Kinetic and Mechanistic Aspects of Osmium(VIII) Catalyzed Oxidation of DLornithine by Copper(III) Periodate Complex in Aqueous Alkaline Medium

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(Received October 20, 2009; accepted April 9, 2010)

Ornithine / Diperiodatocuprate(III) / Os(VIII) Catalysis / Oxidation / Kinetics

The oxidation of DL-ornithine monohydrochloride (OMH) by diperiodatocuprate(III) (DPC) has been investigated in the presence of osmium(VIII) catalyst in aqueous alkaline medium at a constant ionic strength of 0.20 mol dm⁻³ spectrophotometrically. The reaction exhibits 1:4 stoichiometry i.e., [OMH]: [DPC]. The order of the reaction with respect to [DPC] was unity while the order with respect to [OMH] was less than unity over the concentration range studied. The rate increased with an increase in [OH⁻] and decreased with an increase in [IO₄⁻]. The order with respect to [Os(VIII)] was unity. The reaction rates revealed that Os(VIII) catalyzed reaction was about nine-fold faster than the uncatalyzed reaction. The oxidation products were identified by spectral analysis. Suitable mechanism has been proposed. The reaction constants involved in the different steps of the reaction mechanism were calculated. The catalytic constant (K_C) was also calculated at different temperatures. The activation parameters with respect to slow step of the mechanism and also the thermodynamic quantities were determined. Kinetic experiments suggest that $[OsO_4(OH)_2]^{2-}$ is the reactive Os(VIII) species and $[Cu(H_2IO_6)(H_2O)_2]$ is the reactive copper(III) species.

1. Introduction

Ornithine is a non-protein amino acid [1], derived from the breakdown of arginine during the citric acid cycle. It helps to build muscle and reduce body fat, especially when combined with the amino acids arginine and carnitine. It is also needed for the formation of citrulline, proline and glutamic acid. Ornithine helps to remove toxic ammonia from the liver, and reduces the effects of cirrhosis of

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the liver and disorders associated with liver malfunction. Ornithine is the major source of polyamines in mammalian physiological systems [2]. Increased urinary polyamine levels have been demonstrated in humans with varied types of cancers. The metabolism of DL-[1-¹⁴C]ornithine monohydrochloride in rats with either Walker 256 carcinoma or chemically induced methylcholanthrene tumors was studied, whose attempts showed to develop ornithine as a biological marker of cancer [3, 4].

Transition metals in their higher oxidation states can generally be stabilized by chelation with suitable polydentate ligands. These metal chelates such as diperiodatocuprate(III) [5], diperiodatoargentate(III)[6] and diperiodatonickelate(IV) [7] are good oxidants in a medium with an appropriate pH value. Diperiodatocuprate(III) is a versatile one-electron oxidant and the oxidation study of DPC is scanty in view of its limited solubility and stability in aqueous medium. Its use as an analytical reagent is now well recognized [8]. Copper complexes have a major role in oxidation chemistry due to their abundance and relevance in biological chemistry [9–11]. Copper(III) is involved in many biological electron transfer reactions [12]. When Copper(III) periodate complex is the oxidant and multiple equilibria between different copper(III) species are involved, it would be interesting to know which of the species is the active oxidant.

Transition metals are known to catalyze many oxidation - reduction reactions since they involve multiple oxidation states. In recent years the use of transition metal ions such as osmium, ruthenium, palladium, manganese, chromium, iridium, either alone or as binary mixtures, as catalysts in various redox processes have attracted considerable interest [13]. The role of osmium(VIII) as a catalyst in some redox reactions has been reviewed [14]. Although the mechanism of catalysis depends on the nature of the substrate, the oxidant and experimental conditions, it has been shown that metal ions act as catalysts by one of these different paths such as the formation of complexes with reactants or oxidation of the substrate itself or through the formation of free radicals. Osmium(VIII) catalysis in redox reactions involves different degrees of complexity, due to the formation of different intermediate complexes and different oxidation states of osmium.

The uncatalysed reaction of oxidation of DL-ornithine monohydrochloride $[(\pm)-2,5$ -Diaminopentanoic acid monohydrochloride] has been studied [15]. Literature survey revealed that the role of osmium(VIII) catalyst on the oxidation of this ubiquitous amino acid has not been examined. We have observed that osmium(VIII) in micro amounts catalyzes the oxidation of OMH by DPC in alkaline medium. Such studies are of much significance in understanding the mechanistic profile of ornithine in redox reactions and provide an insight into the interaction of metal ions with the substrate and its mode of action in biological systems. Also to know the active species of Cu(III) and catalyst Os(VIII), to compute the activity of the catalyst and the complexity of the reaction, a detailed study of the title reaction becomes important. Hence, the present investigation is aimed at checking the reactivity of OMH towards DPC in the presence of

2. Experimental

2.1 Chemicals and solutions

All reagents were of analytical reagent grade and Millipore water was used throughout the work. A solution of DL-ornithine monohydrochloride (HiMedia Laboratories) was prepared by dissolving an appropriate amount of recrystallized sample in Millipore water. The purity of OMH was checked by comparing its IR spectrum with literature data and with its m.p. 232-234°C. The required concentration of OMH was obtained from its stock solution. A standard stock solution of Os(VIII) was prepared by dissolving OsO4 (Johnson Matthey) in 0.50 mol dm^{-3} NaOH. The concentration of Os(VIII) was ascertained [16] by determining the unreacted ferrocyanide solution with standard cerium(IV) solution in an acidic medium. The copper(III) periodate complex was prepared [17, 18] and standardized by a standard procedure [19]. The UV-vis spectrum with maximum absorption at 415 nm verified the existence of copper(III) complex. The ionic strength was maintained by adding KNO₃ (AR) solution and the pH value was regulated with KOH (BDH) solution. A stock solution of IO₄⁻ was prepared by dissolving a known weight of KIO₄ (Riedel-de-Hean) in hot water and used after keeping for 24 h to attain the equilibrium. Its concentration was ascertained iodometrically [20], at neutral pH maintained using phosphate buffer. The pH of the medium in the solution was measured by ELICO (LI120) pH meter. Solutions of OMH and DPC were always freshly prepared before use.

2.2 Instruments used

(i) For kinetics measurements, a CARY 50 Bio UV–vis Spectrophotometer (Varian, Victoria-3170, Australia) was used.

(ii) For product analysis, a QP-2010S Shimadzu gas chromatograph mass spectrometer, Nicolet 5700-FT-IR spectrometer (Thermo, U.S.A.), 300 MHz ¹H NMR spectrophotometer (Bruker, Switzerland) were used and for pH measurements, an Elico pH meter model LI120 was used.

2.3 Kinetic measurements

The kinetics was followed under pseudo-first-order condition where [OMH] > [DPC] at 25.0 \pm 0.1°C, unless otherwise specified. The reaction was initiated by mixing DPC with the OMH solution which also contained the required concentration of KNO₃, KOH, KIO₄, and Os(VIII) catalyst. The progress of the reaction was monitored spectrophotometrically at 415 nm (i.e., decrease in absorbance due to DPC with the molar absorbency index, ' ε ' to be 6231 \pm 100 dm³ mol⁻¹ cm⁻¹(Liter-



Fig. 1. UV-vis. spectral changes during the oxidation of DL-ornithine by alkaline diperiodatocuprate(III) at 298K, [DPC] = 5.0×10^{-5} , [OMH] = 5.0×10^{-4} , [OH⁻] = 0.08, [Os(VIII)] = 8.0×10^{-7} and I = 0.20 mol dm⁻³ with scanning time of: (1) 0.5, (2) 1.0, (3) 1.5, (4) 2.0, (5) 2.5 and (6) 3.0 min.

ature $\varepsilon = 6230$ [21]) which is the maximum absorption wavelength of DPC. The spectral changes during the chemical reaction for the standard condition at 298 K are shown in Fig. 1. It is evident from the figure that the concentration of DPC decreases at 415 nm. It was verified that there was almost no interference from other species in the reaction mixture at this wavelength.

The pseudo-first order rate constants, ' k_T ', were determined from the log (absorbance) vs time plots. The plots were linear up to 85% completion of reaction under the range of $[OH^-]$ used. During the kinetics, a constant concentration viz. 1.0×10^{-5} mol dm⁻³ of KIO₄ was used throughout the study unless otherwise stated. Since excess of periodate is present in DPC, the possibility of oxidation of OMH by periodate in alkaline medium at 25°C was tested and found that there was no significant interference due to KIO₄ under experimental conditions. The total concentrations of periodate and OH⁻ was calculated by considering the amount present in DPC solution and that additionally added. Kinetic runs were also carried out in N₂ atmosphere in order to understand the effect of dissolved oxygen on the rate of the reaction. No significant difference in the results was obtained under a N₂ atmosphere and in the presence of air. In view of the ubiquitous contamination of carbonate in the basic medium, the effect of carbonate was also studied. The added carbonate had no effect on the reaction rates.

Regression analysis of experimental data to obtain regression coefficient r and the standard deviation S, of points from the regression line, was performed with the Microsoft office Excel 2003 program.

$$H_{2}N \longrightarrow O + 4 [Cu(H_{2}|O_{6})(H_{2}O)_{2}] + 3 OH^{-} \longrightarrow H_{2}N - CH_{2} - CH_{2} - CH_{2} - CH_{2} - COH + CO_{2}$$

$$H_{2}N - CH_{2} -$$

Scheme 1.

3. Results

3.1 Stoichiometry and product analysis

Different sets of reaction mixtures containing varying ratios of DPC to OMH in presence of constant amount of OH^- , KIO_4 , KNO_3 and Os(VIII) were kept for 6 h in a closed vessel under nitrogen atmosphere. The remaining concentration of DPC was assayed by measuring the absorbance at 415 nm. The results indicated 1:4 stoichiometry as given in Scheme 1.

After completion of reaction, the reaction mixture was acidified, concentrated and extracted with ether. The reaction product was further recrystallized from aqueous alcohol. The main reaction product was identified as 4-aminobutyric acid. This was the only organic product obtained in the oxidation which was confirmed by a single spot on thin layer chromatography and was characterized by FT-IR, GC-MS and ¹H NMR spectral studies.

The IR spectroscopy showed a >C = O stretching of carboxylic acid at 1708 cm⁻¹ indicating the presence of acidic C = O group, O-H stretching of carboxylic acid at 2848 cm⁻¹ indicating the presence of acidic – OH group, and also N-H stretching at 3427 cm⁻¹ indicating the presence of -NH₂ group in 4-aminobutyric acid. GC-MS data was obtained on a QP-2010S Shimadzu gas chromatograph mass spectrometer. The mass spectral data showed a molecular ion peak at 103 m/z confirming the presence of 4-aminobutyric acid (Fig. 2). All other peaks observed in GC-MS can be interpreted in accordance with the observed structure of 4-aminobutyric acid. It was also subjected to ¹H NMR spectrum (CDCl₃), two triplet at 2.31 δ (a) and 2.69 δ (c) and a multiplet at 1.84 δ (due to (b) CH₂), 5.44 δ (s, 2H due to - NH₂) and 11.6 δ (s, H due to -COOH). -NH₂ and -OH disappeared on D₂O exchange.

The byproducts were identified as ammonia by Nessler's reagent [19] and CO₂ was qualitatively detected by bubbling nitrogen gas through the acidified reaction mixture and passing the liberated gas through the tube containing limewater. Finally copper(II) was identified by UV-vis spectra.

3.2 Reaction orders

As the diperiodatocuprate(III) oxidation of DL-ornithine in alkaline medium proceeds with a measurable rate in the absence of Os(VIII), the catalyzed reaction is understood to occur in parallel paths with contributions from both the catalyzed and uncatalyzed paths. Thus the total rate constant (k_T) is equal to the sum



Fig. 2. Mass spectrum of reaction product, 4-aminobutyric acid with its molecular ion peak at 103 m/z.

of the rate constants of the catalyzed ($k_{\rm C}$) and uncatalyzed ($k_{\rm U}$) reactions, so $k_{\rm C} = k_{\rm T} - k_{\rm U}$. Hence the reaction orders have been determined from the slopes of log k_C vs log (concentration) plots by varying the concentrations of OMH, IO₄⁻, OH⁻, and catalyst Os(VIII), in turn while keeping others constant. The uncatalyzed reaction was followed under the condition, [DPC] = 5.0×10^{-5} , [OMH] = 5.0×10^{-4} , [OH⁻] = 0.08, [IO₄⁻] = 1.0×10^{-5} , I = 0.20 / mol dm⁻³. The rate constant of uncatalyzed reaction ($k_{\rm U}$) was obtained by the plot of log (absorbance) vs time by following the progress of the reaction spectrophotometrically at 415 nm.

3.3 Evaluation of pseudo first order rate constants

The oxidant [DPC] was varied in the range of 1.0×10^{-5} to 1.0×10^{-4} and the linearity of the plots of log (absorbance) *vs* time up to 85% completion of the reaction ($r \ge 0.9549$, $S \le 0.016$) indicates a reaction order of unity in [DPC]. This is also confirmed by varying [DPC], which did not result in any change in the pseudo-first-order rate constants, $k_{\rm C}$ (Table 1).

3.4 The dependence of rate on the concentration of DL-ornithine

The effect of OMH was studied in the range of 6.0×10^{-5} to 6.0×10^{-4} mol dm⁻³ at constant concentrations of DPC, OH⁻, IO₄⁻ and a constant ionic strength of 0.20 mol dm⁻³ in the presence of Os(VIII) catalyst. At constant temperature, the $k_{\rm C}$ values increased with increase in [OMH] indicating the order with respect to [OMH] as less than unity (Table 1) (r \ge 0.9997, $S \le$ 0.009). This was also



Fig. 3. Plots of $k_{\rm C}$ vs [OMH] ^{0.55} and $k_{\rm C}$ vs [OMH] (conditions as in Table 1).

confirmed by the plot of $k_{\rm C} vs$ [OMH]^{0.55} which were linear rather than the direct plot of $k_{\rm C} vs$ [OMH] (Fig.3).

3.5 The dependence of rate on the concentration of OH⁻

The effect of alkali was studied in the range of 0.02 - 0.20 mol dm⁻³ at constant concentrations of DPC, OMH, IO_4^- and ionic strength in the presence of Os(VIII) catalyst. The rate constants increased with increase in [alkali]and the order was found to be less than unity i.e., 0.41 (Table 1) ($r \ge 0.9973$, $S \le 0.007$). This was also confirmed by the plot $k_C vs$ [OH⁻]^{0.40} which were linear rather than the direct plot of $k_C vs$ [OH⁻] (Fig 4).

3.6 The dependence of rate on the concentration of IO_4^-

The effect of periodate was studied in the range of 5.0×10^{-6} to 5.0×10^{-5} mol dm⁻³ at constant concentrations of DPC, OMH, OH⁻ and ionic strength in the presence of Os(VIII) catalyst. The experimental results indicated that the $k_{\rm C}$ values decreased with increase in [IO₄⁻]. The order with respect to IO₄⁻ was negative fractional i.e., -0.45 (Table 1) (r ≥ 0.9957 , $S \le 0.004$).

3.7 The dependence of rate on [Os(VIII)]

The [Os(VIII)] concentration was varied from 2.0×10^{-7} to 2.0×10^{-6} mol dm⁻³ range, at constant concentration of DPC, OMH, and alkali and constant ionic strength. The order in [Os(VIII)] was found to be unity from the linearity of the plot of $k_{\rm C} vs$ [Os(VIII)] (Table 1) (Fig 5).



Fig. 4. Plots of $k_{\rm C} vs [OH^-]^{0.40}$ and $k_{\rm C} vs [OH^-]$ (conditions as in Table 1).



Fig. 5. Unit order plot of $k_{\rm C} vs$ [Os(VIII)].

3.8 The dependence of rate on ionic strength (I) and dielectric constant (D)

The effect of ionic strength (I) was studied by varying [KNO₃]. The dielectric constant of the medium (D) was studied by varying the t-butyl alcohol and water percentage. It was found that there was no significant effect of ionic strength and dielectric constant of the medium on the rate of the reaction.

10 ⁵ [DPC] mol dm ⁻³	10^4 [OMH] mol dm ⁻³	$10^{1}[OH^{-}]$ mol dm ⁻³	$10^{5} [IO_{4}^{-}]$ mol dm ⁻³	10 ⁷ [Os(VIII)]	$\frac{10^2 k_{\rm T}}{{\rm s}^{-1}}$	$\frac{10^{3}k_{\rm U}}{{\rm s}^{-1}}$	$\frac{10^2 k_{\rm C}}{{\rm s}^{-1}}$	
				mol dm^{-3}			Found	Calculated
1.0	5.0	0.8	1.0	8.0	2.61	2.90	2.31	2.46
3.0	5.0	0.8	1.0	8.0	2.67	3.00	2.37	2.46
5.0	5.0	0.8	1.0	8.0	2.74	2.88	2.45	2.46
8.0	5.0	0.8	1.0	8.0	2.56	2.53	2.30	2.46
10.0	5.0	0.8	1.0	8.0	2.57	2.30	2.34	2.46
5.0	0.6	0.8	1.0	8.0	0.80	0.85	0.72	0.70
5.0	1.0	0.8	1.0	8.0	1.20	1.28	1.07	1.03
5.0	2.0	0.8	1.0	8.0	1.90	2.08	1.69	1.62
5.0	5.0	0.8	1.0	8.0	2.74	2.88	2.45	2.46
5.0	6.0	0.8	1.0	8.0	3.01	3.38	2.67	2.62
5.0	5.0	0.2	1.0	8.0	1.40	1.48	1.25	1.23
5.0	5.0	0.4	1.0	8.0	2.01	2.15	1.79	1.85
5.0	5.0	0.8	1.0	8.0	2.74	2.88	2.45	2.46
5.0	5.0	1.0	1.0	8.0	3.00	3.36	2.66	2.64
5.0	5.0	2.0	1.0	8.0	3.52	3.74	3.15	3.07
5.0	5.0	0.8	0.5	8.0	3.51	3.80	3.12	3.00
5.0	5.0	0.8	0.8	8.0	2.82	3.30	2.49	2.64
5.0	5.0	0.8	1.0	8.0	2.74	2.88	2.45	2.46
5.0	5.0	0.8	3.0	8.0	1.70	1.85	1.52	1.48
5.0	5.0	0.8	5.0	8.0	1.19	1.33	1.05	1.06
5.0	5.0	0.8	1.0	2.0	0.90	2.88	0.61	0.61
5.0	5.0	0.8	1.0	5.0	1.83	2.88	1.55	1.54
5.0	5.0	0.8	1.0	8.0	2.74	2.88	2.45	2.46
5.0	5.0	0.8	1.0	10.0	3.37	2.88	3.09	3.08
5.0	5.0	0.8	1.0	20.0	6.45	2.88	6.17	6.16

Table 1. Effect of variation of [DPC], [OMH], [OH⁻], $[IO_4^-]$ and [Os(VIII)] on the osmium(VIII) catalysed oxidation of DL-ornithine by diperiodatocuprate(III) in aqueous alkaline medium at 298 K and I = 0.20 mol dm⁻³.

3.9. Effect of initially added products

Initially added products, copper(II) (CuSO₄) and 4-aminobutyric acid did not have any significant effect on the rate of reaction.

Thus, from the observed experimental results, the rate law for Os(VIII) catalyzed reaction is given as:

Rate =
$$k_{\rm C} [{\rm DPC}]^{1.0} [{\rm OMH}]^{0.55} [{\rm OH}^{-}]^{0.41} [{\rm Os}({\rm VIII})]^{1.0} [{\rm IO_4}^{-}]^{-0.45}$$

3.10 Polymerization study

The possibility of free radicals was detected as follows: the reaction mixture, to which a known quantity of acrylonitrile (scavenger) had been added initially, was kept for 2 h in an inert atmosphere. On diluting the reaction mixture with methanol, a white precipitate was formed, indicating the intervention of free radicals in the reactions. The blank experiments of either DPC or DL-ornithine alone with acrylonitrile did not induce any polymerization under the same condi-

tion as those induced for the reaction mixture. Initially added acrylonitrile decreases the rate of reaction indicating free radical intervention, which is the case in earlier work [22].

3.11 Effect of temperature

The kinetics was studied at four different temperatures 288 K, 298 K, 308 K and 318 K under varying concentrations of DL-ornithine, alkali and periodate, and osmium(VIII), keeping other conditions constant. The rate constants, (*k*), of the slow step of Scheme 3 were obtained from the slopes and the intercepts of the plots of $[Os(VIII)]/k_C vs 1/[OMH]$ at four different temperatures. The values are given in Table 2. The energy of activation for the rate determining step was obtained by the least - squares method of plot of log k vs 1/T and other activation parameters calculated for the reaction are presented in Table 2.

3.12 Catalytic activity

It has been pointed out by Moelwyn-Hughes [23] that in the presence of catalyst, the uncatalyzed and catalyzed reactions proceed simultaneously, so that,

$$k_{\rm T} = k_{\rm U} + K_{\rm C} \left[Os(\rm VIII) \right]^{\rm x}$$
⁽¹⁾

Here $k_{\rm T}$ is the observed pseudo first-order rate constant in the presence of Os(VIII) catalyst; $k_{\rm U}$, the pseudo-first-order rate constant for uncatalyzed; $K_{\rm C}$, the catalytic constant and 'x' the order of the reaction with respect to Os(VIII). In the present investigations; x values for the standard run were found to be unity.

Then, the value of $K_{\rm C}$ is calculated using the equation,

$$K_{\rm C} = \frac{k_{\rm T} - k_{\rm U}}{\left[\mathrm{Os}(\mathrm{VIII})\right]^x} = \frac{k_{\rm C}}{\left[\mathrm{Os}(\mathrm{VIII})\right]} \quad (\text{where } k_{\rm T} - k_{\rm U} = k_{\rm C})]$$
(2)

The values of $K_{\rm C}$ were evaluated for Os(VIII) catalyst at different temperatures and were found to vary at different temperatures. Further, plots of log $K_{\rm C}$ vs 1/T were linear and the values of energy of activation and other activation parameters with reference to catalyst were computed. These results are summarized in Table 3. The value of $K_{\rm C}$ is 3.07×10^4 at 298 K.

4. Discussion

The water-soluble copper(III) periodate complex is reported [24]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] (3)–(5) depending on the pH of the solution.

$$H_5IO_6 \rightleftharpoons H_4IO_6^- + H^+$$
 (3)

Table 2. Activation parameters and thermodynamic quantities for the osmium(VIII) catalysed oxidation of OMH by diperiodatocuprate(III) in aqueous alkaline medium with respect to the slow step of Scheme 3: (A) effect of temperature, (B) activation parameters (Scheme 3), (C) effect of temperature on K_1 , K_2 and K_3 for the osmium(VIII) catalysed oxidation of OMH by diperiodatocuprate(III) in aqueous alkaline medium, (D) thermodynamic quantities using K_1 , K_2 and K_3 .

Temperature / K		10	$k / dm^3 mol^{-1} s^{-1}$			
(A)						
288			0.23			
298			0.47			
308			0.80			
318			1.58			
Parameters		Values				
(B)						
$E_a / \text{kJ mol}^{-1}$		47 ± 2				
$\Delta H^{\#}/ \text{ kJ mol}^{-1}$		44.8 ± 0.5				
$\Delta S^{\#} / JK^{-1} mol^{-1}$		-5.01 ± 1.0				
$\Delta G^{\#} / \text{kJ mol}^{-1}$		46 ± 5				
log A		12.9 ± 0.2				
Temperature / K 10	$0^{1}K_{1} / \mathrm{dm}^{3} \mathrm{mol}^{-1}$	$10^4 K_2 / \text{moldm}^{-3}$	$\frac{10^{-4}K_3}{\text{dm}^3 \text{ mol}^{-1}}$			
(C)						
288 0.2	28	2.59	6.51			
298 0.:	51	1.36	7.06			
308 0.9	91	0.68	7.88			
318 1.4	48	0.37	8.75			
Thermodynamic quantities	Values from K_1	Values from K_2	Values from K_3			
(D)						
$\Delta H / \text{kJ mol}^{-1}$	42	-49.1	7.56			
$\Delta S / JK^{-1} mol^{-1}$	116	-239	118			
$\Delta G_{298} / \text{kJ mol}^{-1}$	7.36	22	-27.6			

$$\mathrm{H}_{4}\mathrm{IO}_{6}^{-} \rightleftharpoons \mathrm{H}_{3}\mathrm{IO}_{6}^{2-} + \mathrm{H}^{+} \tag{4}$$

$$H_3IO_6^{2-} \rightleftharpoons H_2IO_6^{3-} + H^+$$
(5)

Periodic acid exists as H_5IO_6 in an acid medium 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 dimerise. 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), $[Cu(H_2IO_6)(H_3IO_6)]^{2-}$, a conclusion also supported by earlier work [26, 27].

Table 3.	Values	of c	catalytic	constant	$(K_{\rm C})$	at	different	temperatures	and	activation	parameters
calculated	l using	K _C v	values.					-			-

Temperature / K	$10^{-5}K_{\rm C}$
288	0.15
298	0.30
308	0.61
318	1.22
$E_a / \text{kJ mol}^{-1}$	52
$\Delta H^{\#}/ \text{ kJ mol}^{-1}$	50.3
$\Delta S^{\#}$ / JK ⁻¹ mol ⁻¹	9.68
$\Delta G^{\#} / \text{kJ mol}^{-1}$	47.4
log A	13.7



Scheme 2.

It is known that DL-ornithine exists in the form of Zwitterion [28] in aqueous medium. In highly acidic medium it exists in the protonated form, where as in highly basic medium it is in the deprotonated form [28] (Scheme 2).

Osmium(VIII) is known to form different complexes at different OH^- concentrations, $[OsO_4(OH)_2]^{2-}$ and $[OsO_5(OH)]^{3-}$. At higher concentration of OH^- , $[OsO_5(OH)]^{3-}$ is significant. At lower concentrations of OH^- , as employed in the present study and since the rate of oxidation increased with increase in $[OH^-]$, it is reasonable that $[OsO_4(OH)_2]^{2-}$ was operative and its formation is important in the reaction.

Lister [29] proposed the copper(III) periodate in alkaline medium into three forms as diperiodatocuprate(III) (DPC), monoperiodatocuprate(III) (MPC) and tetrahydroxocuprate(III). The latter is ruled out as its equilibrium constant is 8.0×10^{-11} at 40°C. Hence, in the present study, in view of the negative less than unit order in periodate on rate of reaction, monoperiodatocuprate(III) MPC is considered to be the active species of copper(III) periodate complex. The results of increase in the rate with increase in alkali concentration and decrease in the rate with increase in periodate complexes are possible as in Eq. (6) and (7).

$$\left[\operatorname{Cu}(\operatorname{H}_{3}\operatorname{IO}_{6})_{2}\right]^{-} + \operatorname{OH}^{-} \rightleftharpoons \left[\operatorname{Cu}(\operatorname{H}_{2}\operatorname{IO}_{6})(\operatorname{H}_{3}\operatorname{IO}_{6})\right]^{2-} + \operatorname{H}_{2}\operatorname{O}$$
(6)

 $[Cu(H_2IO_6)(H_3IO_6)]^{2-} + 2H_2O \iff [Cu(H_2IO_6)(H_2O)_2] + [H_3IO_6^{2-}]$ (7)

The inverse fractional order in $[IO_4^-]$ might also be due to this reason. The reaction between DPC and OMH in alkaline medium presents [DPC]/[OMH] = 1:4 stoichiometry. Since the reaction was enhanced by $[OH^-]$, added periodate retarded the rate and first order dependency in [DPC] and [Os(VIII)] and fractional order in [OMH] and $[OH^-]$, a plausible reaction mechanism has been proposed which also explains all other experimental observations as shown in Scheme 3.

Anionic species of OMH reacts with osmium(VIII) active species to form a complex (C) which further reacts with one mole of MPC in a slow step to give the free radical species of OMH, Cu(II) with regeneration of catalyst, osmium(VIII). Further this free radical species of OMH reacts with one more molecule of MPC species in a fast step to form 4-aminobutaraldehyde intermediate. This 4-aminobutaraldehyde then reacts with two more moles of MPC in a further fast step to form products such as 4-aminobutyric acid, Cu(II) and periodate. All these results may be interpreted in the form of Scheme 3. The probable structure of the complex (C) is given below.



Spectroscopic evidence for the complex formation between Os(VIII) and OMH was obtained from UV - vis spectra of OMH (5.0×10^{-4}) , Os(VIII) $(8.0 \times 10^{-7}, [OH^{-1}] = 0.08 \text{ mol } dm^{-3})$ and a mixture of both. A bathochromic shift of about 4 nm from 364 to 368 nm in the spectra of Os(VIII) to the mixture of Os(VIII) and OMH was observed. The Michaelis-Menten plot proved the complex formation between catalyst and substrate, which explains less than unit order in [OMH]. Such a complex between a catalyst and substrate has also been observed in other studies[30].

From Scheme 3, the rate law (9) can be derived.

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

$$= \frac{k K_1 K_2 K_3 [DPC][OMH][OH^-][Os(VIII)]}{[H_3 IO_6^{2^-}] + K_1 K_2 [OH^-] + K_1 K_2 K_3 [OH^-][OMH]}$$

$$= \frac{k K_1 K_2 K_3 [OMH][OH^-][Os(VIII)]}{[H_3 IO_6^{2^-}] + K_1 K_2 [OH^-] + K_1 K_2 K_3 [OH^-][OMH]}$$
(9)



Scheme 3. Detailed Scheme for Os(VIII) catalyzed oxidation of DL-ornithine by alkaline diperidatocuprate(III).

+ 2 H₂IO₆³⁻ + 5 H₂O

which explains all the observed kinetic orders of different species.

+ 20H⁻

The rate law (9) can be rearranged into the following form which is suitable for verification.

$$\frac{[\text{Os}(\text{VIII})]}{k_{\text{C}}} = \frac{[\text{H}_{3}\text{IO}_{6}^{2^{-}}]}{kK_{1}K_{2}K_{3}[\text{OH}^{-}][\text{OMH}]} + \frac{[\text{H}_{3}\text{IO}_{6}^{2^{-}}]}{kK_{2}K_{3}[\text{OMH}]} + \frac{1}{kK_{3}[\text{OMH}]} + \frac{1}{k} \quad (10)$$

According to Eq. (10), other conditions being constant, plots of $[Os(VIII)]/k_C vs 1/[OMH], 1/[OH⁻] and <math>[H_3IO_6^{2-}]$ should be linear and are found to be so at different temperatures (Fig. 6). The slopes and intercepts of such plots lead to the values of K_1 , K_2 , K_3 and k (Table 2). The value of K_1 and K_2 are in good agreement with the literature [31]. Using these constants, the rate constants were calculated and compared with the experimental k_C values. There was a reasonable

agreement with each other (Table 1), which fortifies the proposed mechanism (Scheme 3).

The negligible effect of ionic strength and dielectric constant of medium on the rate explains qualitatively the reaction between neutral and negatively charged ions, as seen in Scheme 3. The thermodynamic quantities for the different equilibrium steps, in Scheme 3 can be evaluated as follows. The [OMH], $[OH^{-}]$ and $[H_3IO_6^{2-}]$ (Table 1) were varied at four different temperatures. The plots of $[Os(VIII)]/k_C vs 1/[OMH], [Os(VIII)]/k_C vs 1/[OH⁻] and [Os(VIII)]/$ $k_{\rm C}$ vs [H₃IO₆²⁻] should be linear and are found to be so. From the slopes and intercepts, the values of K_1 , K_2 and K_3 were calculated at four different temperatures. A vant Hoff's plot was made for the variation of K_1 , K_2 and K_3 with temperature (log K_1 vs 1/T, log K_2 vs 1/T and log K_3 vs 1/T). 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 Table 2. A comparison of the ΔH value (42.08 kJ mol⁻¹) from K_1 with that of $\Delta H^{\#}$ (47.29 kJ mol⁻¹) of rate- limiting step supports that the reaction before the rate determining step is fairly fast as it involves low activation energy [32, 33], The negative value of $\Delta S^{\#}(-5.01 \text{ JK}^{-1} \text{ mol}^{-1})$ suggests that intermediate complex is more ordered than the reactants [34]. The observed modest enthalpy of activation and higher rate constant for the slow step indicate that the oxidation presumably occurs via an inner-sphere mechanism. This conclusion is supported by earlier observation [35]. The activation parameters evaluated for the catalyzed and uncatalyzed reactions explain the catalytic effect on the reaction. The catalyst Os(VIII) forms the complex (C) with substrate, which enhances the reducing property of substrate than that without catalyst. Further, the catalyst Os(VIII) modifies the reaction path by lowering the energy of activation.

5. Conclusion

Among the various species of copper(III) in alkaline medium. $[Cu(H_2IO_6)(H_2O)_2]$ is considered to be the active species for the title reaction. The active species of Os(VIII) is found to be $[OsO_4(OH)_2]^{2-}$. The reaction rates revealed that Os(VIII) catalysed reaction is about nine-fold faster than the uncatalysed reaction. . It becomes apparent that, in carrying out this reaction, the role of reaction medium is crucial. Activation parameters were evaluated for the catalyzed reaction. 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.



Fig. 6. Verification of rate law (9) for the oxidation of DL-ornithine by diperiodatocuprate(III). Plots of (A) $[Os(VIII)]/k_C vs 1/[OMH]$, (B) $[Os(VIII)]/k_C vs 1/[OH^-]$, (C) $[Os(VIII)]/k_C vs [H_3IO_6^{-2}]$ at four different temperatures (conditions as in Table 1).

Appendix

Derivation of rate law

According to Scheme 3,

$$\operatorname{Rate} = -\frac{d[DPC]}{dt} = k[C] = \frac{kK_1K_2K_3[DPC][OMH][OH^-][Os(VIII)]}{[H_3IO_6^{2^-}]}$$
(11)

The total concentration of [DPC]_T is given by

$$[DPC]_{T} = [DPC]_{f} + [Cu(H_{2}IO_{6})(H_{3}IO_{6})]^{2-} + [Cu(H_{2}IO_{6})(H_{2}O)_{2}]$$
(12)
where T and f refer to total and free concentrations

$$[DPC]_{f} = \frac{[DPC]_{T}[H_{3}IO_{6}^{2^{-}}]}{[H_{3}IO_{6}^{2^{-}}] + K_{1}[H_{3}IO_{6}^{2^{-}}][OH^{-}] + K_{1}K_{2}[OH^{-}]}$$

Similarly
$$[OMH]_{f} = \frac{[OMH]_{T}}{1 + K_{3}[Os(VIII)]}]$$

In view of low concentrations of Osmium(VIII) used,

$$[OMH]_{f} = [OMH]_{T}$$
⁽¹³⁾

Similarly,

$$[Os(VIII)]_{f} = [Os(VIII)]_{T}$$
(14)

$$[OH^{-}]_{T} = [OH^{-}]_{f} + [Cu(H_{2}IO_{6})(H_{3}IO_{6})]^{2^{-}} + [Cu(H_{2}IO_{6})(H_{2}O)_{2}]$$

= [OH^{-}]_{f} + K_{1}[OH^{-}][DPC] + \frac{K_{1}K_{2}[DPC][OH^{-}]}{[H_{3}IO_{6}^{2^{-}}]}

In view of low concentration of [DPC] and $[H_3IO_6^{2-}]$ used,

$$[OH^{-}]_{T} = [OH^{-}]_{f}]$$

$$\tag{15}$$

Substituting equations (12), (13), (14) and (15) in equation (11), and omitting subscripts, the final form of the equation obtained is,

$$\frac{\text{Rate}}{[\text{DPC}]} = \frac{k_{\text{C}} = k_{\text{T}} - k_{\text{U}}}{[\text{H}_{3}\text{IO}_{6}^{2^{-}}] + K_{1}[\text{OH}^{-}][\text{H}_{3}\text{IO}_{6}^{2^{-}}] + K_{1}K_{2}[\text{OH}^{-}] + K_{1}K_{2}[\text{OH}^{-}] + K_{1}K_{2}K_{3}[\text{OH}^{-}][\text{OMH}]}$$

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