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Thermodynamic, kinetic and mechanistic investigations of Piperazine oxidation by Diperiodatocuprate(III) complex in aqueous alkaline medium

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Abstract. The kinetics of oxidation of piperazine by the copper complex, diperiodatocuprate(III) in alkaline medium was studied at 298 K, at an ionic strength of 2.0 x 10^{-2} mol dm^{-3}. The reaction between piperazine and diperiodatocuprate(III) in aqueous alkaline medium exhibited 1:2 stoichiometry. The oxidation products were identified by UV-Visible, GC-MS and IR spectral studies. In the present study we have obtained different kinetic observations. The reaction exhibited unit order in case of diperiodatocuprate(III), while less than unit order with respect to piperazine. The addition of alkali and periodate retarded the rate of reaction. The effects of added products, ionic strength and dielectric constant on the rate of the reaction were also studied. The active species of diperiodatocuprate(III) in alkaline media is $[Cu(OH)_2(H_3IO_6)]^-$. The activation parameters with respect to the rate determining step and the thermodynamic quantities with respect to the equilibrium steps were evaluated and discussed. The plausible mechanism consistent with the experimental results was proposed and discussed in detail.

Keywords. Kinetics; oxidation; mechanism; diperiodatocuprate(III); piperazine.

1. Introduction

The oxidation by diperiodatocuprate(III) (DPC) is new and restricted to a few cases due to its limited solubility and stability in aqueous medium. A metal chelate, DPC is a good oxidant[1] in a medium with an appropriate pH value. The synthesis, structural determination and characterization of DPC have been reported.[2,3] Periodate complexes of copper in its trivalent state have been extensively used in the analysis of several organic compounds.[4] The kinetics of self-decomposition of these complexes was studied in some detail.[5] Copper complexes have occupied a major place in oxidation chemistry due to their abundance and relevance in biological chemistry.[6] Copper(III) is an intermediate in the copper(II) catalyzed oxidation of amino acids by peroxy disulfate.[7] DPC is a versatile one-electron oxidant for various organic compounds in alkaline medium and its use as an analytical reagent is now well recognized.[8] When the copper(III) periodate complex is the oxidant, multiple equilibria between different copper(III) species are involved. It would be interesting to know which of the species is the active oxidant.

Piperazine (PPZ) belongs to the family of medicines called anthelmintics. Anthelmintics are used in the treatment of worm infections.[9] PPZ is a heterocyclic nitrogenous compound[10] that has two NH groups in the ring. PPZ and its salts, as an γ-aminobutyric acid (GABA)-like substance, induce a reversible flaccid paralysis in the nematode parasites. It is an excellent solvent for uric acid and used in the treatment of gout.[9,11] In humans, serious adverse effects are rare and are generally reported with evidence of overdose or impaired excretion. PPZ derivatives fall into three broad categories i.e., gastrointestinal, neurological and allergic. Piperazine is a respiratory sensitizer. Some piperazines have been investigated for the treatment of anginapectoris,[12] cancer[13,14] and radiation sickness.[15]

In earlier reports[16,17] on DPC oxidation, periodate had a retarding effect and the order in [OH$^-$] was found to be less than unity in most of the reactions. However, in the present study we have obtained entirely different kinetic observations. The kinetics of oxidation of PPZ by some oxidants is reported in the literature.[18,19] To the best of our knowledge, oxidation of PPZ by DPC has not been reported yet. In view of the medicinal value and potential pharmaceutical importance of PPZ and lack of literature on the oxidation mechanism

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of this drug by DPC, there is a need for understanding the oxidation mechanism of this bioactive compound. Thus, the study could throw some light on the fate of the compound in biological system. We have undertaken a careful study of oxidation of PPZ by DPC in aqueous alkaline medium. The aims of the present work are, (1) to establish a rate law through kinetic measurements, (2) to propose a suitable reaction mechanism, (3) to identify the reactive species of DPC, (4) to identify the oxidation products of PPZ and (5) to calculate the thermodynamic quantities of various steps of mechanism.

2. Experimental

2.1 *Materials and Reagents*

All the chemicals used were of reagent grade. Double distilled water was used throughout the work. A solution of Piperazine (Sigma Aldrich, India) was prepared by dissolving an appropriate amount in double distilled water. The required concentration of PPZ was used from its aqueous stock solution. KNO_3 and KOH were used to maintain ionic strength and alkalinity of the reaction respectively. 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 keeping it for 24 h. Its concentration was ascertained iodometrically[20] at neutral pH by phosphate buffer. The pH of the medium was measured by ELICO LI613 pH meter.

2.2 *Preparation of DPC*

The copper(III) periodate complex was prepared by standard procedure.[21,22] Existence of copper(III) complex was verified by its UV–Vis spectrum, which showed an absorption band with maximum absorption at 418 nm. The aqueous solution of copper(III) was standardized by iodometric titration and gravimetrically by the thiocyanate[23] method.

2.3 *Kinetic Measurements*

Kinetics was followed under pseudo first order conditions where [PPZ] > [DPC] at $25 \pm 0.1°C$, unless otherwise specified. The reaction was initiated by mixing the DPC to PPZ solution, which also contained the required concentration of KNO_3, KOH, and KIO_4. The progress of the reaction was followed spectrophotometrically at 418 nm by monitoring the decrease in absorbance due to DPC with the molar extinction coefficient ε to be $6240 \pm 100 \, dm^3 \, mol^{-1} \, cm^{-1}$ (Kiran *et al.*[17], $\varepsilon = 6235 \, dm^3 \, mol^{-1} \, cm^{-1}$). It was verified that there is negligible interference from other species

Table 1. Effect of [DPC], [PPZ], IO_4^- and [OH^-] on the oxidation of piperazine by diperiodatocuprate(III) in alkaline medium at 25°C, I = 0.02 mol dm^{-3}.

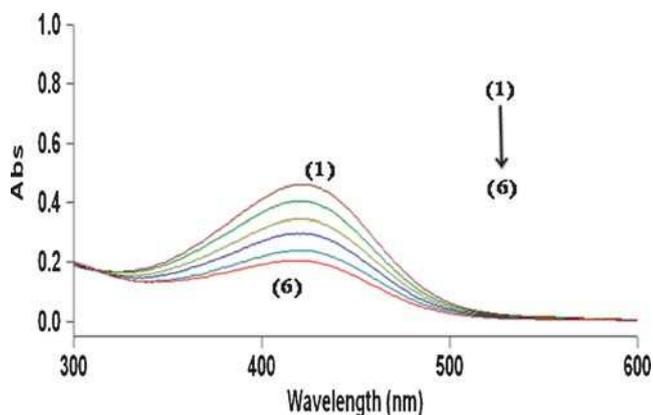| [DPC]x10^4 (mol dm^{-3})	[PPZ]x10^3 (mol dm^{-3})	[OH^-] (mol dm^{-3})	[IO_4^-]x10^5 (mol dm^{-3})	k_{obs}x10^2 (s^{-1})	k_{Cal}x10^2 (s^{-1})
0.2	1.0	0.01	4.0	2.13	2.20
0.6	1.0	0.01	4.0	2.13	2.20
1.0	1.0	0.01	4.0	2.13	2.20
1.5	1.0	0.01	4.0	2.13	2.20
2.0	1.0	0.01	4.0	2.13	2.20
1.0	0.2	0.01	4.0	0.53	0.55
1.0	0.6	0.01	4.0	1.37	1.46
1.0	1.0	0.01	4.0	2.13	2.20
1.0	1.5	0.01	4.0	2.88	2.93
1.0	2.0	0.01	4.0	3.59	3.52
1.0	1.0	0.002	4.0	2.89	2.83
1.0	1.0	0.006	4.0	2.49	2.48
1.0	1.0	0.01	4.0	2.13	2.20
1.0	1.0	0.015	4.0	1.86	1.93
1.0	1.0	0.02	4.0	1.73	1.72
1.0	1.0	0.01	0.5	4.53	4.48
1.0	1.0	0.01	1.0	3.82	3.90
1.0	1.0	0.01	2.0	2.56	2.57
1.0	1.0	0.01	4.0	2.13	2.20
1.0	1.0	0.01	5.0	1.90	1.92

Figure 1. Spectroscopic changes occurring in the oxidation of PPZ by DPC at 298 K, [DPC] = 1.0×10^{-4} mol dm^{-3}, [PPZ] = 1.0×10^{-3} mol dm^{-3}, [IO$_4^-$] = 4.0×10^{-5} mol dm^{-3}, [OH$^-$] = 0.01 mol dm^{-3} and I = 0.02 mol dm^{-3} with scanning time interval of 30 seconds.
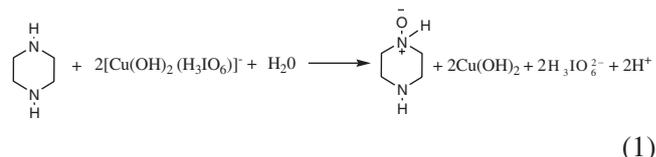
present in the reaction mixture at this wavelength. The pseudo first order rate constants, k$_{obs}$, were determined from the log (absorbance) versus time plots and were the average of duplicate runs (table 1). The plots were linear up to 80% completion of reaction under the range of [OH$^-$] used and the rate constants were reproducible to within ±5%.

In view of the modest concentration of alkali used in the reaction medium, attention was also directed to the effect of the reaction vessel surface on the kinetics. Use of polythene/acrylic wares and quartz or polyacrylate cells gave the same results, indicating that the surface does not have any significant effect on the reaction rates. The spectroscopic changes during the reaction are shown in figure 1. It is evident from the figure 1 that the concentration of DPC decreases at 418 nm. Regression analysis of the experimental data to obtain the regression coefficient r and standard deviation S of points from the regression line was performed using Microsoft 2003 Excel program.

3. Results and Discussion

3.1 *Stoichiometry and product analysis*

Different sets of reaction mixtures containing varying ratios of DPC to PPZ in the presence of constant amount of OH$^-$ and KNO$_3$ in the reaction were kept for 2 h in a closed vessel under nitrogen atmosphere. The remaining concentration of DPC was estimated spectrophotometrically at 418 nm. The results indicated 1:2 stoichiometry (PPZ: DPC) as given in Eq. 1.

$$\text{(structure)} + 2[\text{Cu(OH)}_2 (\text{H}_3\text{IO}_6)]^- + \text{H}_2\text{O} \longrightarrow \text{(structure)} + 2\text{Cu(OH)}_2 + 2\text{H}_3\text{IO}_6^{2-} + 2\text{H}^+$$

(1)

The stoichiometric ratio suggests that the main product is piperazine-N-oxide. The product was extracted with ether and recrystallized from aqueous alcohol. It was characterized by FT-IR and GC–MS spectral studies.

The presence of NO bond was confirmed by IR spectroscopy which showed N-O stretching at 1358.36 cm^{-1} indicating the presence of NO bond and N-H stretching at 3418.64 cm^{-1} indicating the presence of –NH group in the product of piperazine-N-oxide. Further, the product was subjected to GC–MS spectral analysis (figure 2). GC-MS data was obtained on a QP-2010S Shimadzu gas chromatograph mass spectrometer. The mass spectrum showed a molecular ion peak at 102 m/z confirming the presence of piperazine-N-oxide. The byproduct, Cu (II) was identified by UV-Vis spectra. The reaction products did not undergo further oxidation under the present kinetic conditions.

3.2 *Reaction Orders*

The reaction orders were determined from the slope of log k_{obs} versus log (concentration) plots by varying
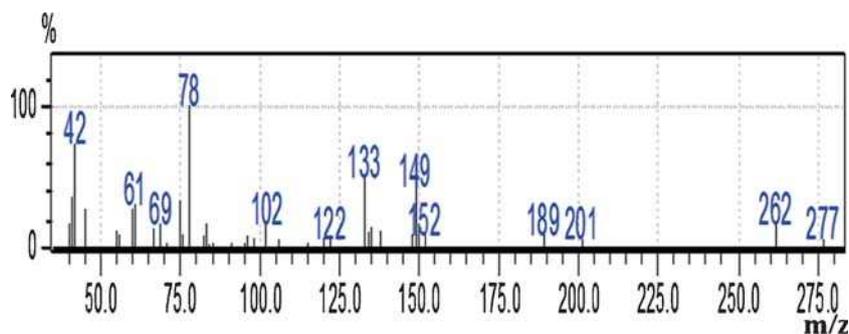

Figure 2. GC-MS spectrum showing a molecular ion peak (m/z) at 102 amu, confirming the presence of piperazine-N-oxide.

the concentration of DPC, PPZ, alkali, and periodate in turn, while keeping all other concentrations and conditions constant.

3.3 *Influence of concentration of DPC(III) on the Reaction Rate*

The concentration of the oxidant, DPC was varied in the range of 2.0×10^{-5} to 20.0×10^{-5} mol dm^{-3} at constant concentrations of PPZ, OH$^-$ and IO$_4^-$. The fairly constant k_{obs} values (table 1) indicate that the order with respect to DPC concentration was unity. This was also confirmed by the linearity of the plots of log(Abs) versus time upto 80% completion of reaction.

3.4 *Influence of concentration of Piperazine on the Reaction Rate*

The effect of piperazine was studied in the range of 2.0×10^{-4} to 2.0×10^{-3} mol dm^{-3} at 25°C and at constant concentrations of DPC, alkali and ionic strength. The rate of the reaction increased with increase in concentration of PPZ (table 1). The order with respect to PPZ concentration was obtained from the plot of log k_{obs} versus log [PPZ] and found to be less than unity (0.84). This was also confirmed by the plot of k_{obs} versus [PPZ]$^{0.84}$, which is linear rather than the direct plot of k_{obs} versus [PPZ] (figure 3).

3.5 *Influence of concentration of Alkali on the Reaction Rate*

The effect of alkali concentration was studied in the range of 2.0×10^{-2} to 20.0×10^{-2} mol dm^{-3} at 25°C and at con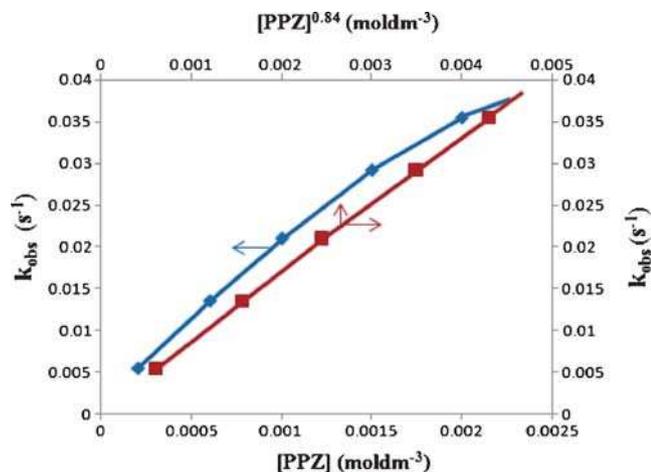stant concentrations of DPC, PPZ and ionic strength. The rate of the reaction decreased with increase in the concentration of alkali (table 1). The order with respect to alkali concentration was obtained from the plot of log k_{obs} versus log [OH$^-$] (figure S1 in Supplementary Information) and was found to be –0.23.

3.6 *Influence of concentration of IO$_4^-$ on the Reaction Rate*

The effect of periodate concentration was studied in the range of 0.5×10^{-5} to 5.0×10^{-5} mol dm^{-3} at 25°C and at constant concentrations of DPC, PPZ, alkali and ionic strength. The rate of the reaction decreased with increase in the concentration of IO$_4^-$ (table 1), which shows that periodate retards the rate of reaction (figure S2 in SI). The order with respect to [IO$_4^-$] was found to be -0.38.

Under the experimental conditions, the rate law is given as,

Rate $= k_{obs}$ [DPC] [PPZ]$^{0.84}$ [OH$^-$]$^{-0.23}$[IO$_4^-$]$^{-0.38}$
(Here k_{obs} refers to the observed rate constant under the experimental conditions).

3.7 *Effect of Ionic Strength (I) and Dielectric Constant (D) on the Reaction Rate*

The addition of KNO$_3$ at constant [DPC], [PPZ], [OH$^-$], and [IO$_4^-$] was found that increasing ionic strength had negligible effect on the rate of the reaction.

Dielectric constant of the medium, D, was varied by varying percentage of water and t-butyl alcohol. The D values were calculated from the equation $D = D_w V_w + D_B V_B$, where D_w and D_B are dielectric constants of pure water and t-butyl alcohol, respectively, and V_w and V_B are the volume fractions of components water and t-butyl alcohol, respectively, in the mixture. The decrease in dielectric constant of the reaction medium had no effect on the rate of reaction. The oxidation of water and t-butyl alcohol mixture with DPC under the experimental conditions did not occur.

3.8 *Effect of Initially Added Product*

The externally added product, copper(II) (CuSO$_4$) in the range 1.0×10^{-4} to 1.0×10^{-3} mol dm^{-3} did not have any significant effect on the rate of the reaction.

3.9 *Polymerization Study*

The intervention of free radicals in the reaction was examined as follows. The reaction mixture, to which a known quantity of acrylonitrile monomer was initially added, was kept for 2 h in an inert atmosphere. On

Figure 3. Plots of k_{obs} *vs.* [PPZ]$^{0.84}$ and k_{obs} *vs.* [PPZ] (from table 1).

diluting the reaction mixture with methanol, a white precipitate was formed, indicating the intervention of free radicals in the reaction. The blank experiments of either DPC or PPZ alone with acrylonitrile did not induce any polymerization under the same condition as those induced for the reaction mixture. To confirm free radical intervention, experiments were performed in absence and presence of acrylonitrile monomer (1.0 x 10^{-4} M). The rate constant decreased[24] from $2.06 \times 10^{-2}\,s^{-1}$ to $1.72 \times 10^{-2}\,s^{-1}$ under the experimental condition.

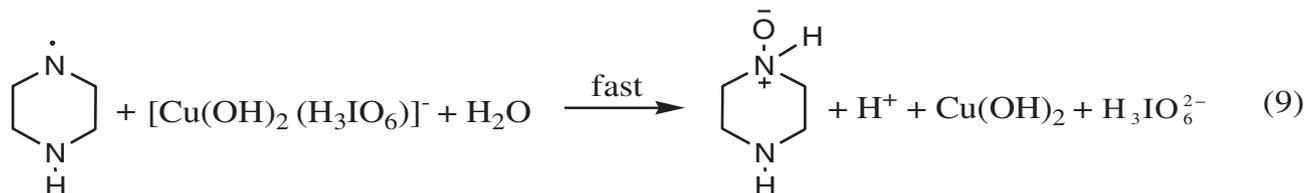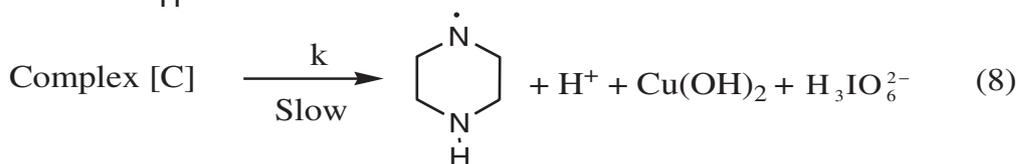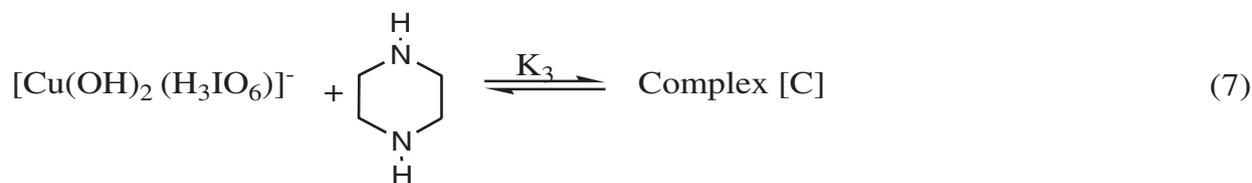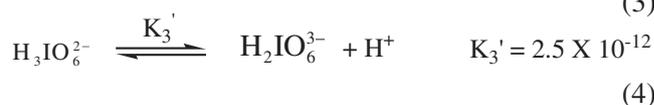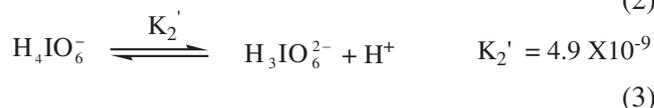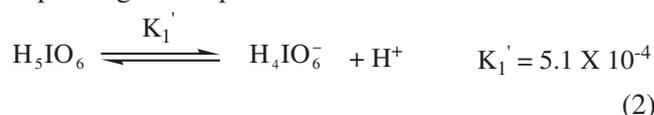### 3.10 *Effect of temperature*

The rate of the reaction was measured at four different temperatures under varying concentrations of PPZ, alkali and periodate, keeping other conditions constant. The rate constants of the slow step (k) of scheme 1 were obtained from the slopes and intercepts of plots of $1/k_{obs}$ versus $1/[PPZ]$ ($r \geq 0.998$, $S \geq 0.008$), $1/k_{obs}$ versus $[H_3IO_6^{2-}]$ ($r \geq 0.996$, $S \geq 0.010$) and $1/k_{obs}$ versus $[OH^-]$ ($r \geq 0.985$, $S \geq 0.006$), at four different temperatures. The data are subjected into least square analysis which is given in tables 2A and 2B. From the plot of log k vs 1/T, activation energy, E_a was obtained and other

activation parameters have also been calculated and tabulated in tables 2A and 2B. The comparison of activation parameters for the oxidation of PPZ by DPC and Bromamine- T (BAT)[19] is shown in table 2B. The low value of enthalpy of activation in DPC oxidation compared to Bromamine-T (BAT) oxidation shows more favorable reaction in DPC.

3.11 *Discussion of Mechanism*

The water soluble copper(III) periodate complex is reported[22] to be $[Cu(HIO_6)_2(OH)_2]^{7-}$. However, in an aqueous alkaline medium and at a 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[25] ((2)–(4)) depending on the pH of the solution.

$$H_5IO_6 \xrightleftharpoons{K_1{'}} H_4IO_6^- + H^+ \qquad K_1{'} = 5.1 \times 10^{-4} \tag{2}$$

$$H_4IO_6^- \xrightleftharpoons{K_2{'}} H_3IO_6^{2-} + H^+ \qquad K_2{'} = 4.9 \times 10^{-9} \tag{3}$$

$$H_3IO_6^{2-} \xrightleftharpoons{K_3{'}} H_2IO_6^{3-} + H^+ \qquad K_3{'} = 2.5 \times 10^{-12} \tag{4}$$

$$[Cu(OH)_2\,(H_3IO_6)\,(H_2IO_6)]^{4-} + H_2O \xrightleftharpoons{K_1} [Cu(OH)_2\,(H_3IO_6)_2]^{3-} + OH^- \tag{5}$$

$$[Cu\,(OH)_2\,(H_3IO_6)_2]^{3-} \xrightleftharpoons{K_2} [Cu(OH)_2\,(H_3IO_6)]^- + H_3IO_6^{2-} \tag{6}$$

$$[Cu(OH)_2\,(H_3IO_6)]^- + \text{(piperazine)} \xrightleftharpoons{K_3} \text{Complex [C]} \tag{7}$$

$$\text{Complex [C]} \xrightarrow[\text{Slow}]{k} \text{(piperazine radical)} + H^+ + Cu(OH)_2 + H_3IO_6^{2-} \tag{8}$$

$$\text{(piperazine radical)} + [Cu(OH)_2\,(H_3IO_6)]^- + H_2O \xrightarrow{\text{fast}} \text{(product)} + H^+ + Cu(OH)_2 + H_3IO_6^{2-} \tag{9}$$

$$H^+ + OH^- \xrightarrow{\text{fast}} H_2O \tag{10}$$

Scheme 1. Detailed mechanistic pathways for the oxidation of PPZ by alkaline diperiodatocuprate (III).

Table 2A. Effect of temperature on k for the oxidation of PPZ by diperiodatocuprate(III) in aqueous alkaline medium.

Temperature (K)	k x 10^2(s^{-1})
288	5.6
293	7.4
298	8.8
303	10.3

Table 2B. Activation parameters for the oxidation of PPZ by diperiodatocuprate (III) in aqueous alkaline medium and Bromamine-T in acidic medium.[19]

Parameters	DPC	Bromamine-T
E_a (k J mol^{-1})	10.3 ± 2	81.6
$\Delta H^{\#}$ (k J mol^{-1})	9.4 ± 2	79.0
$\Delta S^{\#}$ (J K^{-1} mol^{-1})	-30.5 ± 1	-55.6
$\Delta G^{\#}_{298K}$ (k J mol^{-1})	18.5 ± 0.8	95.4
Log A (s^{-1})	6.5 ± 0.2	—

Periodic acid exists in acid medium as H_5IO_6 and as $H_4IO_6^-$ 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 dimerize.[26] 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), $[Cu(OH)_2(H_3IO_6)_2]^{3-}$, also supported by earlier work.[15,17]

3.11a *Mechanism*: The reaction between the diperiodatocuprate(III) complex and PPZ in alkaline medium has the stoichiometry 1:2 (PPZ:DPC) with a first-order dependence on [DPC] and an apparent order of less than unity in [PPZ], negative fractional order dependence on the [alkali] and periodate. No effect of added products was observed. Based on the experimental results, a mechanism is proposed for which all the observed orders in each constituent such as [oxidant], [reductant], [OH^-], and [IO_4^-] may be well accommodated. Lister[27] proposed three forms of copper(III) periodate in alkaline medium as diperiodatocuprate(III) (DPC), monoperiodatocuprate(III) (MPC), and tetrahydroxocuprate(III). Hence, in the present study, DPC and MPC are to be considered as active forms of copper(III) periodate complex.

In most of the reports[16,17] on DPC oxidation, periodate had a retarding effect and OH^- had an increasing effect on the rate of the reaction. However in the present kinetic study, different kinetic results have

been obtained. In this study both OH^- and periodate retarded the rate of the reaction. The result of decrease in rate of reaction with increase in alkalinity (table 1) can be explained in terms of prevailing equilibrium of formation of $[Cu(OH)_2(H_3IO_6)]^{3-}$ from $[Cu(OH)_2(H_3IO_6)(H_2IO_6)]^{4-}$ hydrolysis as given in Eq. (5) of scheme 1.

Also, the decrease in rate with increase in $H_3IO_6^{2-}$ (table 1) suggests the displacement of periodate species to form monoperiodatocuprate(III) (MPC) species as given in Eq. (6) of scheme 1.

Such types of equilibria (5) and (6) of scheme 1, have been well noted in the literature.[28] It may be expected that a lower periodate complex such as monoperiodatocuptrate(III) (MPC) is more important in the reaction than the DPC in view of its participation in the reaction as given in scheme 1. The inverse fractional order in $H_3IO_6^{2-}$ might also be due to this reason. Therefore, MPC might be the main reactive form of the oxidant.

The less than unit order in [PPZ] presumably results from formation of a complex (C) between the oxidant, MPC species and PPZ prior to the formation of the products. K_3 is the composite equilibrium constant comprising the equilibrium to bind active species of PPZ to MPC species to form a complex (C). Then, this complex (C) decomposes in a slow step to form a free radical derived from PPZ. This free radical species further reacts with another molecule of MPC species in a fast step to yield the products such as piperazine-N-oxide, Cu(II) and periodate. So, the detailed mechanistic scheme for the oxidation of PPZ by diperiodatocuprate(III) is presented in scheme 1.

Since scheme 1 is in accordance with the 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.[29] Spectroscopic evidence for the complex formation between oxidant and substrate was obtained from UV–Vis spectra of PPZ (1.0×10^{-3} mol dm^{-3}), DPC (1.0×10^{-4} mol dm^{-3}), [OH^-] (0.01 mol dm^{-3}) and mixture of both. A bathochromic about 5 nm from 257 to 262 nm in the spectrum of DPC was observed (figure 4).

The Michaelis–Menten plot also proved the complex formation between DPC and PPZ, which explains the less than unit order dependence on [PPZ]. Such a complex between a substrate and an oxidant has been observed in other studies.[30] The probable structure of the complex is given in scheme 2.
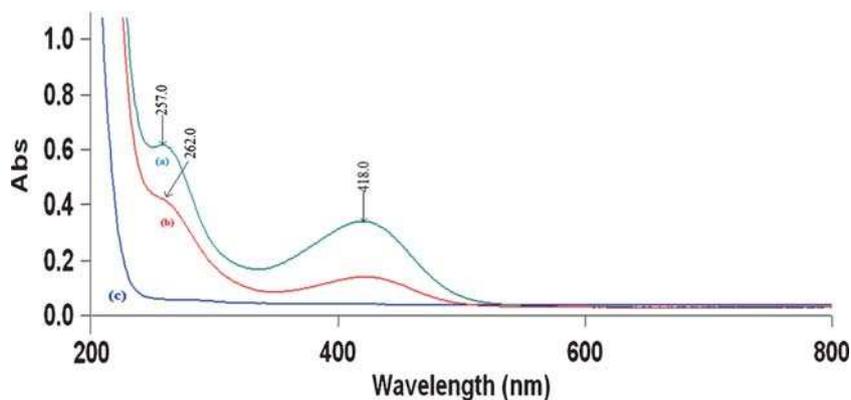
Figure 4. Spectroscopic evidence for the complex formation between DPC and PPZ. (a) UV–Vis spectrum of DPC complex (257.0 nm), (b) UV–Vis spectrum of mixture of DPA and PPZ (262.0 nm), and (c) UV–Vis spectrum of PPZ.

Scheme 1 leads to the rate law eq. (11):

$$\text{Rate} = -\frac{d[\text{DPC}]}{dt}$$

$$= \frac{kK_1K_2K_3[\text{PPZ}]_T[\text{DPC}]_T}{[\text{H}_3\text{IO}_6^{2-}][\text{OH}^-] + K_1[\text{H}_3\text{IO}_6^{2-}] + K_1K_2 + K_1K_2K_3[\text{PPZ}]} \quad (11)$$

This explains all the observed kinetic orders of different species. PPZ shows positive less than unit order since the concentration term of PPZ was present in both numerator and denominator. But the negative, less than unit order in alkali and periodate can be explained by the presence of $[\text{OH}^-]$ and $[\text{IO}_4^-]$ terms in the denominator only (shown in Eq. 11).

The eq. 12 for k_{obs} can be rearranged into eq. 13, which is suitable for verification.

$$k_{obs} = \frac{\text{Rate}}{[\text{DPC}]}$$

$$= \frac{kK_1K_2K_3[\text{PPZ}]_T}{[\text{H}_3\text{IO}_6^{2-}][\text{OH}^-] + K_1[\text{H}_3\text{IO}_6^{2-}] + K_1K_2 + K_1K_2K_3[\text{PPZ}]} \quad (12)$$

$$\frac{1}{k_{obs}} = \frac{[\text{H}_3\text{IO}_6^{2-}][\text{OH}^-]}{kK_1K_2K_3[\text{PPZ}]} + \frac{[\text{H}_3\text{IO}_6^{2-}]}{kK_2K_3[\text{PPZ}]}$$

$$+ \frac{1}{kK_3[\text{PPZ}]} + \frac{1}{k} \quad (13)$$
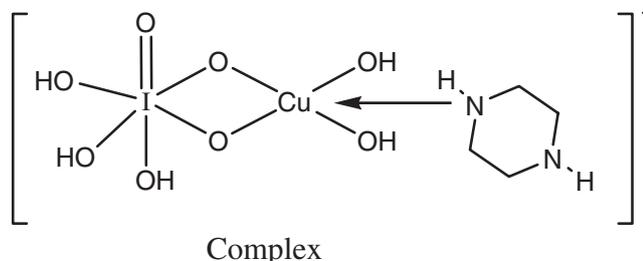
Complex

Scheme 2. The probable structure of the complex [C].

According to eq. 13, other conditions being constant, plots of $1/k_{obs}$ versus $1/[\text{PPZ}]$ (r ≥ 0.999, S ≤ 0.011), $1/k_{obs}$ versus $[\text{H}_3\text{IO}_6^{2-}]$ (r ≥ 0.995, S ≤ 0.013) and $1/k_{obs}$ versus $[\text{OH}^-]$ (r ≥ 0.926, S ≤ 0.019) should be linear, as verified in figures 5A-C. The slopes and intercepts of such plots lead to the values of K_1, K_2, K_3 and k as $(1.02 \pm 0.2) \times 10^{-2}\,\text{mol}\,\text{dm}^{-3}$, $(2.23 \pm 0.5) \times 10^{-5}\,\text{mol}\,\text{dm}^{-3}$, $(1.4 \pm 0.3) \times 10^3\,\text{dm}^3\,\text{mol}^{-1}$ and $(0.8 \pm 0.02) \times 10^{-1}\,\text{s}^{-1}$, respectively. These constants were used to calculate the rate constants and compared with the experimental values, and found to be in reasonable agreement with each other (table 1), which further supports scheme 1. The equilibrium constant K_1 is far greater than K_2. This may be attributed to the greater tendency of DPC to undergo hydrolysis compared to the dissociation of hydrolyzed species in an alkaline medium. The effect of ionic strength and dielectric constant of the medium on the rate qualitatively explains the reaction involving a neutral species, as seen in scheme 1.

K_1, K_2, K_3, and k values were calculated at four different temperatures and are given in tables 3A and 3B. The van't Hoff's plots were made for variation of K_1, K_2, K_3 with temperature (log K_1 vs. 1/T (r ≥ 0.950, S ≤ 0.008), log K_2 vs. 1/T (r ≥ 0.911, S ≤ 0.009), log K_3 vs. 1/T (r ≥ 0.975, S ≤ 0.006),) and the values of enthalpy of reaction ΔH, entropy of reaction ΔS and free energy of reaction ΔG were calculated for the first, second and third equilibrium steps. These values are given in tables 3A and 3B. The value of $\Delta S^{\#}$ is within the range for a radical reaction and has been ascribed to the nature of electron pairing and unpairing processes and to the loss of degrees of freedom formerly available to the reactants upon the formation of rigid transition state.[31] The negative value of $\Delta S^{\#}$ indicates that the
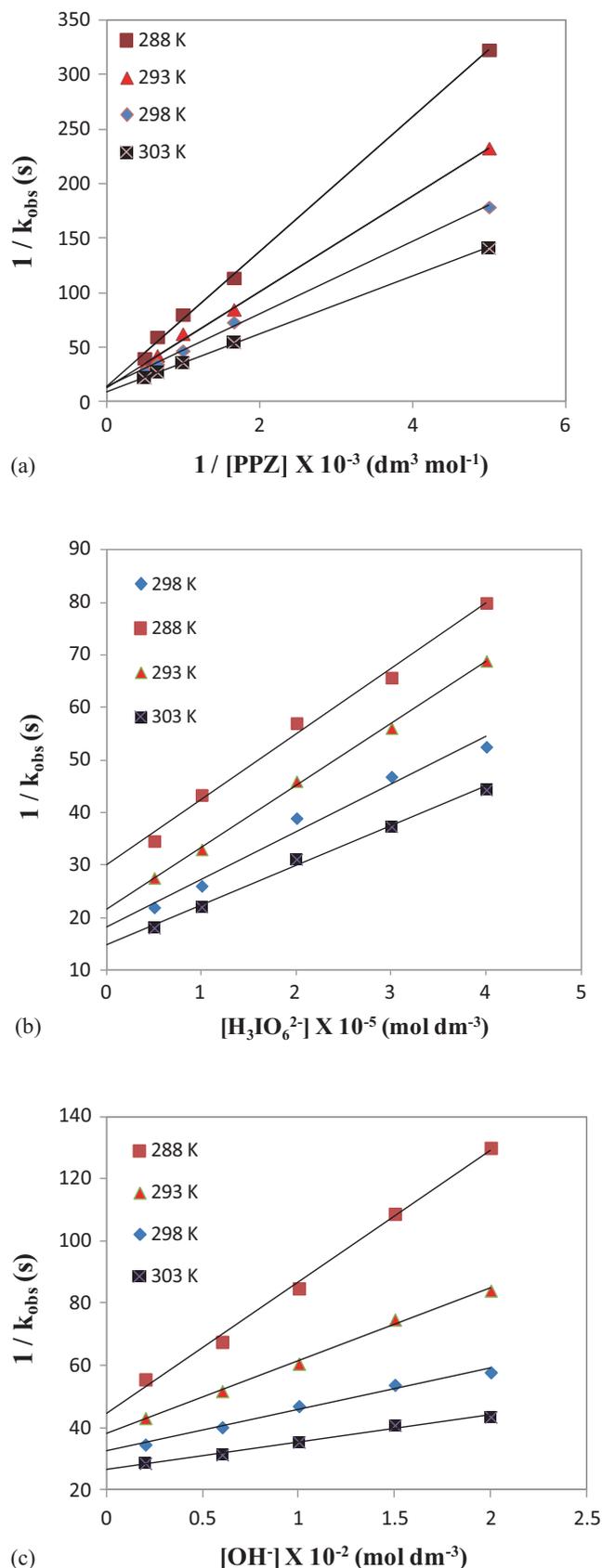
(a)

(b)

(c)

Figure 5. Verification of rate law (eq. 13) for the oxidation of PPZ by diperiodatocuprate(III). (A) Plot of $1/k_{obs}$ vs $1/[PPZ]$, (B) Plot of $1/k_{obs}$ vs $[H_3IO_6^{2-}]$ and (C) Plot of $1/k_{obs}$ vs $[OH^-]$ at four different temperatures.

Table 3A. Effect of temperature on equilibrium constants of Scheme 1 for the oxidation of PPZ by diperiodatocuprate (III) in aqueous alkaline medium.

Temperature (K)	$K_1 \times 10^2$ (mol dm^{-3})	$K_2 \times 10^5$ (mol dm^{-3})	$K_3 \times 10^{-3}$ (dm^3 mol^{-1})
288	0.3	4.0	1.3
293	0.6	2.5	1.4
298	1.0	2.3	1.5
303	1.3	2.1	1.7

Table 3B. Thermodynamic quantities with respect to 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})	15.8 ± 2	-7.9 ± 3	1.9 ± 3
ΔS (J K^{-1} mol^{-1})	-14.9 ± 4	-106.3 ± 4	-37.5 ± 2
ΔG (kJ mol^{-1})	20.1 ± 0.1	23.5 ± 1.8	13.0 ± 0.5

complex (C) is more ordered than the reactants.[32] The observed modest enthalpy of activation and a relatively low value of the entropy of activation, as well as higher rate constant of the slow step, indicate that the oxidation presumably occurs via inner-sphere mechanism.[33]

4. Conclusions

Among various species of DPC in alkaline medium, monoperiodatocuprate(III) (MPC) $[Cu(OH)_2(H_3IO_6)]^-$ is considered as active species for the title reaction. The results indicate that the role of pH in the reaction medium is crucial. The rate constant of the slow step and other equilibrium constants involved in the mechanism were evaluated and activation parameters with respect to slow step of reaction were computed.

Supplementary Information

The order with respect to alkali concentration and periodate concentration were obtained from the plot of log k_{obs} versus log $[OH^-]$ (figure S1) and log k_{obs} versus $\log[IO_4^-]$ (figure S2). Supplementary Information is available at www.ias.ac.in/chemsci.

Appendix

$$\text{Rate} = -d[DPC]_T/dt = k[C]$$
$$= kK_1K_2K_3[PPZ][DPC]_f/([OH][H_3IO_6^{2-}]) \quad (A1)$$

$[DPC]_f$ and $[DPC]_T$ are given as,

$$[DPC]_f = [Cu(OH)_2(H_3IO_6)(H_2IO_6)^{4-}] \quad (A2)$$

$$[DPC]_T = [DPC]_f + [Cu(OH)_2(H_3IO_6)_2]^{3-}$$
$$+ [Cu(OH)_2(H_3IO_6)]^- + [C] \quad (A3)$$

where, C denotes {DPC-PPZ} complex.

$$[DPC]_T = [DPC]_f\{1 + K_1/[OH^-]$$
$$+ K_1K_2/[H_3IO_6^{2-}][OH^-]$$
$$+ K_1K_2K_3[PPZ]/[H_3IO_6^{2-}][OH^-]\} \quad (A4)$$

$$[DPC]_f = [DPC]_T[H_3IO_6^{2-}][OH^-]/\{[H_3IO_6^{2-}][OH^-]$$
$$+ K_1[H_3IO_6^{2-}] + K_1K_2$$
$$+ K_1K_2K_3[PPZ]\} \quad (A5)$$

Under the experimental conditions, $[OH^-]_f \sim 10^3[DPC]_T$ and $[PPZ]_T \sim (2-10)[DPC]_T$ (see table 1). Hence, corrections for $[OH^-]_f$ and $[PPZ]_f$ due to interaction with DPC were not applied (i. e., $[KOH]_{added} = [OH^-]_f$ and $[PPZ]_f = [PPZ]_T$ were assumed).

Substituting equation (A5) in equation (A1), we get,

$$\text{Rate} = -d[DPC]_T/dt = kK_1K_2K_3[PPZ]_T[DPC]_T/$$
$$\{[H_3IO_6^{2-}][OH^-] + K_1[H_3IO_6^{2-}] + K_1K_2$$
$$+ K_1K_2K_3[PPZ]_T\} \quad (A6)$$

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