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ORIGINAL ARTICLE

Kinetic Effect of Novel Osmium(VIII) for the Oxidation of Pyrazinamide by a Copper(III) Complex and Their Mechanistic Aspects

Umar Farooq R. Bagwan[1] · **Amit B. Teradale**[2] · **Irfan N. Shaikh**[1] · **Abdulazizkhan L. Harihar**[3]

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Abstract
The oxidation of an anti-tuberculosis drug, Pyrazinamide (PYZ) by Cu(III) complex has been investigated with and without Osmium(VIII) catalyst in aqueous alkaline media at constant ionic strength using spectrophotometer. The stoichiometric ratio was found to be 1:2 in both the cases. The reaction was unit order with respect to DPC and Os(VIII), whereas less than unity with respect to PYZ. The rate increased with increase in concentration of alkali and retarding effect was observed with increase in periodate concentration in both the cases. The oxidation product was identified and characterized by spectral analysis. A plausible mechanism was proposed and physical quantities such as activation parameters and thermodynamic quantities were determined with respect to slow step. Active species for Cu(III) and Os(VIII) were $[Cu(H_2IO_6)(H_20)_2]$ and $[OsO_4(OH)_2]^{-2}$ respectively. The reaction constants involved in different steps were calculated for both the cases. The catalytic constant (K_C) for catalyzed reaction was calculated at different temperatures.

Keywords Pyrazinamide · Osmium(VIII) · Kinetics · Reaction mechanism

1 Introduction

Pyrazinamide is a potent anti-tuberculosis drug [1] which is administered in early stages of TB to shorten [2–4] the course of chemotherapy. It has unique property of killing non replicating [5] bacteria. Pyrazinamide is prescribed to patients in combination with Rifampin and Isoniazid [6]. The active form of pyrazinamide is pyarazinoic acid which acts against TB causing bacteria 'Mycobacterium tuberculosis' at little less than neutral pH. Even though the mode of action is not clearly inferred [7], but reports are available for conversion of pyrazmide into pyrazinoic acid [8] by the enzyme pyraziamidase present in cytoplasm of the bacteria, where it inhibits fatty acid synthase. This restricts the ability of bacterium to synthesize new fatty acids which are essential for growth and multiplication [9].

The intake of pyrazinamide has also shown some of the side effects such as liver injury, arthralgia, anorexia, nausea, vomiting, dysuria, malaise, fever and sideroblastic anemia [10]. Therefore, monitoring the PYZ level in human body fluids is quite significant to find the possible lowest relative concentration that could provide nominal therapeutic dosage and toxicity [11]. It is also important to control the dosage of PYZ in biological fluids to minimize the harmful effects.

Several analytical methods have been developed, such as multivariate standardization methods [12], capillary electrophoresis [13] and chromatographic methods [14]. Its determination and *in vivo* study of metabolites were carried out by using HPLC technique [15] and electroanalytical technique [16]. From past few decades, oxidizing property of transition metals in higher oxidation state has acquired substantial attention of many researchers. The transitional metals in higher oxidation states are stabilized by using chelating ligands. Periodate complex of Cu(III) [17], Ag(III) [18] and Ni(III) [19] have been synthesized and found to have fairly good oxidizing property in alkaline media. Moreover, Cu(III) is a fine oxidant which shows better oxidizing property particularly, in alkaline media. Ramreddy et.al., [20] reported, Copper(III) as an intermediate in the copper(II) catalyzed oxidation of amino acids by peroxydisulphate. The oxidation reactions usually involve the copper(II)

✉ Abdulazizkhan L. Harihar
dralharihar@rediffmail.com

[1] Department of Chemistry, SECAB Institute of Engineering and Technology, Vijayapur, Karnataka 586101, India

[2] P.G. Department of Studies in Chemistry, S.B Arts KCP Science College, Vijaypur, Karnataka 586103, India

[3] Department of Chemistry, Kittel Science College, Dharwad, Karnataka 580003, India

copper(I) couple and such aspects are detailed in different reviews [21]. The copper has acquired significant place in oxidative study owing to its bioavailability and involvement in biological electron transfer reactions [22, 23]. The diperiodatecuprate(III) DPC is versatile and rare case due to its low solubility and stability. DPC shows multiple equilibria in alkali media and it would be interesting to know which is an active species.

In recent years, transition metal ions such as Os, Ru, Pd, Mn, Cr and Ir have been used as catalysts in redox reactions [24]. The effect of Osmium(VIII) as a catalyst on rate of redox reaction have been studied [25]. However, the mechanism of catalysis is governed by nature of substrate, oxidant and conditions employed during the experiment. It is observed that catalysis may proceed through by forming complex with substrate or oxidation of substrate itself or by free radicals. The oxidation of PYZ by DPC has been reported earlier in absence of catalyst [26], but there are no reports on Osmium(VIII) catalyzed oxidation of PYZ by DPC. Hence, a comparative study of Os(VIII) catalyzed and uncatalyzed oxidation of PYZ by DPC has been undertaken which perhaps helps further in exploring drug action mechanism.

2 Experimental

2.1 Chemicals and Reagents

All chemicals employed in the experiment are of analytical grade and mili pore water was used throughout the experiment to prepare the solutions. Pyrazinamide (Sigma Aldrich) was used as received. The copper (III) periodate complex was prepared [27] and ascertained by referring to standard procedure [28]. Potassium periodate solution was prepared by dissolving required amount in warm water and it was kept for 24 h [28]. Alkalinity and ionic strength were maintained in the reaction mixture by adding required quantity of KOH and KNO_3 respectively. Standard solution of Os(VIII) was prepared by dissolving required amount of OsO_4 in NaOH. Its concentration was determined by referring to standard procedure [29].

2.2 Preparation of Diperiodatocuprate(III) Complex

Diperiodatocuprate(III) complex was synthesized by oxidation of copper sulphate using potassium persulphate in an alkaline media. $CuSO_4$ (3.54 g), KIO_4 (6.8 g), $K_2S_2O_8$ (2.2 g) and KOH (9 g) were added to 250 ml water. The reaction mixture was heated till it turned reddish brown and the solution was boiled for another 20 min to ensure the decomposition of excess of potassium persulphate. The resultant solution was filtered through a sintered glass crucible (G-4) after cooling to ambient temperature and the same was diluted to 250 ml. The Diperiodatocuprate(III) complex (DPC) is susceptible to undergo photochemical reaction which was avoided by storing in amber colored volumetric flask and keeping in dark. It remained stable at ambient temperature for months together. The UV Visible spectrum of DPC showed two strong broad absorption bands at 416 and 265 nm which ensures the existence Cu(III) in complex. Iodometric and gravimetric [30] methods were used to standardize the complex. Since, periodate is an oxidant, it may react with pyrazinamide. The reaction was tested iodometrically but no such reaction was observed in experimentally employed condition.

2.3 Experimental Details of Kinetic Measurements

The kinetics of reaction between PYZ and DPC was studied at pseudo-first order condition where the concentration of PYZ was greater than DPC {[PYZ] >[DPC]} at 25 ± 0.1 °C, unless specified, using Analytika Jena, Germany, a double beam UV–visible spectrophotometer with Win ASPECT software. The reaction was instigated by adding DPC to the PYZ solution which was having 0.1 mol dm^{-3} KNO_3, 0.05 mol dm^{-3} KOH and 1×10^{-5} mol dm^{-3} KIO_4. In case of catalyzed reaction, Os(VIII) solution with concentration 8×10^{-7} mol dm^{-3} was added in reaction mixture. The course of reaction was tracked spectrophotometrically in both uncatalyzed and catalyzed reaction, by measuring decrease in the optical density of DPC at 416 nm with the molar absorbance coefficient index, 'ε' to be 6250 ± 50 dm^3 mol^{-1} cm^{-1} which is close to literature ε = 6500 ± dm^3 mol^{-1} cm^{-1} [31]. The reaction progressed without any interference from any other species present in the reaction mixture at 416 nm. The plots of log (absorbance) against time were linear up to 80% completion of reaction as shown in Fig. 1 and the same were used to determine pseudo first order rate constants. The order with respect to different species such as PYZ, KOH, KIO_4 and ionic strength were obtained from slopes of plots of log k_{obs} against concentration of each species. The 'k_{obs}' with respect to DPC remained constant as anticipated for pseudo first order condition.

The concentration of KIO_4 is kept constant, 1×10^{-5} mol dm^{-3} and ionic strength of 0.1 mol dm^{-3} was kept constant throughout the experiment unless otherwise stated. The amount of alkali, periodate present in DPC solution

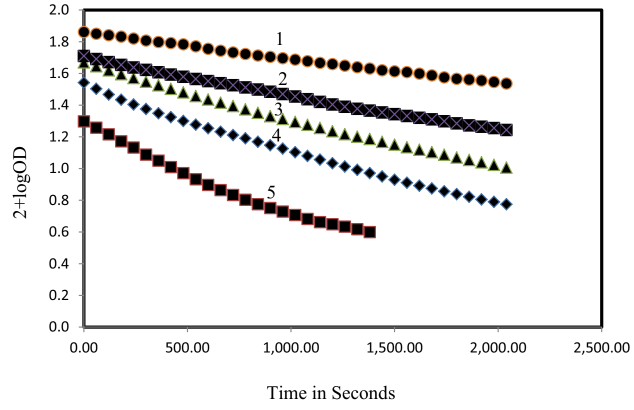


Fig. 1 First order plots for the oxidation of pyrazinamide by diperiodatocuprate(III) in aqueous alkaline medium. [diperiodatocuprate(III)] $\times 10^5$ (mol dm^{-3}): (1) 1.0, (2) 3.0, (3) 5.0, (4) 8.0 and (5) 10.0

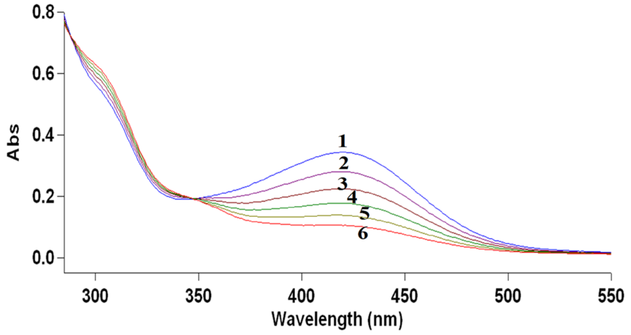
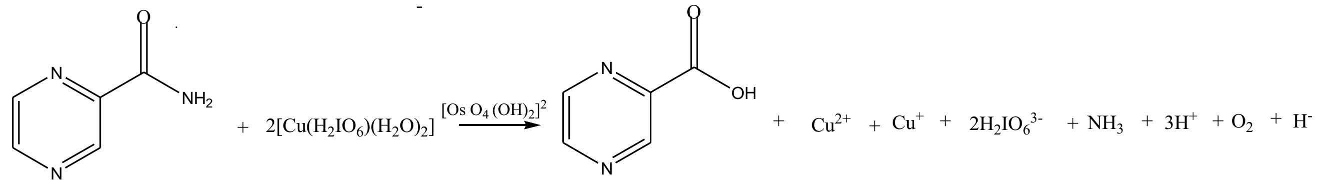


Fig. 2 Spectroscopic changes occurring in the oxidation of PZA by DPC at 298 K [DPC] = 5.0×10^{-5} mol dm^{-3}; [PZA] = 5.0×10^{-4} mol dm^{-3}; [OH^-] = 0.05 mol dm^{-3}; and $I = 0.1$ mol dm^{-3} with scanning time interval of 1 min



were taken into account while calculating total concentration required to maintain in the reaction mixture. Kinetics of reaction was also monitored in presence of nitrogen atmosphere to understand the effect of dissolved oxygen on rate of reaction, but no disparities in results were obtained between presence of nitrogen and air. In view of contamination of carbonate in the basic medium, the effect of carbonate was also studied. The rate of reaction was not affected in presence of carbonate. The decrease in concentration of DPC at 416 nm during the course of reaction is shown in Fig. 2. All kinetic data were evaluated by the method of least square regression analysis using Microsoft Excel 2007 program.

3 Results

3.1 Stoichiometry and Identification of Products

In order to find out the stoichiometry of reaction, different sets of reaction mixture containing varying ratios of DPC to PYZ were taken along with constant amount of all other reactants. The reaction mixtures were kept in closed vessel for 4 h under inert atmosphere. This procedure was followed for uncatalyzed and catalyzed reaction separately. The remaining DPC was determined spectrophotometrically at 416 nm. From results we obtained 1:2 (PYZ:DPC) stoichiometry in both the cases.

The oxidation product was identified using TLC and isolated by separation techniques. The product was characterized using FT-IR, ^{1}H NMR and LC–ESI–MS spectra. The FT-IR spectrum (Fig. 3c) showed C=O stretching frequency at 1680 cm^{-1}, broad OH stretching peak was observed at 3480 cm^{-1}. From ^{1}H NMR spectrum (Fig. 3b), we observed a broad singlet at δ 11.1 ppm which confirms the complete oxidation of pyrazinamide to pyrazonic acid. The C_5–H and C_6–H of pyrazonic acid appeared as doublet at δ 8.5 ppm. Whereas, the proton at C_3–H appeared as singlet at δ 9.1 ppm. The molecular ion peak at m/z 123 (m + 1) was observed which corresponds to pyrazinoic acid was in agreement with the molecular formula observed in LC–MS spectra (Fig. 3a).

3.2 Order of Reaction

It is assumed that catalyzed reaction is driven by both uncatalyzed and catalyzed pathways simultaneously. Therefore, total rate constant of the reaction is considered as sum of uncatalyzed and catalyzed rate constants ($k_T = k_U + k_C$). Herein, the order of reaction with respect to different reactants involved were determined from the slopes obtained from graphs of log(*kc*) vs log (concentration) by varying the concentration of substrate, oxidant, alkali, ionic strength, periodate and Os(VIII). The concentration of all other reagents were maintained constant in each case.

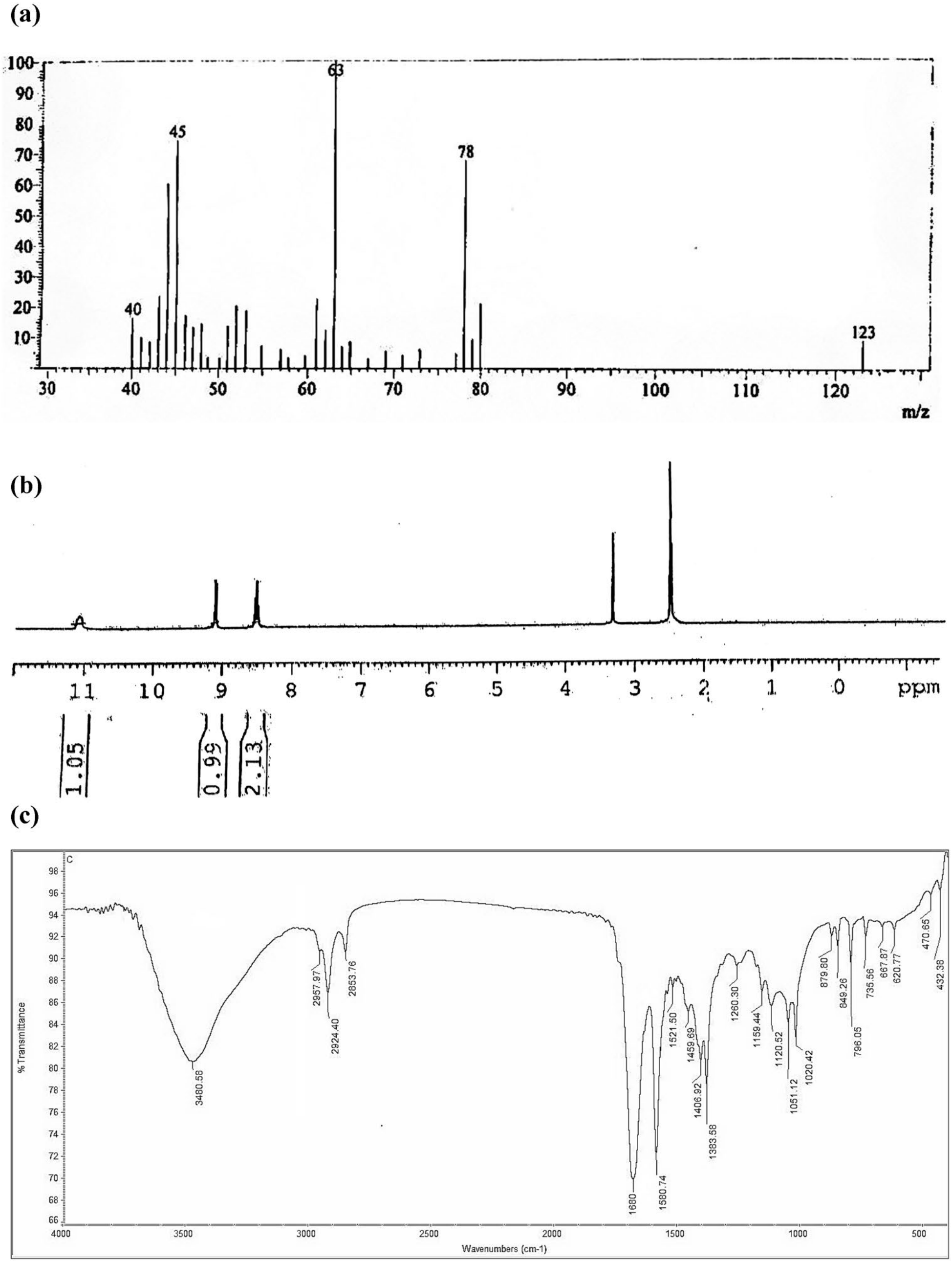


Fig. 3 **a** Mass spectrum of reaction product, pyrazinoic acid at 123 ± 1 amu. **b** ^{1}H NMR spectrum of pyrazinoic acid in DMSO. **c** FTIR spectrum of pyrazinoic acid

3.3 Effect of DPC on Rate of Reaction

The effect of DPC on rate of reaction was studied in both the cases, by varying the concentration of DPC in range between 1×10^{-5} to 10×10^{-5} mol dm^{-3} at 25 °C under constant concentrations of other reactants. The rate constants k_u for uncatalyzed and k_c for catalyzed reactions were determined from the plots of log(absorbance) against time which were linear up to 80% completion of reaction as expected for pseudo first order condition. We observed that, the rate constants obtained were fairly constant in both the cases (k_U and k_C) indicating unit order with respect to DPC. ($r \geq 0.9932$, $S \leq 0.015$).

3.4 Effect of Pyrazinamide on Rate of Reaction

The rate constants (k_U and k_C) increased for both uncatalyzed and catalyzed reactions with increase in the concentration of PYZ which is represented in Tables 1 and 2. The concentration of PYZ was varied in the range from 1×10^{-4} to 10×10^{-4} mol dm^{-3} and the concentrations of all other reactants were kept constant. We have observed, the order was less than unity for both the cases. ($r \geq 0.9972$, $S \leq 0.009$).

Table 1 Effect of [DPC], [PZA], $[OH^-]$ and $[IO_4^-]$ on the oxidation of pyrazinamide by DPC in alkaline medium at 298 K $I = 0.1$ mol dm^{-3}

$[DPC] \times 10^5$ (mol dm^3)	$[PZA] \times 10^4$ (mol dm^{-3})	$[OH^-]$ (mol dm^{-3})	$[IO_4] \times 10^5$ (mol dm^{-3})	k_U (10^3 s^{-1})	
				Found	Calculated
1.0	5.0	0.05	1.0	3.92	3.97
3.0	5.0	0.05	1.0	3.78	3.82
5.0	5.0	0.05	1.0	3.88	3.91
8.0	5.0	0.05	1.0	3.73	3.76
10.0	5.0	0.05	1.0	3. 83	3.87
5.0	1.0	0.05	1.0	1.21	1.1
5.0	3.0	0.05	1.0	2.34	2.8
5.0	5.0	0.05	1.0	3.53	4.0
5.0	8.0	0.05	1.0	4.96	5.23
5.0	10.0	0.05	1.0	5.98	5.8
5.0	5.0	0.01	1.0	2.62	2.4
5.0	5.0	0.03	1.0	3.41	3.5
5.0	5.0	0.05	1.0	3.85	4.0
5.0	5.0	0.08	1.0	4.27	4.2
5.0	5.0	0.1	1.0	4.43	4.6
5.0	5.0	0.05	0.5	4.53	4.4
5.0	5.0	0.05	0.8	4.24	4.2
5.0	5.0	0.05	1.0	3.82	4.0
5.0	5.0	0.05	3.0	2.91	3.0
5.0	5.0	0.05	5.0	2.34	2.3

3.5 Effect of Alkali on Rate of Reaction

Here, we observed that the rate constants (k_U and k_C) increased in both uncatalyzed and catalyzed reactions, with increase in concentration of KOH. The concentration of alkali was varied in the range from 0.01 to 0.1 mol dm^{-3} at constant concentration of substrate, oxidant, catalyst, periodate and at constant ionic strength. The order was found to be less than unity for both the cases. ($r \geq 0.9954$, $S \leq 0.008$).

3.6 Effect of Periodate on Rate of Reaction

The k_U and k_C values decreased with increase in periodate concentration which was varied from 0.5×10^{-5} to 5.0×10^{-5} mol dm^{-3} at constant concentration of substrate, oxidant, catalyst, alkali and at constant ionic strength. The order was negative fractional with respect to periodate in both the cases. ($r \geq 0.9927$, $S \leq 0.005$).

3.7 Effect of Catalyst on Rate of Reaction

For the effect of catalyst, we have varied the concentration of Os(VIII) from 3.0×10^{-7} to 30×10^{-7} mol dm^{-3} and concentration of remaining reactants such as substrate, oxidant, alkali, periodate and at constant ionic strength were kept constants. The values of k_C increased with increase in concentration of catalyst. Herein, we found unit order with respect to Os(VIII) (Fig. 4).

3.8 Effect of Ionic Strength and Dielectric Constant on Rate of Reaction

The effect of ionic strength on rate of reaction was studied by varying the concentration of potassium nitrate and keeping all other concentrations constant. There was no any significant effect on both uncatalyzed and catalyzed reactions. The effect of dielectric constant of reaction medium was also studied by using mixture of t-butyl alcohol and water in which t-butyl alcohol was varied. The values for dielectric constant (D) were calculated from equation.

$D = D_W V_W + D_B V_B$, where D_W and D_B are dielectric constant values of water and t-butyl alcohol respectively and V_W and V_B are volume fractions of water and t-butanol, respectively in total mixture. It was found that the rate of reaction decreased with decrease in dielectric constant and plot of log k_{obs} against 1/D was linear with negative slope for both the cases which is shown in Fig. 5.

3.9 Test for Any Free Radical

In order to infer whether the reaction is following free radical pathway, an acrylonitrile as free radical scavenger [17] was added to reaction mixture and kept for 2 h in inert atmosphere and later on diluted with methanol, but there was no formation of precipitate, hence intervention of free radical in reaction mechanism was ruled out. Further, the initially added acrylonitrile added in the reaction mixture increased

Table 2 Effect of variation of [DPC], [PYZ], [OH$^-$], [IO$_4^-$] and Os(VIII) on the Os(VIII) catalyzed oxidation of pyrazinamide by DPC in alkaline medium at 298 K $I = 0.1$ mol dm^{-3}

[DPC] × 10^5 (mol dm^3)	[PZA] × 10^4 (mol dm^{-3})	[OH$^-$] (mol dm^{-3})	[IO$_4$] × 10^5 (mol dm^{-3})	Os(VIII) (× 10^7)	k_T	k_U × 10^3 s^{-1}	K_c × 10^2 (s^{-1})	
							Found	Calculated
1.0	5.0	0.05	1.0	8.0	3.01	3.92	2.54	2.62
3.0	5.0	0.05	1.0	8.0	2.9	3.88	2.61	2.64
5.0	5.0	0.05	1.0	8.0	3.1	3.98	2.65	2.63
8.0	5.0	0.05	1.0	8.0	3.05	3.73	2.52	2.62
10.0	5.0	0.05	1.0	8.0	3.07	3.83	2.56	2.64
5.0	1.0	0.05	1.0	8.0	0.90	1.21	0.85	0.82
5.0	3.0	0.05	1.0	8.0	2.50	2.34	1.58	1.47
5.0	5.0	0.05	1.0	8.0	3.1	3.53	2.12	2.03
5.0	8.0	0.05	1.0	8.0	4.4	4.96	2.97	2.78
5.0	10.0	0.05	1.0	8.0	5.2	5.98	3.85	3.80
5.0	5.0	0.01	1.0	8.0	2.3	2.62	1.15	1.12
5.0	5.0	0.03	1.0	8.0	3.0	3.41	2.43	2.41
5.0	5.0	0.05	1.0	8.0	3.3	3.85	2.94	2.87
5.0	5.0	0.08	1.0	8.0	3.8	4.27	3.43	3.39
5.0	5.0	0.1	1.0	8.0	4.0	4.43	3.59	3.54
5.0	5.0	0.05	0.5	8.0	4.1	4.53	3.43	3.37
5.0	5.0	0.05	0.8	8.0	3.8	4.24	3.10	3.09
5.0	5.0	0.05	1.0	8.0	3.3	3.82	2.93	2.85
5.0	5.0	0.05	3.0	8.0	2.57	2.91	2.68	2.57
5.0	5.0	0.05	5.0	8.0	1.84	2.34	1.95	1.68
5.0	5.0	0.05	1.0	3.0	1.43	3.82	1.54	1.25
5.0	5.0	0.05	1.0	7.0	2.36	3.83	2.21	2.09
5.0	5.0	0.05	1.0	10.0	3.24	3.78	2.63	2.45
5.0	5.0	0.05	1.0	20.0	3.75	3.82	3.91	3.60
5.0	5.0	0.05	1.0	30.0	5.61	3.99	5.53	5.61

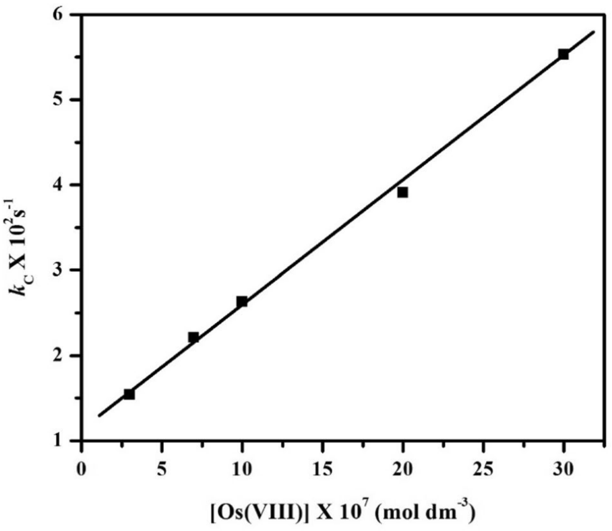


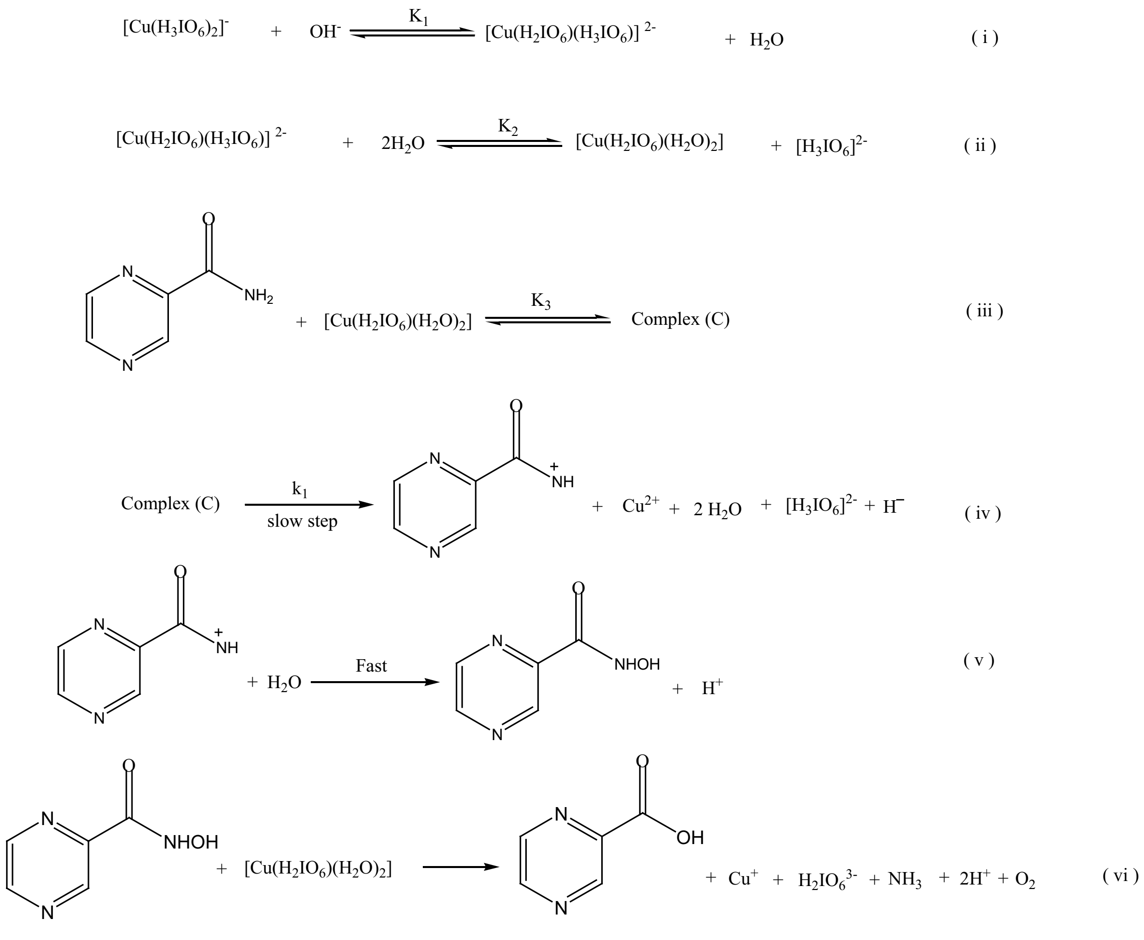
Fig. 4 Unit order plot of [Os(VIII)] versus k_C

the rate of reaction indicating no intervention of any free radical. Such observations have been reported earlier [32].

3.10 Effect of Temperature

For the effect of temperature, the kinetic study was carried out at four different temperatures 293, 298, 305 and 308 K for both the cases with varying concentration of PYZ, DPC, alkali, periodate and concentration of all other reagents were maintained constant in each case. The rate constant values (k_1) for the slow step of Scheme 1 were obtained from the slopes and intercepts of the plots of 1/k_U against 1/[PYZ] at four different temperatures and values are tabulated in the Table 3a. The energy of activation for the slow step was obtained using plots of log k_1 vs 1/T and the activation parameters were calculated and are given in the Table 3b.

Similarly, the rate constants (k_2) for the slow step of Scheme 2 were obtained from the slopes and intercepts of the plots of of [Os(VIII)]/k_C vs 1/[PYZ] at four different temperatures and the values are mentioned in Table 4a. The activation parameters were calculated and mentioned in



Scheme 1 *Uncatalyzed oxidation of PYZ by DPC*

Table 4b. Based on experimental observations the rate law for uncatalyzed reaction could be given as

$$\text{Rate } = k_U[\text{DPC}]^{1.0}[\text{PYZ}]^{0.63}[\text{OH}^-]^{0.32}\left[\text{IO}_4^-\right]^{-0.26} \tag{1}$$

Similarly, for catlaysed reaction the rate is given in following way.

$$\text{Rate} = k_U[\text{DPC}]^{1.0}[\text{PYZ}]^{0.66}[\text{OH}^-]^{0.28}[\text{Os(VIII)}]^{1.0}\left[\text{IO}_4^-\right]^{-0.25} \tag{2}$$

3.11 Catalytic Activity

When a reaction is carried out in presence of catalyst, according to Moelwyn-Huges [33] the reaction proceeds through both uncatalyzed and catalyzed pathways simultaneously. The relation between observed pseudo-first order rate constant of catalyzed reaction and that of uncatalyzed reaction is given by the equation

$$k_T = k_U + K_C\left[\text{Catalyst}\right]^x \tag{3}$$

where k_T is observed pseudo-first order rate constant of catalyzed reaction and k_U is observed pseudo-first order rate constant of uncatalyzed reaction. K_C is the catalytic constant and 'x' is the order of reaction with respect to catalyst, Os(VIII). In this study, the values of x were found to be unity for standard run. The values of K_C were calculated by the equation given below.

$$K_C = \frac{k_T - k_U}{[\text{Os(VIII)}]^X} = \frac{k_T}{[\text{Os(VIII)}]^X} \tag{4}$$

The values of K_C were calculated for Os(VIII) at different temperatures and it varies at different temperature. Further, plots of log K_C vs 1/T were linear, the activation energy and other activation parameters were calculated and given in Table 5. The value of K_C was found to be 3.41×10^{-4} at 298 K.

Table 3 With respect to the slow step of Scheme 1: (a) effect of temperature, (b) activation parameters (Scheme 1), (c) effect of temperature on K_1, K_2, K_3 for the oxidation of PYZ by DPC in aqueous alkaline medium, (d) thermodynamic parameters using K_1, K_2, K_3

(a) Effect of temperature

Temperature (K)	$K_1 \times 10^2$ (s^{-1})
293	0.39
298	0.52
305	0.66
308	0.84

(b) Activation parameters (Scheme 1)

Parameters	Value
E_a (kJ mol^{-1})	38.80
ΔH^* (kJ mol^{-1})	36.30
ΔS^* (JK^{-1} mol^{-1})	−161.10
ΔG^* (kJ mol^{-1})	84.34
Log A	4.82

(c) Effect of temperature to calculate K_1, K_2 and K_3 for the oxidation of pyrazinamide by DPC in alkaline medium

Temperature (K)	K_1 (dm^3 mol^{-1})	$K_2 \times 10^3$ (mol dm^{-3})	$K_3 \times 10^{-3}$ (dm^3 mol^{-1})
293	0.43	0.74	2.32
298	0.63	0.57	3.06
305	0.88	0.41	3.66
308	1.22	0.32	4.49

(d) Thermodynamic parameters using K_1, K_2 and K_3

Thermodynamic parameters	Values from K_1	Values from K_2	Values from K_3
ΔH (kJ mol^{-1})	53.38	−40.36	32.60
ΔS (J K^{-1} mol^{-1})	178.14	−198.39	177.63
ΔG (kJ mol^{-1})	−0.455	17.81	−19.25

4 Discussion

The Cu(III) periodate complex is water soluble and reported as $[Cu(HIO_6)_2(OH)_2]^{7-}$ [34]. But periodate exists as HIO_6^{4-} in alkaline medium which is the present employed condition. However, periodate shows multiple equilibria [35] depending upon pH of the solution as given below.

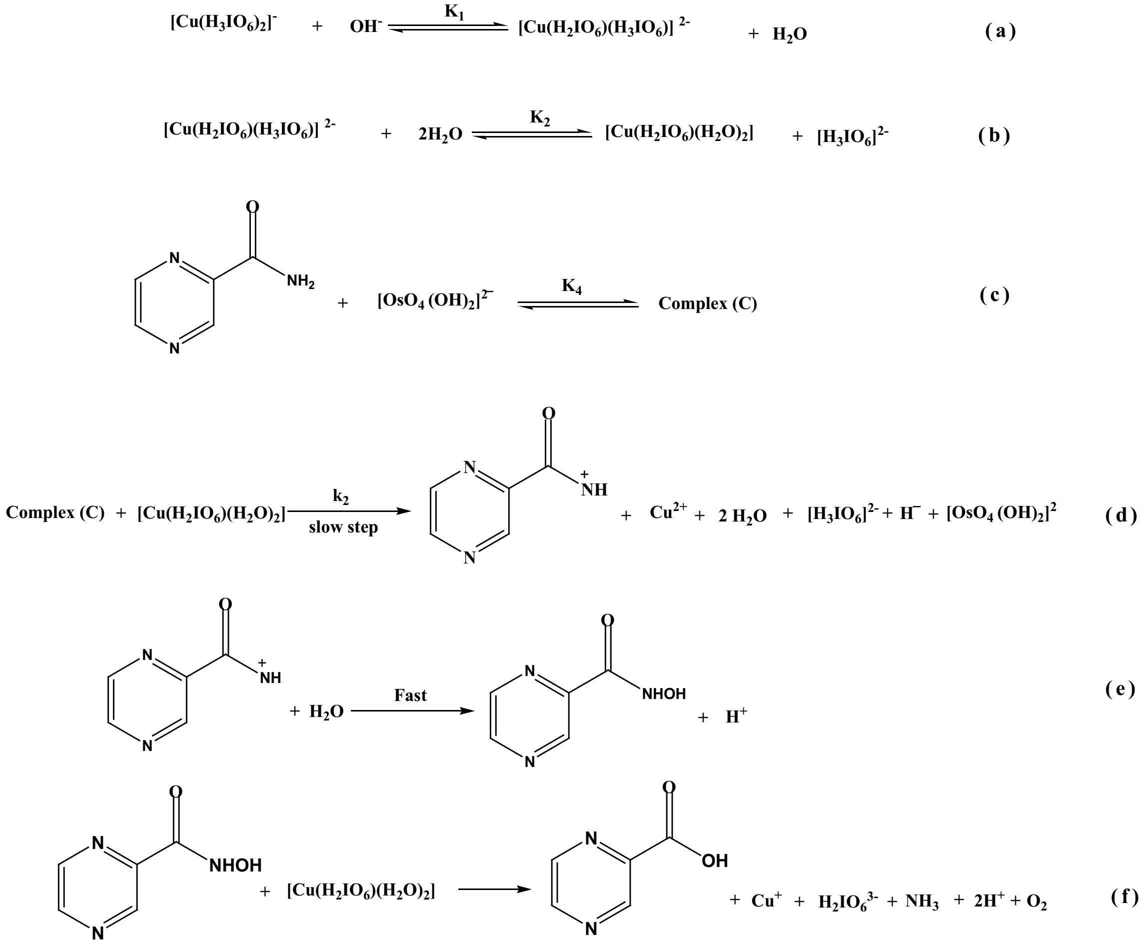
$$H_5IO_6 \rightleftharpoons H_4IO_6^- + H^+ \tag{5}$$

$$H_4IO_6^- \rightleftharpoons H_3IO_6^{2-} + H^+ \tag{6}$$

$$H_3IO_6^{2-} \rightleftharpoons H_2IO_6^{3-} + H^+ \tag{7}$$

Generally periodic acid exists as H_5IO_6 in acid media and as $H_3IO_6^{2-}$ near pH 7. Hence, under experimentally employed conditions, the expected species are $H_3IO_6^{2-}$ and $H_2IO_6^{3-}$. Periodate also tend to dimerise at higher concentration, but such possibility is ruled out in present experimental conditions. The Cu(III) complex might exist as diperiodatocuprate(III), $[Cu(OH)_2(H_3IO_6)_2]^{3-}$, a conclusion is also supported by earlier work [36]. The Copper(III) periodate complex exists in three different forms particularly in alkaline media [37] viz; diperiodatocuprate(III), monoperiodatocuprate(III), and tetrahydroxocuprate(III) which has equilibrium constant of 8×10^{-11} at 40 °C. Hence the existence of tetrahydroxocuprate(III) is ruled out.

The reaction between DPC and PYZ was found to be 1:2 stoichiometry (PZA:DPC) in both uncatalyzed and catalyzed reactions. The order with respect to DPC was unity and less than unit order in PYZ, KOH, whereas negative fractional order was observed with respect to KIO_4. Externally added products had no any significant change in kinetics of reaction. The rate of reaction increased with increase in concentration of alkali and periodate showed retarding effect on rate of reaction (Table 1). Such inference was obtained probably due to existence of following equilibria.



Scheme 2 *Os(VIII) catalyzed oxidation of PYZ by DPC*

$$[Cu(H_3IO_6)_2]^- + OH^- \overset{K_1}{\rightleftharpoons} [Cu(H_2IO_6)(H_3IO_6)]^{2-} \tag{8}$$

$$[Cu(H_2IO_6)(H_3IO_6)]^{2-} + 2H_2O \overset{K_2}{\rightleftharpoons} [Cu(H_2IO_6)(H_2O)_2] + [H_3IO_6]^{2-} \tag{9}$$

The increase in rate with the concentration of alkali and decrease in rate with increase in concentration of periodate could be due to equilibrium (8) and (9) respectively. Existence of such equilibria (8) and (9) have been claimed in earlier work [20]. The existence of monoperiodatocuptrate(III) (MPC) is more significant in the reaction than the DPC. The inverse fractional order with respect to $H_3IO_6^{2-}$ might also be due to this reason. Therefore, MPC might be the main reactive form of the oxidant.

4.1 Mechanism for Uncatalyzed Reaction

The Scheme 1 is based on principle of non-complementary oxidation. The possibility of any parallel reaction along with interaction between PYZ and DPC was ruled out due to non-linear curve obtained from the plot of k_{obs} vs [PYZ]. The fractional order with respect to pyrazinamide is probably due to formation of complex between PYZ and MPC prior to slow step which has also reflected in value of intercept obtained from the plot of $1/k_{obs}$ vs 1/[PYZ]. The value was found to be in close agreement with complex formation. In step (1) OH^- abstracts one proton from DPC to give deprotonated diperiodatocuprate(III) (DDPC) complex which explains positive fractional order with respect to [OH^-]. Now in step (2) the DDPC exchanges one periodate ligand with water molecule in the inner sphere to give monoperiodatocuprate(III) (MPC) which fortifies retarding effect on rate with respect to [$H_3IO_6^{2-}$]. Further, in step (3), the MPC forms a complex with one molecule of pyrazinamide to give a complex(I) which decomposes in a slow step (4) to give pyrazinium cation and Cu^{2+} ions. The pyrazinium cation in subsequent step (5) undergo hydrolysis to form pyrazinium hydroxide which further reacts with another molecule of MPC in fast step (6) to give pyrazinoic acid

Table 4 Activation parameters and thermodynamic quantities for Os(VIII) catalyzed oxidation of PYZ by DPC in aqueous alkaline medium with respect to the slow step of Scheme 2: (a) effect of temperature, (b) activation parameters (Scheme 2), (c) effect of temperature on K_1, K_2, K_4 for Os(VIII) catalyzed oxidation of PYZ by DPC in aqueous alkaline medium, (d) thermodynamic parameters using K_1, K_2, K_4

(a) Effect of temperature

Temperature (K)	$K_2 \times 10^2$ (s^{-1})
293	0.38
298	0.48
305	0.42
308	0.54

(b) Activation parameters (Scheme 2)

Parameters	Value
E_a (kJ mol^{-1})	32.10
ΔH^* (kJ mol^{-1})	29.20
ΔS^* (JK^{-1} mol^{-1})	−91.10
ΔG^* (kJ mol^{-1})	49.34
Log A	11.2

(c) Effect of temperature to calculate K_1, K_2 and K_4 for the oxidation of pyrazinamide by DPC in alkaline medium

Temperature (K)	K_1 (dm^3 mol^{-1})	$K_2 \times 10^3$ (mol dm^{-3})	$K_4 \times 10^{-3}$ (dm^3 mol^{-1})
293	0.24	6.19	0.53
298	0.79	1.87	1.31
305	1.21	0.63	3.20
308	3.27	0.23	4.49

(d) Thermodynamic parameters using K_1, K_2 and K_4

Thermodynamic parameters	Values from K_1	Values from K_2	Values from K_4
ΔH (kJ mol^{-1})	66.28	−72.36	38.12
ΔS (J K^{-1} mol^{-1})	195.14	−329.49	208.36
ΔG (kJ mol^{-1})	−0.655	15.34	−16.67

Table 5 Values of catalytic constant (K_C) at different temperatures and activation parameters calculated using K_C values

Temperature	$K_C \times 10^{-4}$
293	2.97
298	3.41
305	5.98
308	8.53
E_a (kJ mol^{-1})	37.8
ΔH^* (kJ mol^{-1})	36.5
ΔS^* (JK^{-1} mol^{-1})	−152.63
ΔG^* (kJ mol^{-1})	81.23
log A	6.21

and Cu^+ species. All results may be interpreted as depicted in Scheme 1.

The formation of complex between MPC and PYZ was confirmed by recording UV–visible spectrum of DPC only and comparing it with the spectrum of mixture containing DPC (5.0×10^{-5} mol dm^{-3}), PYZ (5.0×10^{-4} mol dm^{-3}), OH

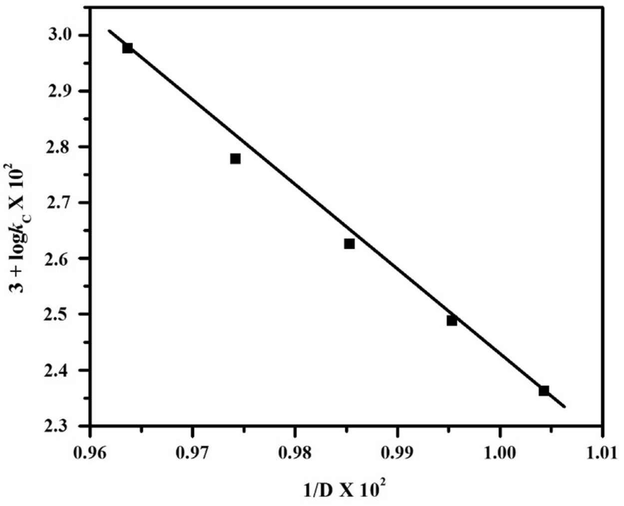


Fig. 5 Effect of dielectric constant of the medium on the oxidation of pyrazinamide at 298 K

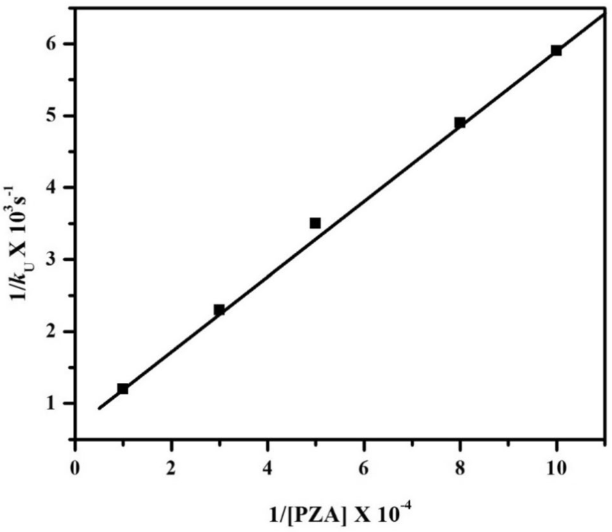


Fig. 6 Verification of rate law (12) for the uncatalyzed oxidation of pyrazinamide by diperiodatocuprate(III)

(0.05 mol dm^{-3}) and KIO$_4$ (1.0×10^{-5}mol dm^{-3}). There was hypsochromic shift of about 8 nm from 288 nm to 280 nm. The formation of complex between oxidant and substrate was also proved by Michalis-Menton plot. Such type of complex formation has been well documented in some earlier reports [38]. The following rate law is derived from Scheme 1.

$$\text{Rate} = \frac{-\text{d[DPC]}}{\text{dt}} = \frac{k_1K_1K_2K_3[\text{PYZ}][\text{OH}^-][\text{DPC}]}{[\text{H}_3\text{IO}_6^{2-}] + K_1[\text{OH}^-][\text{H}_3\text{IO}_6^{2-}] + K_1K_2[\text{OH}^-] + K_1K_2K_3[\text{PYZ}][\text{OH}^-]} \tag{10}$$

$$k_U = \frac{-\text{d[DPC]}}{\text{dt}} = \frac{k_1K_1K_2K_3[\text{PYZ}][\text{OH}^-]}{[\text{H}_3\text{IO}_6^{2-}] + K_1[\text{OH}^-][\text{H}_3\text{IO}_6^{2-}] + K_1K_2[\text{OH}^-] + K_1K_2K_3[\text{PYZ}][\text{OH}^-]} \tag{11}$$

The Eq. (11) explains all observed kinetic orders of different species and it can be rearranged into Eq. (12) which would be sutiable for verification (Fig. 6).

$$\frac{1}{k_U} = \frac{[\text{H}_3\text{IO}_6^{2-}]}{k_1K_1K_2K_3[\text{PYZ}][\text{OH}^-]} + \frac{[\text{H}_3\text{IO}_6^{2-}]}{k_1K_2K_3[\text{PYZ}]} + \frac{1}{k_1K_3[\text{PYZ}]} + \frac{1}{k_1} \tag{12}$$

From Eq. (12) the values of k_1, K_1, K_2, K_3 were calculated (Table 3a, c) by using intercepts and slopes obtained from the plots of $1/k_U$ vs 1/[PZA], $1/k_U$ vs 1/[OH] and $1/k_U$ vs [H$_3$IO$_6^{2-}$], which were supposed to be linear and are found so. The values of K_1 *and* K_2 are in close agreement with those reported earlier in literature. These constants were used to calculate the rate constant and compared with k_U values obtained from experiment. The values are reasonably in agreement which fortifies the Scheme 1. The change in enthalpy (ΔH), change in entropy (ΔS) and free energy change (ΔG) for all the three equilibrium steps were calculated from Vant Hoff plots (log K_1 vs 1/T$_1$, log K_2 vs 1/T$_2$, log K_3 vs 1/T$_3$) and given in Table 3d.

A comparison of ΔH value (-40.36 kJ mol^{-1}, Table 3d) of K$_2$ with that of ΔH^* (36.30 kJ mol^{-1}, Table 3c) of rate limiting step suggests that the reaction before rate determining step is fairly fast as it involves low activation energy [39]. The values ΔH^* and ΔS^* support for the electron transfer processes. The ΔS^* was found to be negative indicating that the intermediate complex (C$_1$) formed during reaction is more ordered than the reactant [34]. The observed modest enthalpy of activation and a higher rate constant for the slow step indicates that the oxidation perhaps proceeds via an inner-sphere mechanism. This conclusion is supported by earlier observations [40].

4.2 Mechanism of Os(VIII) Catalyzed Reaction

Osmium(VIII) forms a complex with OH$^-$ in different ways and it depends on concentration of OH$^-$ ions [39]. [OsO$_5$(OH)]$^{3-}$ is formed at high OH$^-$ concentration, whereas [OsO$_4$(OH)$_2$]$^{2-}$ at low concentration as maintained in this study. The rate increased with increase in OH$^-$ ion concentration. Hence, [OsO$_4$(OH)$_2$]$^{2-}$ is considered as possible form of catalyst and its formation is important aspect in reaction [41].

The reaction between PYZ and DPC showed 1:2 stoichiometry (PYZ: DPC) and unit order dependency for both DPC and Os(VIII), while fractional order in case of [PYZ]. The rate was enhanced by [OH$^-$] and retarded by [H$_3$IO$_6$]$^{2-}$. A Scheme 2 for Os(VIII) catalyzed oxidation of PYZ has been proposed to fortify the above said observations. According to step (a) OH$^-$ ions deprotonates DPC, to give deprotonated diperiodatocuprate(III) (DDPC) complex which explains positive fractional order with respect to [OH$^-$]. Now in step (b) the DDPC exchanges one periodate ligand with water molecule in the inner sphere to give MPC which validates retarding effect on rate with respect to [H$_3$IO$_6$$^{2-}$]. Now in step (c) which is before rate determining step, the hydroxylated species of Os(VIII) coordinates with PYZ to form a intermediate complex (C$_2$), which reacts further with 1 mol of MPC in Step (d) to give pyrazinium cation and Cu^{2+} ions. The pyrazinium cation in subsequent step (e) undergo hydrolysis to form pyrazinium hydroxide. Now it reacts with another molecule of MPC in fast step (f) to give pyrazinoic acid and Cu$^+$ species. All results may be interpreted as depicted in Scheme 2.

The formation of complex between Os(VIII) and PYZ was confirmed by obtaining UV–visible spectrum which showed bathochromic shift of about 5 nm from 288 to 293 nm. The formation of complex between catalyst and substrate was also proved by Michalis-Menton plot, which explains less than unit order in case of [PYZ]. Such type of complex formation between catalyst and substrate have been observed in earlier reports [42].

The following rate law is derived from Scheme 2.

$$\text{Rate} = \frac{-\text{d[DPC]}}{\text{dt}}\frac{-\text{d[DPC]}}{\text{dt}} = \frac{k_2K_1K_2K_4[\text{PYZ}][\text{OH}^-][\text{DPC}][\text{Os(VIII)}]}{[\text{H}_3\text{IO}_6^{2-}] + K_1[\text{OH}^-][\text{H}_3\text{IO}_6^{2-}] + K_1K_2[\text{OH}^-] + K_1K_2K_4[\text{PYZ}][\text{OH}^-]} \tag{13}$$

$$\frac{\text{Rate}}{[\text{DPC}]} = k_C = k_T - k_U = \frac{k_2K_1K_2K_4[\text{PYZ}][\text{OH}^-][\text{DPC}]}{[\text{H}_3\text{IO}_6^{2-}] + K_1[\text{OH}^-][\text{H}_3\text{IO}_6^{2-}] + K_1K_2[\text{OH}^-] + K_1K_2K_4[\text{PYZ}][\text{OH}^-]} \tag{14}$$

The Eq. (14) explains all observed kinetic orders of different species and it can be rearranged into Eq. (15) which would be suitable for verification.

$$\frac{[\text{Os(VIII)}]}{k_C} = \frac{[\text{H}_3\text{IO}_6^{2-}]}{k_2K_1K_2K_4[\text{PYZ}][\text{OH}^-]} + \frac{[\text{H}_3\text{IO}_6^{2-}]}{k_2K_2K_4[\text{PYZ}]} + \frac{1}{K_2K_4[\text{PYZ}]} + \frac{1}{k_2} \tag{15}$$

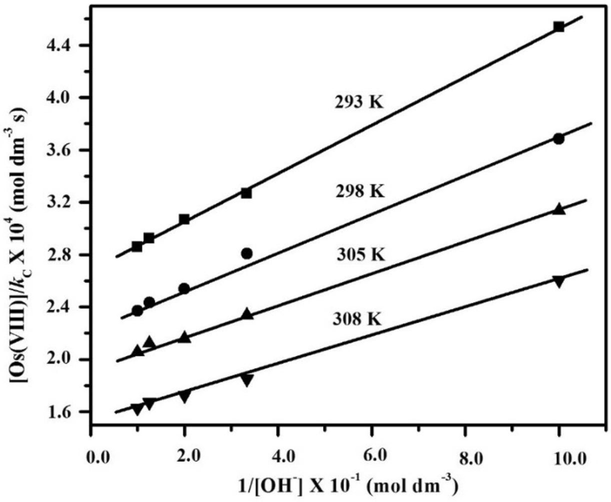


Fig. 8 Verification of rate law (15) for the Os (VIII) catalyzed oxidation of pyrazinamide by DPC. Plot of [Os (VIII)]/k_C versus 1/[OH$^-$] at four different temperatures (conditions as in Table 2)

From Eq. (15) the values of k_2, K_1, K_2, K_4 were calculated (Table 4a, 4c) by using intercepts and slopes obtained from the plots of [Os(VIII)]/k_C vs 1/[PZA], [Os(VIII)]/k_C vs 1/[OH] and [Os(VIII)]/k_C vs [$H_3IO_6^{2-}$] (Figs. 7, 8, 9) which were supposed to be linear and are found so. The values of K_1 *and* K_2 are in close agreement with those reported earlier in literature. These constants were used to calculate the rate constant and compared with k_C values obtained from experiment. The values are reasonably in agreement which fortifies the Scheme 2. The thermodynamic parameters such as ΔH, ΔS and ΔG for all the three equilibrium steps were calculated from Vanthoff plots (log K_1 vs 1/T, log K_2 vs 1/T, log K_4 vs 1/T) and tabulated in Table 4d.

The values ΔH^* and ΔS^* supports for the electron transfer processes. The ΔS^* was found to be negative indicating that the intermediate complex (C_2) formed during reaction is more ordered than the reactant [34]. The observed modest enthalpy of activation and a higher rate constant for the slow

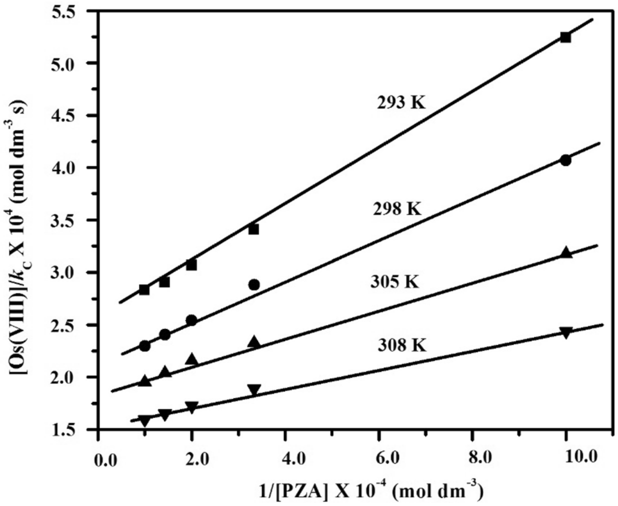


Fig. 7 Verification of rate law (15) for the Os(VIII) catalyzed oxidation of pyrazinamide. Plot of [Os(VIII)]/k_C versus 1/[PYZ] at four different temperatures (conditions as in Table 2)

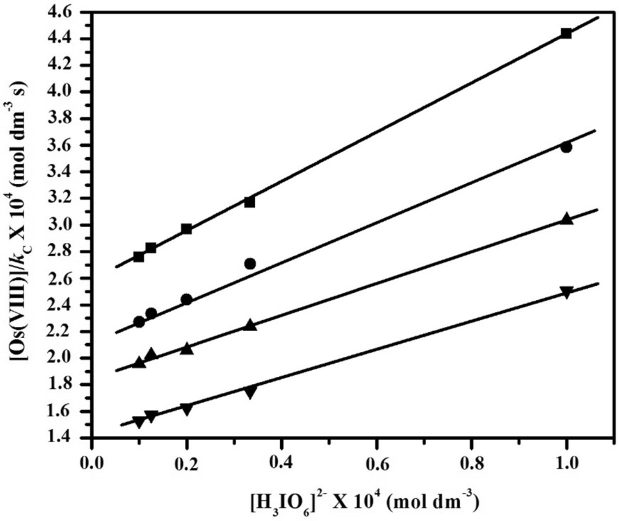


Fig. 9 Verification of rate law (15) for the Os (VIII) catalyzed oxidation of pyrazinamide by DPC. Plot of [Os (VIII)]/k_C versus 1/[$H_3IO_6^{2-}$]at four different temperatures (conditions as in Table 2)

step suggests that the oxidation probably proceeds through an inner-sphere mechanism. This assumption is supported by earlier reports [40]. The activation parameters were evaluated for both the cases, which explains the effect of catalyst on the rate of reaction. In catalyzed reaction, the Os(VIII) enhances the reducing property of the substrate by forming complex (C_2) with it. Further, Os(VIII) alters the reaction path by lowering the activation energy. It's quite interesting to note that, both the uncatalyzed and catalyzed reactions proceed through different pathways with different transient species, but finally lead to the same products. In uncatalyzed reaction the reaction coordinate passes through formation MPC-PYZ complex during transition state which later on decomposes slowly during rate determining step.In case of catalyzed reaction, the reaction proceeds via Os(VIII)-PYZ complex which further reacts with one mole of MPC in the rate determining step. Since MPC was involved as active species of Cu(III) in the mechanisms of both the cases, the products obtained were same.

5 Conclusion

A comparative investigation of uncatalyzed and Os(VIII) catalyzed oxidation of anti-tuberculosis drug Pyrazinamide by diperiodatecuprate(III) was under taken in alkaline medium. Among different forms of Cu(III)periodate in alkaline media, monoperiodatocuprate(III) was considered as active species. The active species of Os(VIII) was $[OsO_4(OH)_2]^2$ and reaction rate was catalyzed six-fold faster compared to uncatalyzed. Catalytic constants and the activation parameters with reference to catalyst were also computed. The overall sequence described here is consistent with all the experimental evidences including the product, spectral, mechanistic and kinetic studies. The oxidative study of pyrazinamide may help in exploring drug action mechanism in biological systems and its metabolism.

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