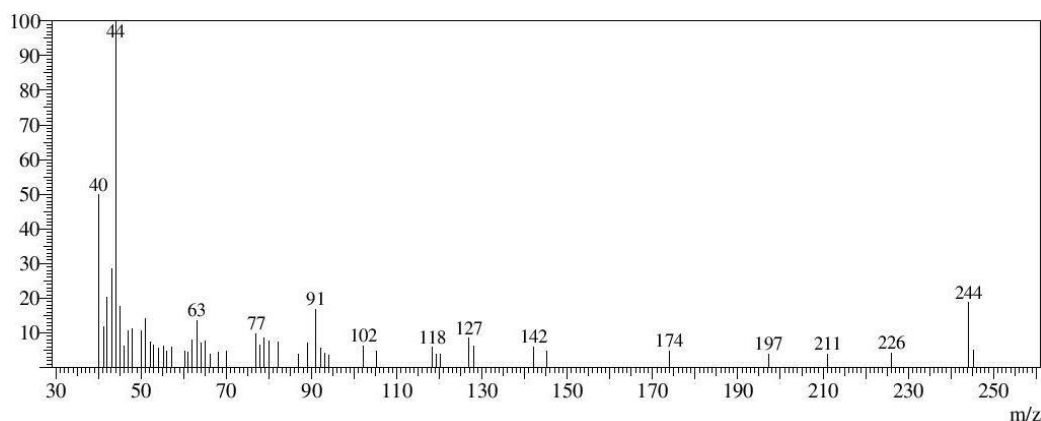
3.2.1. Effect of [DPC]

The oxidant DPC concentration was varied in the range 2.0×10^{-5} to 2.0×10^{-4} mol dm^{-3}, and fairly constant k_{obs} values indicate that order with respect to DPC was unity (Table 2). This was also confirmed by linearity of log [absorbance] versus time up to 60% completion of the reaction (Figure 3).

3.2.2. Effect of [TPH]

The substrate, TPH was varied in the range of 1.0×10^{-3} to 1.0×10^{-2} mol dm^{-3} at 298 K keeping all other reactants, concentrations and conditions constant. The k_{obs} values increased with the increase in concentration of TPH indicating an apparent less than unit order dependence on TPH under the condition of experiment and concentration range used (Table 2) (Figure 4(a)) (r$\geq$ 0.9876, S $\leq$ 0.003) .

3.2.3. Effect of [alkali]

The effect of alkali on the reaction was studied in the range of 0.02 - 0.20 mol dm^{-3} in presence of fixed concentrations of DPC, TPH, IO$_4^-$ and ionic strength of 0.30 mol dm^{-3}. The rate increased with increase in the concentration of alkali (Table 3). The order w.r.t [alkali] was found to be less than unit order. (Figure 4(b)) (r$\geq$ = 0.9915, S$\leq$ 0.002).

3.2.4. Effect of [Periodate]

The effect of increasing concentration of periodate was studied by varying the periodate concentration from 0.1×10^{-4} to 1.0×10^{-4} keeping all other reactant, concentration constants. It was found that added periodate had retarding effect on the rate of reaction (Table 3), the order with respect to periodate concentration being less than unity (Figure 6) (r $\geq$ 0.8256, S $\leq$ 0.003).

Table 2 Effect of variation of [DPC] and [TPH] on the oxidation of tripelennamine hydrochloride by DPC in aqueous alkaline medium at 298 K

$[IO_4^-] = 1.0 \times 10^{-4}$ mol dm^{-3}; $[OH^-] = 0.20$ mol dm^{-3}; $I = 0.30$ mol dm^{-3}

[DPC] $\times 10^4$ (mol dm^{-3})	[TPH] $\times 10^3$ (mol dm^{-3})	$k_{obs} \times 10^4$ (s^{-1})	$k_{cal} \times 10^4$ (s^{-1})
0.2	1.0	2.9	2.5
0.5	1.0	3.1	2.5
1.0	1.0	2.6	2.5
1.5	1.0	2.9	2.5
2.0	1.0	2.8	2.5
1.0	0.2	0.95	0.75
1.0	0.5	1.4	1.6
1.0	1.0	2.6	2.5
1.0	1.5	4.1	3.2
1.0	2.0	5.6	3.6

Figure 3 First order plots for the oxidation of tripelennamine hydrochloride by diperiodatocuprate(III) in aqueous alkaline medium at 298 K. [DPC] $\times 10^4$ (mol dm^{-3}) : (a) 0.2, (b) 0.5, (c) 1.0, (d) 1.5 and (e) 2.0. [TPH] $= 1.0 \times 10^{-3}$; $[IO_4^-] = 1.0 \times 10^{-4}$ mol dm^{-3}; $[OH^-] = 0.20$ mol dm^{-3}; $I = 0.30$ mol dm^{-3}
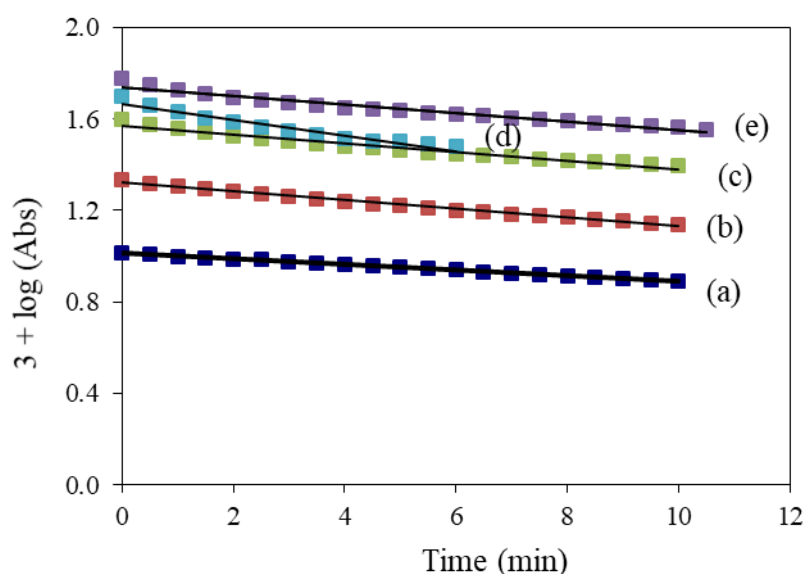
Figure 4 (a) Order with respect to TPH concentration on the oxidation of tripelennamine hydrochloride by diperiodatocuprate(III) in aqueous alkaline medium at 298 K

(Conditions as in Table III (i))
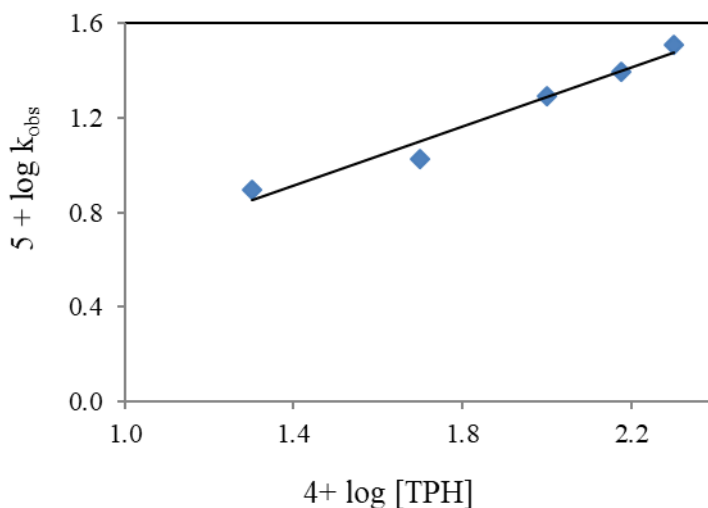
(a) Plots of k_{obs} versus $[TPH]^{0.779}$ and k_{obs} versus [TPH]

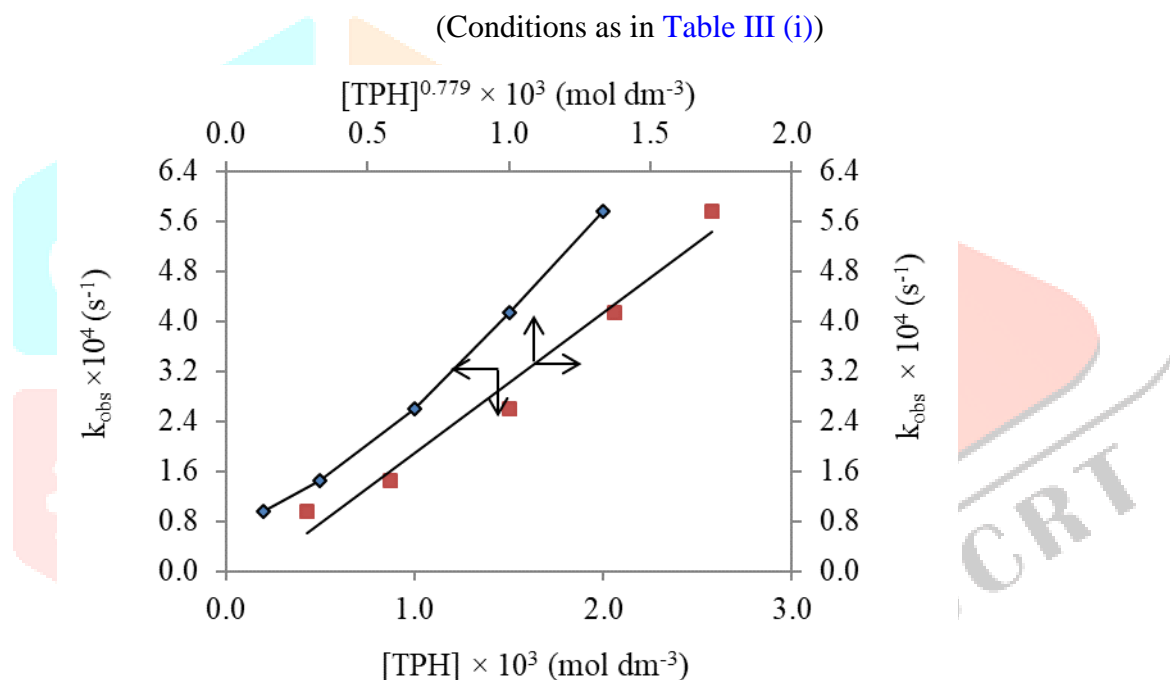(Conditions as in Table III (i))

Table 3 Effect of variation of $[OH^-]$ and $[IO_4^-]$ on the oxidation of tripelennamine hydrochloride by DPC in aqueous alkaline medium at 298 K

$[TPH] = 1.0 \times 10^{-3}$ mol dm^{-3}; $[DPC] = 1.0 \times 10^{-4}$ mol dm^{-3}; I = 0.30 mol dm^{-3}

$[OH^-]$ (mol dm^{-3})	$[IO_4^-] \times 10^4$ (mol dm^{-3})	$k_{obs} \times 10^4$ (s^{-1})	$k_{cal} \times 10^4$ (s^{-1})
0.02	1.0	1.1	1.1
0.05	1.0	1.4	1.7
0.1	1.0	1.8	2.1
0.15	1.0	2.2	2.4

0.2	1.0	2.6	2.5
0.20	0.1	4.7	4.85
0.20	0.3	4.2	4.0
0.20	0.5	3.7	3.5
0.20	0.8	3.3	2.8
0.20	1.0	2.6	2.5

Figure 4 (a) Order with respect to OH^- concentration on the oxidation of tripelennamine hydrochloride by diperiodatocuprate(III) in aqueous alkaline medium at 298 K

(Conditions as in Table III (ii))
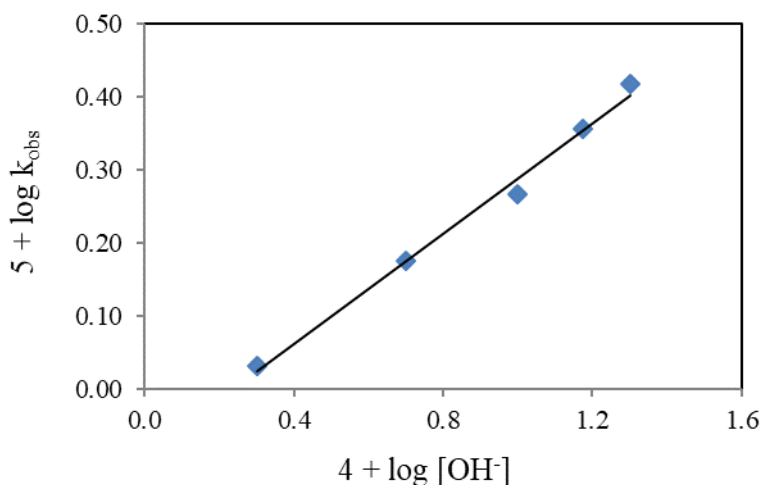
(a) Order with respect to IO_4^- concentration on the oxidation of tripelennamine hydrochloride by diperiodatocuprate(III) in aqueous alkaline medium at 298 K

(Conditions as in Table III (ii))
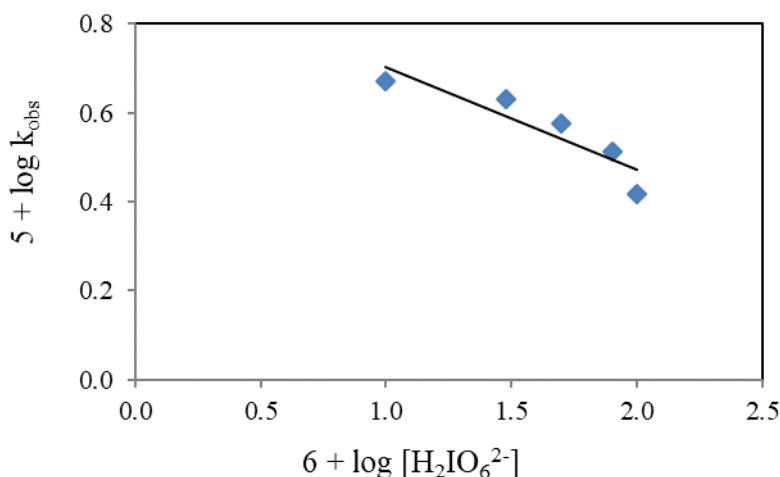
3.2.5. Effect of ionic strength

The effect of ionic strength was studied by varying the KNO_3 concentration. Ionic strength was varied from 0.2 to 0.45 mol dm^{-3} at constant concentrations of DPC, TPH, periodate. It was found that increasing ionic strength had no significant effect on the rate of reaction.

3.2.6. Rate law

Under optimized experimental conditions, the rate law is given by

$$\text{Rate} = k_{obs} \ [TPH]^{0.78} [DPC]^{1} \ [OH^-]^{0.37} \ [IO_4^-]^{-0.22}$$

3.3. Test for free radicals (polymerization)

The involvement of free radicals in the reaction was examined as follows :

The reaction mixture was mixed with acrylonitrile monomer and kept for 2 hour in an inter atmosphere. On dilution with methanol, white precipitate was formed, indicating the involvement of free radicals in the reaction. The blank experiments of either DPC or TPH or alone with acrylonitrile induced the polymerization under the same conditions. Initially added acrylonitrile decreased the rate of reaction indicating free radical intervention, which is the case as in earlier work.

3.4. Effect of temperature (T)

The influence of temperature on the rate of reaction was studied for reaction at different temperatures (288, 298, 308 and 318 K) under varying a concentration of TPH, DPC, periodate and OH$^-$ and keeping other conditions constant. The rate constants were found to increase with temperature. The rate constants (k) of the slow step of the reaction was obtained from the slopes and intercept of plots of $1/k_{obs}$ versus 1/[TPH] at four different temperatures. The energy of activation corresponding to those constants was evaluated from Arrhenius plot of log k versus 1/T [Figure 5] (r≥0.9557, S≤0.003) and other activation parameters obtained are tabulated in Table 4.

Table 4 Effect of temperature on slow step of the mechanism (Scheme 2) for the oxidation of TPH by diperiodatocuprate(III) in aqueous alkaline medium
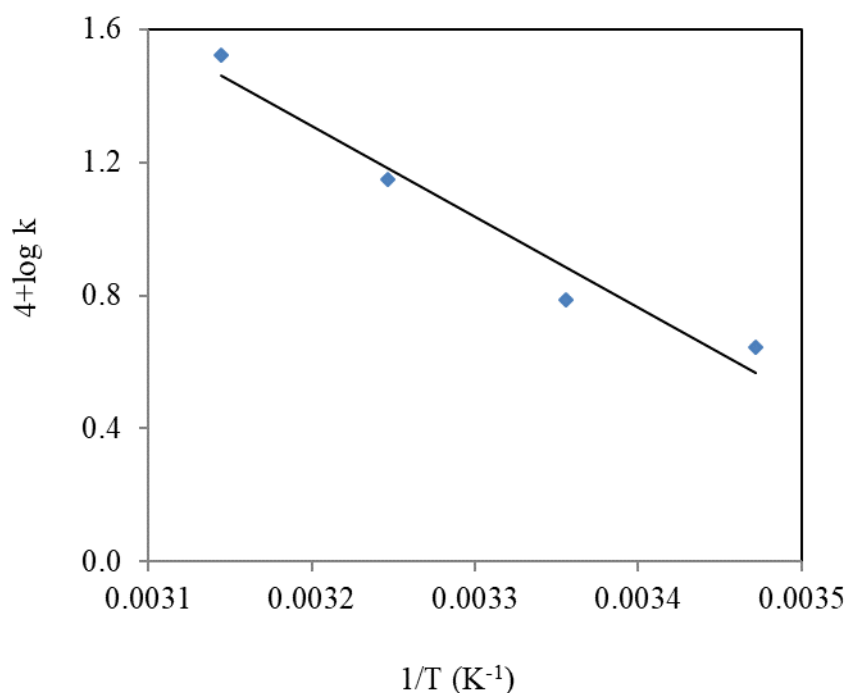
Temperature (K)	k × 10^4 (s^{-1})	log k	1/T × 10^3
288	4.4	-1.7959	3.47

298	6.1	-1.4948	3.35
308	14.1	-1.3372	3.24
318	33.3	-1.1739	3.14

(a) Activation parameters with respect to slow step of Scheme 2

Parameters	Values
E_a (kJ mol^{-1})	52.1 ± 2.6
$\Delta H^\#$ (kJ mol^{-1})	50.0 ± 2.0
$\Delta S^\#$ (JK^{-1} mol^{-1})	-137.0 ± 3.4
$\Delta G^\#$ (kJ mol^{-1})	91.0 ± 2.0
log A	17.0 ± 0.8

Figure III (v) Effect of temperature on the oxidation of TPH by DPC in aqueous alkaline medium
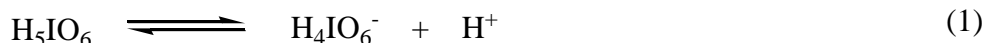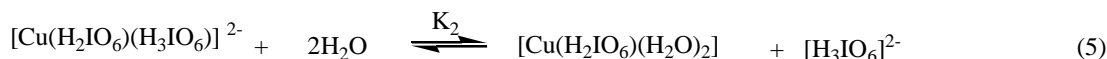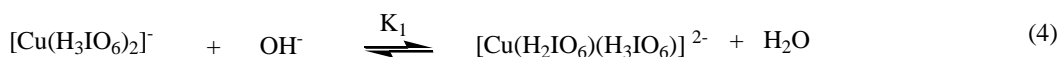

DISCUSSION

4.1. Reaction mechanism

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[4] 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[5], (1) to (3) depending on the pH of the solution, as given below.
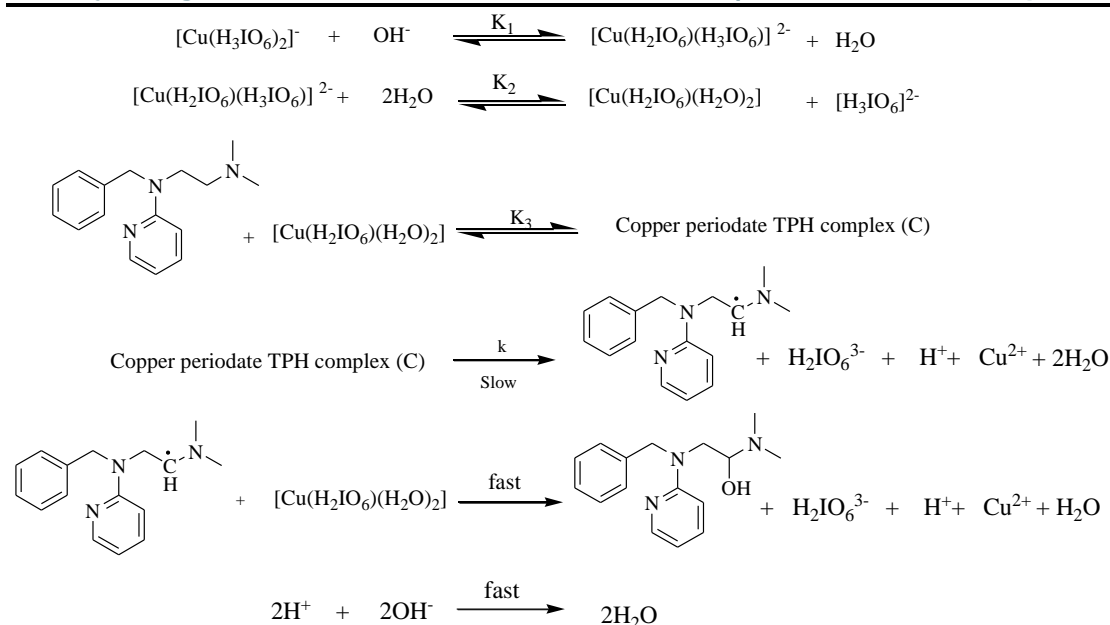
$$H_5IO_6 \rightleftharpoons H_4IO_6^- + H^+ \qquad\qquad (1)$$

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

$$H_3IO_6^{2-} \rightleftharpoons H_2IO_6^{3-} + H^+ \qquad\qquad (3)$$
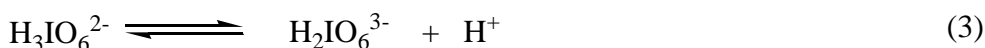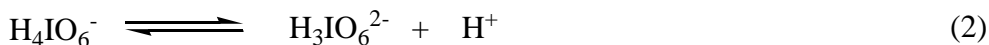
Periodic acid exists in the acid medium as H_5IO_6 and as $H_4IO_6^-$ at around pH 7. Thus under the conditions employed, in alkaline medium the main species are expected to be $H_3IO_6^{2-}$ and $H_2IO_6^{3-}$. At higher concentrations, periodate also tends to dimerise[6]. However, formation of this 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), $[Cu(H_3IO_6)(H_2IO_6)]^{2-}$, the conclusion also supported by earlier study.[6]

Lister[7] 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 40 °C. 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 3) suggest an equilibrium of the copper(III) periodate complex to form a monoperiodatocuptrate(III) (MPC) species as shown in equations (4) and (5). Similar results have been well reported in literature.[8]

$$[Cu(H_3IO_6)_2]^- + OH^- \xrightarrow{K_1} [Cu(H_2IO_6)(H_3IO_6)]^{2-} + H_2O \qquad (4)$$

$$[Cu(H_2IO_6)(H_3IO_6)]^{2-} + 2H_2O \xrightarrow{K_2} [Cu(H_2IO_6)(H_2O)_2] + [H_3IO_6]^{2-} \qquad (5)$$

The reaction between the diperiodatocuprate(III) complex and tripeleneamine hydrochloride in alkaline medium has a 1:2 stoichiometry (TPH: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.

$[Cu(H_3IO_6)_2]^- \;+\; OH^- \;\xrightleftharpoons{K_1}\; [Cu(H_2IO_6)(H_3IO_6)]^{2-} \;+\; H_2O$

$[Cu(H_2IO_6)(H_3IO_6)]^{2-} \;+\; 2H_2O \;\xrightleftharpoons{K_2}\; [Cu(H_2IO_6)(H_2O)_2] \;+\; [H_3IO_6]^{2-}$

$+ \; [Cu(H_2IO_6)(H_2O)_2] \;\xrightleftharpoons{K_3}\; \text{Copper periodate TPH complex (C)}$

Copper periodate TPH complex (C) $\xrightarrow[\text{Slow}]{k}$ $+ \; H_2IO_6^{3-} \;+\; H^+ +\; Cu^{2+} + 2H_2O$

$+ \; [Cu(H_2IO_6)(H_2O)_2] \;\xrightarrow{\text{fast}}\; + \; H_2IO_6^{3-} \;+\; H^+ +\; Cu^{2+} + H_2O$

$2H^+ \;+\; 2OH^- \;\xrightarrow{\text{fast}}\; 2H_2O$

Scheme 2: Detailed scheme for the oxidation of tripeleneamine hydrochloride by DPC

The less than unit order in [TPH] is due to the formation of a complex (C) between the oxidant and TPH prior to the formation of the products. K_3 is the composite equilibrium constant comprising the equilibrium to bind active species of tripeleneamine hydrochloride to MPC species to form a complex (C). Then, this complex (C) decomposes in a slow step to form a free radical derived from tripeleneamine hydrochloride. This free-radical species further reacts with another molecule of monoperiodatocuprate species in a fast step to yield 2-(benzyl(pyridin-2-yl)amino)-1-(dimethylamino)ethanol. The detailed mechanism for the oxidation of tripeleneamine hydrochloride 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 literature.[9, 10] Spectroscopic evidence for the complex formation between oxidant and substrate was obtained from UV–visible spectra of TPH and DPC and mixture of both. A blue shift was observed.[9]

From Scheme 2, rate law (15) can be derived as follows,

$$\text{Rate} \;=\; \frac{-d[DPC]}{dt} \;=\; k\,[\text{Complex}] = k\,[C] \tag{6}$$

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

$$K_3 = \frac{[C]}{[Cu(H_2IO_6)(H_2O)_2]\,[TPH]}$$

This can be rearranged to give

$$[C] = K_3\,[Cu(H_2IO_6)(H_2O)_2]\,[TPH] \tag{7}$$

Equation (7) takes the form upon substituting the [C] from equation (8)

$$\text{Rate} = \frac{-d[DPC]}{dt} = k\,K_3\,[Cu(H_2IO_6)(H_2O)_2]\,[TPH] \tag{8}$$

The second equilibrium constant is given by

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

This can be rearranged to give

$$[Cu(H_2IO_6)(H_2O)_2] = \frac{K_2\,[Cu(H_2IO_6)(H_3IO_6)]^{2-}}{[H_3IO_6^{2-}]} \tag{9}$$

The first equilibrium constant is given by

$$K_1 = \frac{[Cu(H_2IO_6)(H_3IO_6)]^{2-}}{[Cu(H_3IO_6)_2]^-\,[OH^-]}$$

This can be rearranged to give

$$[Cu(H_2IO_6)(H_3IO_6)]^{2-} = K_1\,[[Cu(H_2IO_6)_2]^-\,[OH^-] \tag{10}$$

By substituting the equations (9) to (10) in equation (8), we have

$$\text{rate} = \frac{-d[DPC]}{dt} = \frac{k\,K_1\,K_2\,K_3\,[TPH]_F\,[DPC]_F\,[OH^-]_F}{[H_3IO_6^{2-}]} \tag{11}$$

The total concentration of $[DPC]_T$ is given by,

$$[DPC]_T = [DPC]_F + [Cu(H_2IO_6)(H_3IO_6)]^{2-} + [Cu(H_2IO_6)(H_2O)_2] + [C]$$

where T and F refer to total and free concentrations

$$= [DPC]_F + K_1\,[[Cu(H_2IO_6)_2]^-\,[OH^-] + \frac{K_1K_2\,[[Cu(H_2IO_6)_2]^-\,[OH^-]}{[H_3IO_6^{2-}]}$$

$$+ \frac{K_1\,K_2\,K_3\,[[Cu(H_3IO_6)_2]^-\,[OH^-]\,[TPH]}{[H_3IO_6^{2-}]}$$

$$[DPC]_T = [DPC]_F + K_1\,[DPC]_F\,[OH^-] + \frac{K_1K_2\,[DPC]_F\,[OH^-]}{[H_3IO_6^{2-}]} + \frac{K_1\,K_2\,K_3\,[DPC]_F\,[OH^-]\,[TPH]}{[H_3IO_6^{2-}]}$$

$$[DPC]_T = [DPC]_F \left\{ \frac{[H_3IO_6{}^{2-}] + K_1[OH^-][H_3IO_6{}^{2-}] + K_1K_2[OH^-] + K_1\ K_2\ K_3\ [OH^-][TPH]}{[H_3IO_6{}^{2-}]} \right\}$$

$$[DPC]_F = \frac{[DPC]_T\ [H_3IO_6{}^{2-}]}{[H_3IO_6{}^{2-}] + K_1[OH^-][H_3IO_6{}^{2-}] + K_1K_2[OH^-] + K_1\ K_2\ K_3\ [OH^-][TPH]} \qquad (12)$$

The total concentration of $[OH^-]_T$ is given by,

$$[OH^-]_T = [OH^-]_F + [Cu(H_2IO_6)(H_3IO_6)]^{2-} + [Cu(H_2IO_6)(H_2O)_2] + [C]$$

$$[OH^-]_T = [OH^-]_F + K_1[DPC][OH^-]_F + \frac{K_1K_2[DPC][OH^-]_F}{[H_3IO_6{}^{2-}]} + \frac{K_1K_2K_3[DPC][OH^-]_F[TPH]}{[H_3IO_6{}^{2-}]}$$

$$[OH^-]_T = [OH^-]_F \left\{ 1 + K_1[DPC] + \frac{K_1K_2[DPC]}{[H_3IO_6{}^{2-}]} + \frac{K_1K_2K_3[DPC][TPH]}{[H_3IO_6{}^{2-}]} \right\}$$

In view of low concentrations of DPC and $H_3IO_6{}^{2-}$ used, last three terms in bracket are neglected in comparison with unity.

$$[OH^-]_T = [OH^-]_F$$

(13)

Similarly, the total concentration of [TPH] is given by,

$$[TPH]_T = [TPH]_F + [C]$$

$$[TPH]_T = [TPH]_F + \frac{K_1\ K_2\ K_3[DPC]_F[OH^-][TPH]}{[H_3IO_6{}^{2-}]} \qquad [TPH]_T = [TPH]_F \left[1 + \frac{K_1\ K_2\ K_3[DPC]_F[OH^-]}{[H_3IO_6{}^{2-}]} \right]$$

In view of low concentrations of DPC and $H_3IO_6{}^{2-}$ used

$$[TPH]_T = [TPH]_F \qquad (14)$$

Substituting the values of $[DPC]_F$ from equation (12), $[OH^-]_F$ from equation (13) and $[TPH]_F$ from equation (14) in equation (11) and omitting subscripts T and F we have,

$$rate = \frac{-d[DPC]}{dt} = \frac{kK_1K_2K_3[TPH][OH^-][DPC]}{[H_3IO_6{}^{2-}] + K_1[OH^-][H_3IO_6{}^{2-}] + K_1K_2[OH^-] + K_1K_2K_3[TPH][OH^-]}$$

$$or\ k_{obs} = \frac{rate}{[DPC]} = \frac{kK_1K_2K_3[TPH][OH^-]}{[H_3IO_6{}^{2-}] + K_1[OH^-][H_3IO_6{}^{2-}] + K_1K_2[OH^-] + K_1K_2K_3[TPH][OH^-]} \qquad (15)$$

By rearranging the above equation (15), equation (16) was obtained which is suitable for verification.

$$\frac{1}{k_{obs}} = \frac{[H_3IO_6{}^{2-}]}{kK_1K_2K_3[TPH][OH^-]} + \frac{[H_3IO_6{}^{2-}]}{kK_2K_3[TPH]} + \frac{1}{kK_3[TPH]} + \frac{1}{k} \qquad (16)$$

According to equation (16), other conditions being constant, plots of $1/k_{obs}$ versus $1/[TPH]$ (r ≥ 0.9315, S ≤ 0.006) (Figure 6 (a)), $1/k_{obs}$ versus $1/[OH^-]$ (r ≥ 0.9446, S ≤ 0.002) (Figure 6 (b)) and $1/k_{obs}$

versus [$H_3IO_6^{2-}$] (r ≥ 0.9424, S ≤ 0.004) (Figure 6 (c)) are linear at different temperatures. The slopes and intercepts of such a plots lead to the values of k, K_1, K_2 and K_3 as 6.1×10^{-4} s^{-1}, 1.3×10^1 dm^3 mol^{-1}, 1.3×10^{-5} mol dm^{-3} and 2.0×10^3 dm^3 mol^{-1} respectively at 298 K (Table 5). Using these K_1, K_2, K_3, and k values, the rate constants under different experimental conditions were calculated by equation (15) and compared with experimental data (Table 2 & 3). It was found that there is a good agreement between observed and calculated rate constants which fortifies the proposed Scheme 2. The values of K_1 and K_2 are in good agreement with the literature.[11] 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.

The thermodynamic quantities for the different equilibrium steps in Scheme 2 can be evaluated as follows. The tripeleneamine hydrochloride, periodate and hydroxide ion concentrations (Table 2 & 3) were varied at different temperatures. A van't Hoff's plot was made for variation of K_1 with temperature (log K_1 versus 1/T (r ≥ 0.9447, S ≤ 0.005) 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 4. A comparison of the latter values (ΔH = 36.9 kJ mol^{-1}) with those obtained for the slow step of the reaction (ΔH$^{\#}$ = 49.7 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

Figure IV (ix) Verification of rate law (15) in the form of equation (16) for the oxidation of trippelene hydrochloride by diperiodatocuprate(III).
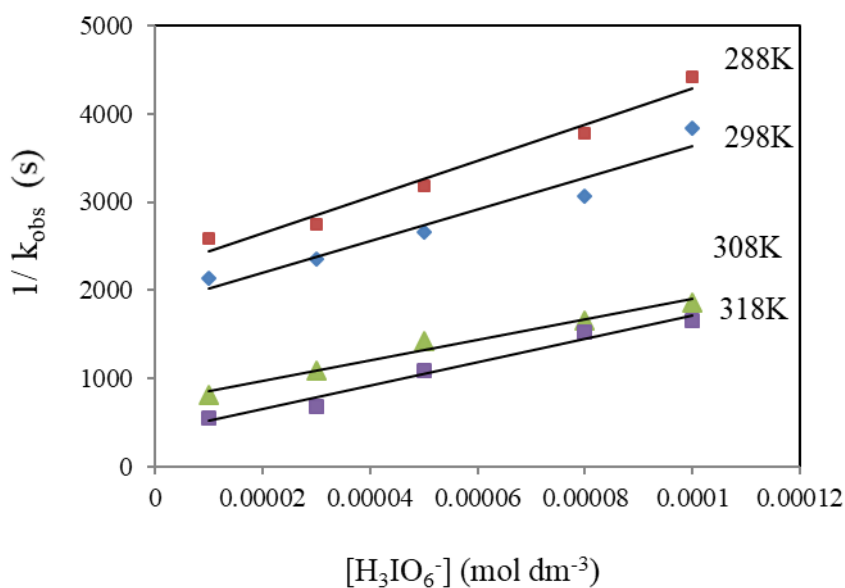
(a)   Plots of $1/k_{obs}$ versus 1/[TPH] at four different temperatures
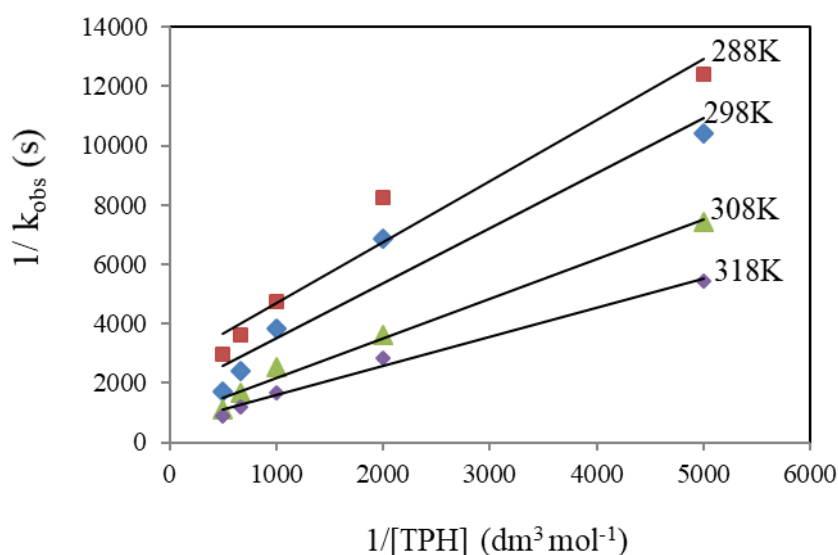
(b) Plots of $1/k_{obs}$ versus [OH$^-$] at four different temperatures
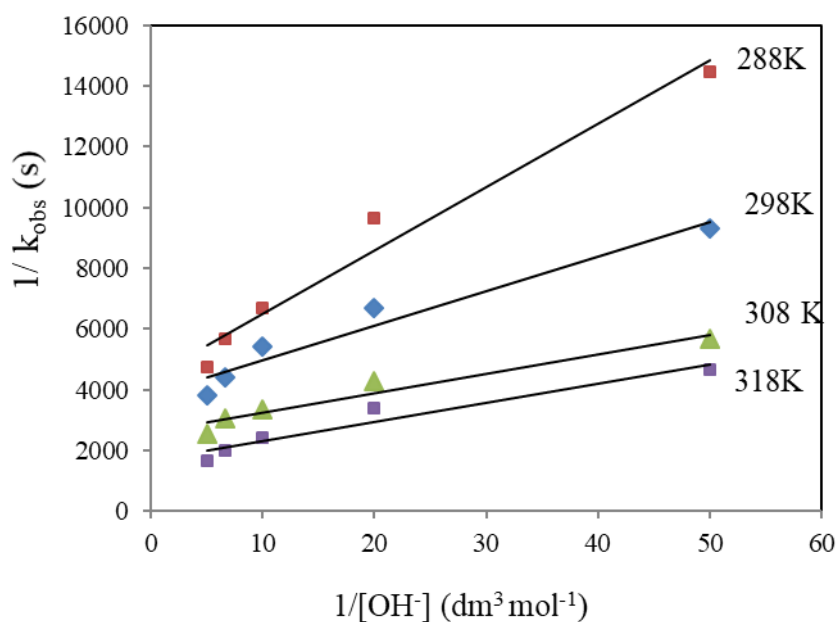
(c) Plots of $1/k_{obs}$ versus [H$_3$IO$_6^{2-}$] at four different temperatures

since it involves low-activation energy.[12] In the same manner, K_2 and K_3 values were calculated at different temperatures Table 4(a) and their corresponding values of the thermodynamic quantities are given in the Table 4 (b). The negligible effect of ionic strength on rate of reaction reveals the involvement of neutral species in reaction as seen in Scheme 2. The effect of solvent on the reaction rate is described in detail in the literature.[13] A high negative value of $\Delta S^{\#}$ (-137.1 JK^{-1}mol^{-1}) suggests that intermediate complex (C) is more ordered than the reactants.[14] The observed modest activation energy and sizeable entropy of activation supports a complex transition state in the reaction.[15]

Table 4 (a) Values of K_1, K_2 and K_3 at different temperatures for the oxidation of tripeleneamine hydrochloride by diperiodatocuprate(III) in alkaline medium

Temperature (K)	$K_1 \times 10^{-1}$ (dm^3 mol^{-1})	$K_2 \times 10^5$ (mol dm^{-3})	$K_3 \times 10^{-3}$ (dm^3 mol^{-1})
288	0.86	2.26	1.30
298	1.3	1.32	8.22
308	2.9	0.21	12.2
318	3.3	0.11	20.2

(b) Thermodynamic quantities from K_1, K_2, and K_3

Thermodynamic quantities	Values from K_1	Values from K_2	Values from K_3
ΔH (kJ mol^{-1})	36.9	83.4	66.3
ΔS (J K^{-1} mol^{-1})	146	262	304
ΔG (kJ mol^{-1})	-6.61	5.29	-19.6

Conclusions:

For the first time the oxidation mechanism of tripelene hydrochloride by diperiodatocuprate(III) in aqueous alkaline medium was studied. Among various species of diperiodatocuprate(III) in alkaline medium, monoperiodatocuprate(III) [Cu (H$_3$IO$_6$)(H$_2$O)$_2$] is considered as the active species for the oxidation reaction of TPH by DPC. Based on experimental observations, a suitable mechanism was proposed. The rate constant of the slow step and other equilibrium constants involved in the mechanism as well as the activation parameters of the reaction have been computed. The description of the mechanism was consistent with all the experimental evidences including kinetic, spectral and product studies.

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