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Osmium(VIII)/Ruthenium(III) Catalysed Oxidation of L-lysine by Diperiodatocuprate(III) in Aqueous Alkaline Medium: A Comparative Mechanistic Approach by Stopped Flow Technique

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Abstract The kinetics of osmium(VIII) and ruthenium(III) catalysed oxidation of L-lysine (L-lys) by diperiodatocuprate(III) (DPC) in alkaline medium at a constant ionic strength of 0.15 mol dm^{-3} was studied spectrophotometrically. The reaction between L-lys and DPC in alkaline medium exhibits 1:2 stoichiometry in both catalysed reaction (L-lys: DPC). The reaction is first order in [DPC] and has less than unit order both in [L-lys] and [alkali]. Increase in periodate concentration decreases the rate. Intervention of free radicals was observed in the reaction. The main products were identified by spot test, IR and GC-MS studies. Probable mechanisms are proposed and discussed. The reaction constants involved in the different steps of the mechanism are calculated. The activation parameters with respect to the slow step of the mechanism are computed and discussed and thermodynamic quantities are also determined. It has been observed that the catalytic efficiency for the present reaction is in the order of Os(VIII) > Ru(III). The active species of catalyst and oxidant have been identified.

Keywords Kinetics · Diperiodatocuprate(III) · Oxidation · L-lysine · Osmium(VIII)/Ruthenium(III) catalysis

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1 Introduction

In recent years, diperiodatocuprate(III) (DPC), is used as an oxidant in alkaline medium [1] and restricted to a few cases due its limited solubility and stability in aqueous medium. Its use as an analytical reagent is now well recognized [2]. The Copper(III) periodate complex exhibits different multiple equilibria involving different copper(III) species in aqueous alkaline medium. It is interesting to know which of the copper(III) species is the active oxidant. Amino acids have been oxidized by a variety of oxidizing agents [3]. The study of amino acids becomes important because of their biological significance and selectivity towards the oxidants to yield different products. L-lysine is a basic amino acid and carries a positive charge at physiological pH.

In recent years, the use of transition metal ions such as osmium, ruthenium and iridium, either alone or as binary mixtures, as catalysts in various redox processes has attracted considerable interest [4]. The role of osmium (VIII) as a catalyst in some redox reactions has been reviewed [5]. Although the mechanism of catalysis depends on the nature of the substrate, oxidant and on the experimental conditions. Osmium(VIII) and ruthenium(III) catalysed redox reactions involve several complexes, different oxidation states of osmium/ruthenium, etc. The reaction between L-lysine and DPC has been studied [6]. There is hardly any work with regard to the kinetics of oxidation of this amino acid in the literature, except in two cases [6, 7]. The authors observed that the microamounts of osmium(VIII) and ruthenium(III) catalyze the reaction between L-lysine and DPC in alkaline medium. In order to understand the active species of oxidant and catalysts, and to propose the appropriate mechanisms, the title reaction is investigated in detail.

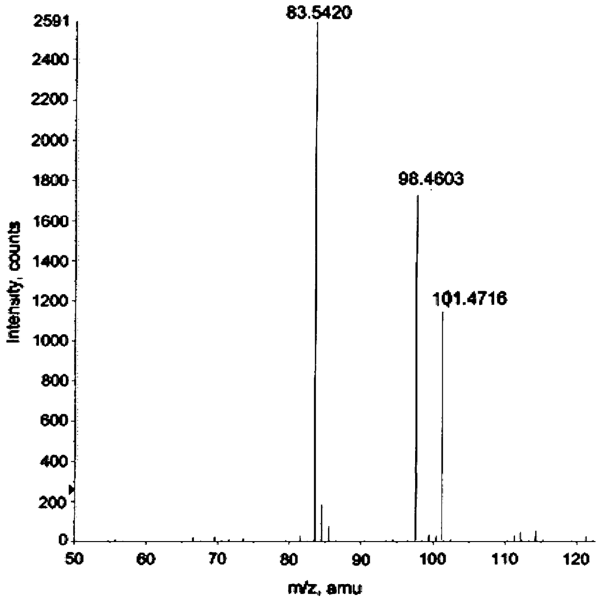


Fig. 1 GC- Mass Spectrum of 5-amino pentanal with its molecular ion peak at 101 amu

2 Experimental and Methods

2.1 Materials and Reagents

All chemicals used were of reagent grade and double distilled water was used throughout the work. A solution of L-lysine (s.d-fine. Chem.) was prepared by dissolving an appropriate amount of recrystallised sample in double distilled water. The purity of L-lys sample was checked by comparing its I.R. spectrum with literature data and with its m.p. 261–263 °C. The osmium(VIII) and ruthenium(III) solutions were prepared by dissolving OsO_4 (Johnson Matthey) and $RuCl_3$ (s.d-fine. Chem.) in 0.50 mol dm^{-3} NaOH and 0.20 mol dm^{-3} HCl respectively and there concentrations were ascertained by known methods [8, 9]. The copper(III) complex was prepared [10] and standardized by known procedure [11]. Periodate solution was prepared by weighing the required amount of sample in hot water and used after 24 h. Its concentration was ascertained iodometrically [12] at neutral pH maintained using a

Table 1 Effects of [DPC], [L-lys], $[OH^-]$ and $[IO_4^-]$ on the ruthenium (III)-catalyzed oxidation of L-lysine by diperiodatocuprate(III) in alkaline medium at 25 °C, I = 0.15 mol dm^{-3}

[DPC] × 10^5 (mol dm^{-3})	[L-lys] × 10^4 (mol dm^{-3})	$[OH^-]$ (mol dm^{-3})	$[IO_4^-]$ × 10^4 (mol dm^{-3})	10^6 [Ru (III)] (mol dm^{-3})	10^2k_T (s^{-1})	10^3k_U (s^{-1})	k_C × 10^2(s^{-1})	
							Found	Calculated
1.0	5.0	0.06	1.0	5.0	4.72	7.52	3.96	4.11
3.0	5.0	0.06	1.0	5.0	4.71	7.50	3.95	4.11
5.0	5.0	0.06	1.0	5.0	4.72	7.51	3.96	4.11
8.0	5.0	0.06	1.0	5.0	4.70	7.53	3.94	4.11
10	5.0	0.06	1.0	5.0	4.72	7.51	3.96	4.11
5.0	1.0	0.06	1.0	5.0	1.35	2.19	1.13	1.24
5.0	3.0	0.06	1.0	5.0	3.25	5.59	2.69	2.97
5.0	5.0	0.06	1.0	5.0	4.72	7.51	3.96	4.11
5.0	8.0	0.06	1.0	5.0	5.92	8.89	5.03	5.26
5.0	10	0.06	1.0	5.0	6.58	9.98	5.59	5.79
5.0	5.0	0.01	1.0	5.0	1.46	2.74	1.19	1.18
5.0	5.0	0.03	1.0	5.0	3.14	5.86	2.55	2.75
5.0	5.0	0.06	1.0	5.0	4.72	7.51	3.96	4.11
5.0	5.0	0.08	1.0	5.0	5.83	8.67	4.96	4.70
5.0	5.0	0.10	1.0	5.0	6.59	9.45	5.64	5.14
5.0	5.0	0.06	0.6	5.0	6.49	8.27	5.66	5.15
5.0	5.0	0.06	0.8	5.0	5.54	7.07	4.83	4.57
5.0	5.0	0.06	1.0	5.0	4.72	7.51	3.96	4.11
5.0	5.0	0.06	3.0	5.0	2.74	5.20	2.22	2.05
5.0	5.0	0.06	5.0	5.0	1.77	3.09	1.46	1.36
5.0	5.0	0.06	1.0	1.0	1.52	7.51	7.73	8.23
5.0	5.0	0.06	1.0	3.0	3.05	7.51	2.30	2.47
5.0	5.0	0.06	1.0	5.0	4.72	7.51	3.96	4.11
5.0	5.0	0.06	1.0	7.0	7.21	7.51	6.46	5.76
5.0	5.0	0.06	1.0	9.0	8.64	7.51	7.89	7.41

$$\mathrm{Cu(HL)_2} + [\mathrm{OH^-}] \rightleftharpoons \mathrm{CuL(HL)} + \mathrm{H_2O}$$

$$\mathrm{CuL(HL)} \rightleftharpoons \mathrm{Cu(HL)} + \mathrm{L}$$

$$\text{L-Lys} + \text{Catalyst} \rightleftharpoons \text{Complex (C)}$$

$$\text{Complex (C)} + \mathrm{CuL(HL)} \longrightarrow \mathrm{I} + \mathrm{Cu(II)} + \text{Catalyst} \quad (\mathrm{I} — \text{Intermediate})$$

$$\mathrm{I} + \mathrm{Cu(HL)} \longrightarrow \text{Products} + \mathrm{Cu(II)}$$

Scheme 1 General mechanistic Scheme for the oxidation of osmium(VIII)/ruthenium(III) catalysed oxidation of L-lysine by diperiodatocuprate(III)

phosphate buffer. KOH and KNO_3 (BDH, AR) were employed to maintain the required alkalinity and ionic strength respectively.

2.2 Kinetic Measurements

The kinetics was followed under pseudo-first order condition where [L-lys] > [DPC] at 25 ± 0.1 °C, unless specified. The reaction was initiated by mixing the DPC to L-lys solution which also contained required concentrations of Os(VIII) or Ru(III), KNO_3, KOH and KIO_4. Since the initial reaction was too fast to be monitored by usual methods, the course of reaction was followed by monitoring the decrease in absorbance of [DPC] in a 1 cm quartz cell placed in the thermostatted compartment of an Hitachi 150-20 UV–Visible spectrophotometer attached to a rapid kinetic accessory (HI-TECH SFA-12) at its absorption maximum of 415 nm. Application of Beer's law had been verified at 415 nm under reaction conditions and the extinction coefficient, € was found to be 6230 ± 100 dm^3 mol^{-1} cm^{-1}. The kinetics were followed more than 90% completion of reaction and good first order kinetics were observed. During the kinetic studies it was observed that, under the present experimental conditions in the absence of osmium(VIII) or ruthenium(III), the oxidation of L-lysine by DPC occurs very slowly, but in a measurable quantities. Hence, during the calculation of the pseudo-first order rate constants, k_c, the uncatalysed rate has also to be taken into account. Due to this, in case of each catalysed kinetic run, parallel kinetic run under similar conditions in the absence of catalysts were also carried out. In both the cases the pseudo–first order rate constants (k_c and k_u) were obtained from the plots of log(absorbance) versus time plots. The plots were linear over 85% completion of the reaction. Thus the total rate constant (k_T) is equal to the sum of rate constants in presence (k_c) and in absence (k_u) of catalysts, i.e.

$$k_T = k_c + k_u$$

$$k_c = k_T - k_u$$

Table 2 Thermodynamic activation parameters for the Ru(III) catalysed oxidation of L-lysine by DPC in aqueous alkaline medium with respect to the slow step of Scheme 2

(A) Effect of temperature

Temperature (K)	$k \times 10^{-3}$ (dm^3 mol^{-1} s^{-1})
298	2.06
303	2.43
308	2.89
313	3.49

(B) Activation parameters (Scheme 2)

Parameters	Values
$\Delta H^{\#}$ (kJ mol^{-1})	24.8 ± 0.5
$\Delta S^{\#}$ (JK^{-1} mol^{-1})	−79 ± 4
$\Delta G^{\#}$ (kJ mol^{-1})	48 ± 2
log A	9.0 ± 0.4

(C) Effect of temperature in calculating K_1, K_2 and K_3 for the Ru(III)-catalysed oxidation of L-lysine by diperiodatocuprate (III) in alkaline medium

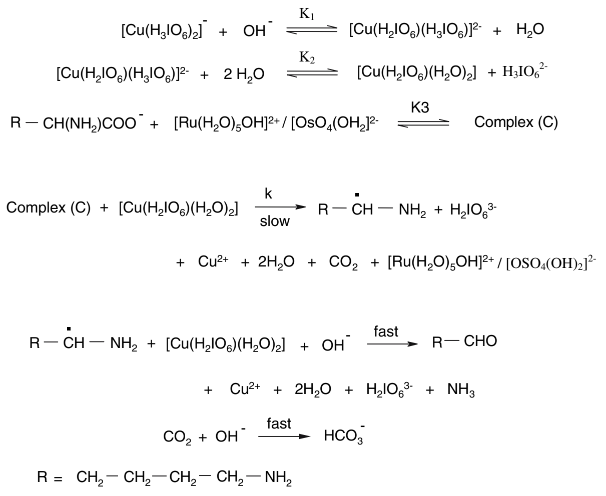
Temperature (K)	K_1 (dm^3 mol^{-1})	$K_2 \times 10^4$ (mol dm^{-3})	$K_3 \times 10^{-4}$ (dm^3 mol^{-1})
298	0.2 ± 0.003	2.9 ± 0.2	1.2 ± 0.05
303	0.7 ± 0.03	2.3 ± 0.1	1.5 ± 0.06
308	1.0 ± 0.05	1.8 ± 0.07	1.8 ± 0.07
313	2.3 ± 0.1	1.4 ± 0.06	2.3 ± 0.1

(D) Thermodynamic quantities using 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})	116 ± 2	−36 ± 1	33 ± 1
ΔS (JK^{-1} mol^{-1})	380 ± 20	−191 ± 10	189 ± 11
ΔG_{298} (kJ mol^{-1})	−2.2 ± 0.1	21.7 ± 0.8	−24.8 ± 0.9

The rate constants k_c obtained in this way were reproducible within ±5%.

Since periodate is present in excess in DPC, the possibility of oxidation of L-lys by periodate in alkaline medium at 25 °C was checked and found that there was no significant reaction under the experimental conditions employed compared to the DPC oxidation of L-lysine. Kinetics runs were also carried out in N_2 atmosphere in order to understand the effect of dissolved oxygen on the rate of reaction. No significant difference in the results were obtained. In view of the ubiquitous contamination of carbonate in the basic medium, the effect of carbonate was also studied. Added carbonate had no effect on the reaction rates.



Scheme 2 Detailed scheme for the oxidation of ruthenium(III)/osmium(VIII) catalysed oxidation of L-lysine by diperiodatocuprate(III)

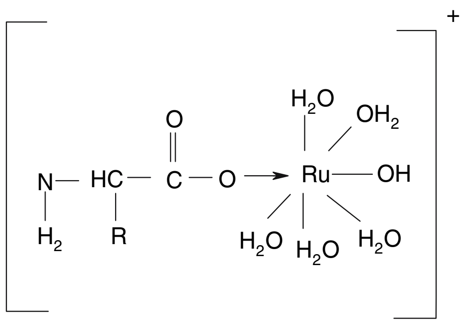


Fig. 2 Probable complex structure of complex for ruthenium(III) catalysed reaction

3 Results

3.1 Stoichiometry and Product Analysis

Different sets of reaction mixtures containing varying ratios of DPC to L-lys in the presence of constant amounts of Os(VIII) or Ru(III), OH^- and KNO_3 were kept for 2 h in closed vessels under nitrogen atmosphere. The remaining concentration of DPC was estimated spectrophotometrically at 415 nm. The results indicated 1:2 stoichiometry as given in Eq. 1.

$$R - CH(NH_2)COO^- + 2[Cu(H_2IO_6)(H_2O)_2] + 2OH^- \xrightarrow{Ru(III)/Os(VIII)} R - CHO + Cu^{2+} + 2H_2O + 2H_2IO_6^{3-} + NH_3 + HCO_3^- \tag{1}$$

$R = CH_2 - CH_2 - CH_2 - CH_2 - NH_2$

The main reaction product was identified as corresponding aldehyde (5-aminopentanal) by its spot test, ammonia by Nessler's reagent [13]. The corresponding aldehyde was identified by preparing its 2,4-DNP derivative. The nature of 5-aminopentanal was confirmed by its IR spectrum which showed a C=O stretching at 1,631 cm^{-1} indicating the presence of C=O, the band at 3,424 cm^{-1} indicating the presence of NH_2 group. It was also confirmed by its melting point 118 °C (lit. m.p. 118–120 °C). Futher, (5-aminopentanal) was subjected to GC-mass spectral analysis. GC-MS data was obtained on a 17A Shimadzu gas chromatograph with a QP-5050A shimadzu mass spectrometer using EI ionization technique. The mass spectrum showed a molecular ion peak at 101 amu confirming the presence of 5-aminopentanal (Fig. 1). All other peaks observed in GC-MS can be interpreted in accordance with observed structure of the product. The product, Cu(II) was identified by UV–Vis spectra. The reaction products do not undergo further oxidation under the present kinetic conditions. Regression analysis of experimental data to obtain the regression coefficient r and standard deviation S of points from the regression line was performed using Microsoft 2003 Excel programme.

3.2 Reaction Orders

The reaction orders have been determined from the slopes of $\log k_c$ versus log(concentration) plots by varying concentrations of L-lysine, OH^-, catalyst (osmium or ruthenium), in turn, while keeping the others constant. The plot of log(absorbance) versus time was linear over three half lives of the reaction for different initial [DPC] which indicates the unit order with respect to [DPC]. This was also confirmed by the constant values of rate constants, k_c for different [DPC] (Tables 1 and 3). The order in osmium(VIII) and ruthenium(III) concentrations were found to be unity under present experimental conditions. In the case of osmium and ruthenium catalysed reaction the L-lysine concentration was varied in the concentration range 1.0×10^{-4}–1.0×10^{-3} mol dm^{-3} and the order with respect to L-lysine concentration was found to be less than unity. Similarly order with respect to hydroxyl and periodate ion concentrations were found to be less than unity and negative fractional (less than unity).

3.3 Effect of Ionic Strength (I) and Dielectric Constant of the Medium (D)

The ionic strength effect was studied by varying the concentration of KNO_3 and found that increasing ionic strength had negligible effect on the rate of reaction. The dielectric constant of the medium, 'D' was varied by varying the t-butyl alcohol and water (V/V). The decrease in dielectric constant of the reaction medium increases the rate of reaction for Os(VIII) catalysis and decreases the rate of reaction for Ru(III) catalysis.

3.4 Effect of Initially Added Products

The externally added products, aldehyde and copper(II) ($CuSO_4$) did not have any significant effect on the rate of the reaction in both the catalysed reactions.

3.5 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 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 L-lysine alone with acrylonitrile did not induce any polymerization under the same condition as those induced for reaction mixture. Initially added acrylonitrile decreases the rate of reaction indicating free radical intervention, which is the case in earlier work [14].

3.6 Effect of Temperature (T)

The influences of temperature on the reaction was studied at four different temperatures. The rate constant (k) of the slow step of Scheme 1 were obtained from the intercepts of [Os(VIII)]/k_C or [Ru(III)]/k_C versus 1/[L-lys] plots at four different temperatures. The values are given in Tables 2 and 4. The activation parameters for the rate-determining step were obtained by the least square method of plot of log k versus 1/T and are given in Tables 2 and 4.

3.7 Catalytical Activity

It has been pointed out by Moelwyn-Hughes [15] that, in the presence of the catalyst, the uncatalysed and catalysed reactions proceed simultaneously, so that

$$k_T = k_U + k_C[\text{catalyst}]^x \tag{2}$$

Here k_T is the observed pseudo first-order rate constant in the presence of Ru(III) or Os(VIII) catalyst, k_U is the pseudo first-order rate constant for the uncatalysed reaction, K_C is the catalytic constant and 'x' is the order of the reaction with respect to [Ru(III)] or [Os(VIII)]. In the present investigations, x values for the standard run were found to be unity for both Ru(III) and Os(VIII) catalysts. Then the value of K_C can be calculated using the equation

$$K_C = \frac{k_T - k_U}{[\text{Catalyst}]^x} = \frac{k_C}{[\text{Catalyst}]^x} \quad (\text{where, } k_T - k_U = k_C) \tag{3}$$

The values of K_C were evaluated for both the catalysts at different temperatures and found to vary at different temperatures. Further, plots of log K_C versus 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 5. The value of K_C for Ru(III) is 1.65×10^3 whereas for Os(VIII) the value is 3.13×10^3. The value of K_C indicates that Os(VIII) is a more efficient catalyst compared to Ru(III) in the oxidation of L-lysine by DPC in alkaline medium.

4 Discussion

The water-soluble copper(III) periodate complex is reported [16] 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 [17] (4)–(6) depending on the pH of the solution.

$$H_5IO_6 \rightleftharpoons H_4IO_6^- + H^+ \tag{4}$$

$$H_4IO_6^- \rightleftharpoons H_3IO_6^{2-} + H^+ \tag{5}$$

$$H_3IO_6^{2-} \rightleftharpoons H_2IO_6^{3-} + H^+ \tag{6}$$

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 [18]. However, formation of this species is negligible under conditions employed for kinetic study. Hence, at the pH employed in this study, the soluble copper(III) periodate complex exists as diperiodatocuprate(III), $[Cu(H_2IO_6)\ (H_3IO_6)]^{2-}$, this conclusion also supported by literature [19]. Based on the experimental rate law, the general mechanism can be proposed (Scheme 1).

4.1 Mechanism of Ruthenium(III) Catalysis

It is interesting to identify the probable ruthenium(III) chloride species in alkaline media. Electronic spectral studies [20] have confirmed that ruthenium(III) chloride exists in hydrated form as $[Ru(H_2O)_6]^{3+}$. In the present study

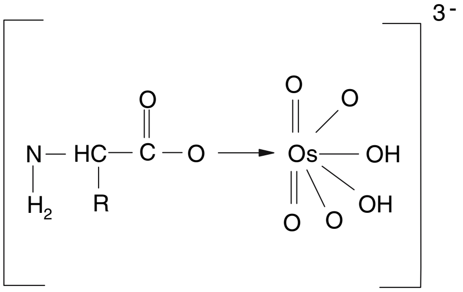


Fig. 3 Probable complex structure of complex for osmium(VIII) catalysed reaction

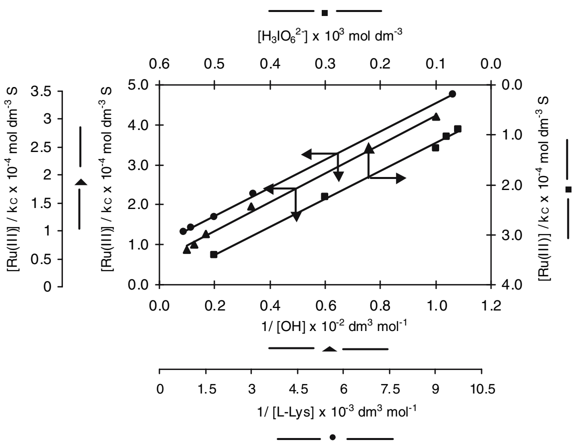


Fig. 4 Verification of rate law (10) of Ru(III)-catalysed oxidation of L-lysine by diperiodatocuprate(III) at 25 °C

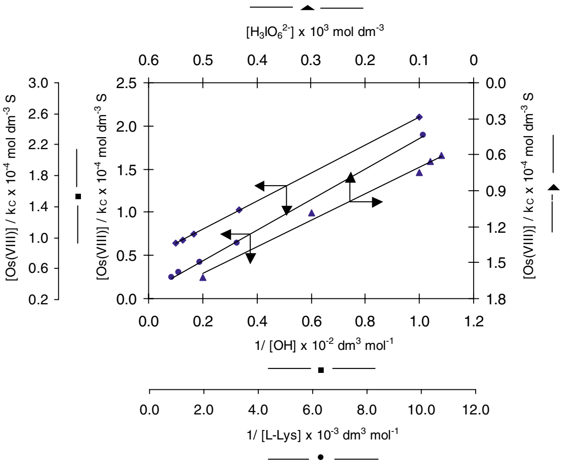


Fig. 5 Verification of rate law (13) of Os(VIII)-catalysed oxidation of L-lysine by diperiodatocuprate(III) at 25 °C

it is quite probable that the $[Ru(H_2O)_5OH]^{2+}$ species might assume the general form $[Ru(III)(OH)_x]^3 - x$. The x value would always be less than six because there are no definite reports of any hexahydroxy ruthenium species. The remainder of the coordination sphere would be filled by water molecules. Hence, under the conditions employed, e.g. $[OH^-] \gg [Ru(III)]$, ruthenium(III) is mostly present as the hydroxylated species, $[Ru(H_2O)_5OH]^{2+}$ [21].

It is known that L-lysine exists in the form of Zwitter ion [22] in aqueous medium. In highly acidic medium, it exists in the protonated form, whereas in highly basic medium it exist as the anionic form according to the following equilibria.

$$\mathrm{R\text{-}CH(NH_2)COOH} \rightleftharpoons \underset{\text{Zwitter ion}}{\mathrm{R\text{-}CH(\overset{+}{N}H_3)COO^-}}$$

$$\mathrm{R\text{-}CH(NH_2)COOH + H^+ \rightleftharpoons R\text{-}CH(\overset{+}{N}H_3)COOH}$$

$$\mathrm{R\text{-}CH(NH_2)COOH + OH^- \rightleftharpoons R\text{-}CH(NH_3)COO^- + H_2O}$$

$$\mathrm{R = CH_2 - CH_2 - CH_2 - CH_2 - NH_2}$$

The reaction between the diperiodatocuprate(III) complex and L-lysine in alkaline medium in the presence of ruthenium(III) has the stoichiometry 1:2 (L-lys: DPC) with a first order dependence on [DPC] and [ruthenium(III)] and an apparent order of less than unity in [substrate], [alkali] and negative fractional order dependence on the periodate. No effect of added products was observed. Based on the experimental results, a mechanism is proposed. Lister [23] proposed the copper(III) periodate in alkaline medium into three forms as diperiodatocuprate(III), monoperiodatocuprate(III) 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, DPC and MPC are to be considered as active forms of copper(III) periodate complex. It may be expected that a lower periodate complex such as monoperiodatocuprate(III) will be more important in the reaction than the DPC, The results of increase in the rate with increase in alkali concentration and decrease in the rate with increase in periodate concentration suggest that equilibria of different copper(III) periodate complexes are possible as in Eqs. 7 and 8.

$$\mathrm{[Cu(H_3IO_6)_2]^- + OH^- \rightleftharpoons [Cu(H_2IO_6)(H_3IO_6)]^{2-} + H2O} \tag{7}$$

$$\mathrm{[Cu(H_2IO_6)(H_3IO_6)]^{2-} + 2H_2O \rightleftharpoons [Cu(H_2IO_6)(H_2O)_2] + [H_3IO_6]^{2-}} \tag{8}$$

The inverse fractional order in $[IO_4^-]$ might also be due to this reason. Anionic species of L-lysine reacts with ruthenium(III) active species to form a complex (C) which futher reacts with one mole of MPC in a slow step to give the free radical species of L-lys, Cu(II) with regeneration of catalyst, ruthenium(III). Further this free radical species of L-lys reacts with one more molecule of

MPC species in a fast step to yield the products as given in Scheme 2.

The probable structure of the complex (C) is also given in Fig. 2. Spectroscopic evidence for the complex formation between ruthenium(III) and substrate was obtained from UV–Vis spectra of L-lys (5.0×10^{-4}), Ru(III) (5.0×10^{-6}), $[OH^-] = 0.06$ mol dm^{-3}) and a mixture of both. A bathochromic shift of about 7 nm from 342 nm to 349 nm in the spectra of L-lys was observed. However, the Michaelis-Menten plot also proved the complex formation between catalyst and reductant, which explains the less than unit order dependence on [L-lys]. Such a complex between a substrate and a oxidant has been observed in other studies [24].

4.2 Mechanism of Osmium (VIII) Catalysis

Osmium(VIII) is known to form different complexes at different OH^- [25] concentrations, $[OsO_4(OH)_2]^{2-}$ and $[OsO_5(OH)]^{3-}$. At higher concentrations of OH^- i.e. > 0.15 mol dm^{-3}, $[OsO_5(OH)]^{3-}$ 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 that its formation is important in the reaction [25].

The equilibrium steps 7 and 8 and the stoichiometry are the same as in case of Ru(III) catalysis. It may be expected that lower Cu(III) periodate species such as MPC is more important in the reaction than the DPC. The inverse fractional order in $[H_3IO_6^{2-}]$ might also be due to this reason. Anionic species of L-lysine reacts with osmium(VIII) species to form a complex (C) which reacts with one mole of the MPC in a slow step to give the free radical of L-lysine and Cu(II) species with regeneration of catalyst, osmium(VIII). Further, this free radical of L-lysine reacts with one more mole of MPC species in a fast step to yield the products as given in Scheme 2.

The probable structure of the complex (C) is given in Fig. 3. Spectroscopic evidence for the complex formation between catalyst and substrate was obtained from UV–Vis spectra of L-lysine (5.0×10^{-4}), Os(VIII) (5.0×10^{-6}, $[OH^-] = 0.06$ mol dm^{-3}) and a mixture of both. A hypsochromic shift of about 6 nm from 439 nm to 433 nm in the spectra of L-lysine was observed. However, the Michaelis-Menten plot proved the complex formation between catalyst and reductant, which explains the less than unit order dependence on [L-lys]. Such a complex between a substrate and a catalyst has been observed in other studies [26]. The negligible small effect of ionic strength and positive effect of dielectric constant of the medium on the rate qualitatively explain the reaction between neutral and negatively charged ions as seen in Scheme 2. Since Scheme 2 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 (see infra). This type of radical intermediate has also been observed in earlier work [26].

From Scheme 2 the general rate law (9) can be derived for ruthenium(III) and osmium(VIII) catalysts.

$$\text{rate} = \frac{-d[DPC]}{dt} = \frac{kK_1K_2K_3[\text{DPC}][\text{L}{-}\text{lys}][\text{OH}^-][\text{Catalyst}]}{\begin{array}{l}[\text{H}_3\text{IO}_6^{2-}] + K_1[\text{OH}^-][\text{H}_3\text{IO}_6^{2-}] + K_1K_2[\text{OH}^-] + K_1K_2K_3[\text{OH}^-][\text{L-lys}] \\ + K_3[\text{H}_3\text{IO}_6^{2-}][\text{L-lys}] + K_1K_3[\text{-lys}][\text{OH}^-][\text{H}_3\text{IO}_6^{2-}]\end{array}} \tag{9}$$

$$\frac{\text{rate}}{[\text{DPC}]} = k_\text{C} = k_\text{T} - k_\text{U} = \frac{kK_1K_2K_3[\text{L}{-}\text{lys}][\text{OH}^-][\text{Catalyst}]}{[\text{H}_3\text{IO}_6^{2-}] + K_1[\text{OH}^-][\text{H}_3\text{IO}_6^{2-}] + K_1K_2[\text{OH}^-] + K_1K_2K_3[\text{OH}^-][\text{L-lys}]} \tag{10}$$

The terms ($K_3[\text{H}_3\text{IO}_6^{2-}][\text{L-lys}]$) and ($K_1K_3[\text{L-lys}][\text{OH}^-][\text{H}_3\text{IO}_6^{2-}]$) in the denominator of Eq. 9 can be neglected in the view of low concentrations of L-lysine and periodate used in the study. Therefore, Eq. 9 becomeswhich explains all the observed kinetic orders of different species.

The rate law (10) can be rearranged into the following form which is suitable for verification.

$$\frac{[\text{Catalyst}]}{K_\text{C}} = \frac{[\text{H}_3\text{IO}_6^{2-}]}{\text{kK}_1K_2K_3[\text{OH}^-][\text{L-lys}]} + \frac{[\text{H}_3\text{IO}_6^{2-}]}{\text{kK}_2K_3[\text{L-lys}]} + \frac{1}{K_3[\text{L-lys}]} + \frac{1}{k} \tag{11}$$

where [Catalyst] = Ru(III)] or [Os(VIII)].

Table 3 Effects of [DPC], [L-Lys], [OH$^-$] and [IO$_4^-$] on the osmium(VIII) catalyzed oxidation of L-lysine by diperiodatocuprate(III) in alkaline medium at 25°C, I = 0.15 mol dm^{-3}

[DPC] × 10^5 (mol dm^{-3})	[L-lys] × 10^4 (mol dm^{-3})	[OH$^-$] (mol dm^{-3})	[IO$_4^-$] × 10^4 (mol dm^{-3})	10^6 [Os(VIII)] (mol dm^{-3})	$10^2 k_T$ (s^{-1})	$10^3 k_U$ (s^{-1})	k_C × 10^2 (s^{-1})	
							Found	Calculated
1.0	5.0	0.06	1.0	5.0	7.42	7.52	6.66	6.64
3.0	5.0	0.06	1.0	5.0	7.41	7.50	6.65	6.64
5.0	5.0	0.06	1.0	5.0	7.42	7.51	6.66	6.64
8.0	5.0	0.06	1.0	5.0	7.40	7.53	6.64	6.64
10	5.0	0.06	1.0	5.0	7.42	7.51	6.65	6.64
5.0	1.0	0.06	1.0	5.0	2.34	2.19	2.12	2.13
5.0	3.0	0.06	1.0	5.0	5.61	5.59	5.05	4.91
5.0	5.0	0.06	1.0	5.0	7.42	7.51	6.66	6.64
5.0	8.0	0.06	1.0	5.0	8.84	8.89	7.95	8.29
5.0	10	0.06	1.0	5.0	9.98	9.98	8.98	9.03
5.0	5.0	0.01	1.0	5.0	2.65	2.74	2.37	2.37
5.0	5.0	0.03	1.0	5.0	5.46	5.86	4.87	4.89
5.0	5.0	0.06	1.0	5.0	7.42	7.51	6.66	6.64
5.0	5.0	0.08	1.0	5.0	8.22	8.67	7.35	7.30
5.0	5.0	0.10	1.0	5.0	8.66	9.45	7.71	7.76
5.0	5.0	0.06	0.6	5.0	9.08	8.27	8.25	7.78
5.0	5.0	0.06	0.8	5.0	8.36	7.07	7.65	7.17
5.0	5.0	0.06	1.0	5.0	7.42	7.51	6.66	6.64
5.0	5.0	0.06	3.0	5.0	5.32	5.20	4.80	3.84
5.0	5.0	0.06	5.0	5.0	3.38	3.09	3.07	2.70
5.0	5.0	0.06	1.0	1.0	1.60	7.51	8.51	8.65
5.0	5.0	0.06	1.0	3.0	4.05	7.51	3.30	3.98
5.0	5.0	0.06	1.0	5.0	7.42	7.51	6.66	6.64
5.0	5.0	0.06	1.0	7.0	7.88	7.51	7.13	7.32
5.0	5.0	0.06	1.0	9.0	9.37	7.51	8.62	8.74

According to Eq.11, other conditions being constant, plots of [Catalyst]/k_c versus 1/[OH$^-$] ($r \geq 0.998$, $S \leq 0.014$), [Catalyst]/k_c versus 1/[L-Lys] ($r \geq 0.997$, $S \leq 0.016$) and [Catalyst]/k_c versus [$H_3IO_6^{2-}$] ($r \geq 0.998$, $S \leq 0.011$) should be linear and are found to be so with an intercept supporting the catalyst-L-lysine complex (Figs. 2 and 3). The slopes and intercepts of such plots (Figs. 4 and 5) lead to the values of K_1, K_2, K_3 and k. In case of ruthenium(III) catalysed reaction (from Fig. 4) the values of K_1, K_2, K_3 and k were found to be as (0.2 ± 0.003) dm^3 mol^{-1}, (2.9 ± 0.1) × 10^{-4} mol dm^3, (1.2 ± 0.05) × 10^4 dm^3 mol^{-1} and (2.6 ± 0.1) × 10^3 dm^3 mol^{-1} s^{-1}, respectively, whereas in case of osmium(VIII) catalysed reaction (from Fig. 5) the values of K_1, K_2, K_3 and k were found to be as (1.0 ± 0.02) dm^3 mol^{-1}, (6.9 ± 0.3) × 10^{-4} mol dm^3, (5.6 ± 0.1) × 10^3 dm^3 mol^{-1} and (2.8 ± 0.1) × 10^3 dm^3 mol^{-1} s^{-1} respectively. 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 hydrolysed species in alkaline medium.

The thermodynamic quantities for the first, second and third equilibrium steps of Scheme 2 can be evaluated in the presence of ruthenium(III) and osmium(VIII) catalysed as follows. The L-lysine and hydroxide ion concentrations (as in Tables 2 and 3) were varied at four different temperatures. The plots of [Catalyst]/k_c versus 1/[OH$^-$] ($r \geq 0.9604$, $S \leq 0.006$) and [Catalyst]/k_c versus 1/[L-lys] ($r \geq 0.9604$, $S \leq 0.006$) should be linear, and are found to be so (Figs. 4 and 5). From the slopes and intercepts, the values of K_1 are calculated at different temperatures and these values are given in Tables 2 and 4. A van't Hoffs plot was made for variation of K_1 with temperature (log K_1 versus 1/T ($r \geq 0.9604$, $S \leq 0.006$) and the values of enthalpy of reaction ΔH, entropy of reaction ΔS and free energy of reaction ΔG, were calculated. These values are also

Table 4 Thermodynamic activation parameters for the Os(VIII) catalysed oxidation of L-lysine by DPC in aqueous alkaline medium with respect to the slow step of Scheme 2

(A) Effect of temperature

Temperature (K)	$k \times 10^{-3}$ ($dm^3\ mol^{-1}\ s^{-1}$)
298	2.81
303	3.08
308	3.52
313	3.97

(B) Activation parameters (Scheme 2)

Parameters	Values
$\Delta H^{\#}$ (kJ mol^{-1})	15.5 ± 0.6
$\Delta S^{\#}$ (JK^{-1} mol^{-1})	−107 ± 8
$\Delta G^{\#}$ (kJ mol^{-1})	47 ± 1
log A	7.6 ± 0.4

(C) Effect of temperature in calculating K_1, K_2 and K_3 for the Os(VIII)-catalysed oxidation of L-lysine by diperiodatocuprate (III) in alkaline medium

Temperature (K)	K_1 ($dm^3\ mol^{-1}$)	$K_2 \times 10^4$ (mol dm^{-3})	$K_3 \times 10^{-3}$ ($dm^3\ mol^{-1}$)
298	1.05 ± 0.02	6.9 ± 0.3	5.6 ± 0.1
303	1.45 ± 0.04	5.5 ± 0.06	6.9 ± 0.3
308	3.14 ± 0.1	4.1 ± 0.03	8.7 ± 0.4
313	4.90 ± 0.2	2.1 ± 0.02	9.5 ± 0.5

(D) Thermodynamic quantities using 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})	63.1 ± 3.0	−58.1 ± 2.0	26.3 ± 0.7
ΔS (JK^{-1} mol^{-1})	279 ± 20	−256 ± 18	167 ± 10
ΔG_{298} (kJ mol^{-1})	−2.3 ± 0.1	20.1 ± 0.9	−22.7 ± 0.8

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

Temperature (K)	$10^{-3}K_C$ (Ru(III))	$10^{-3}K_C$ (Os(VIII))
298	1.65	3.13
303	1.84	3.34
308	2.02	3.57
313	2.23	3.78
Ea (kJ mol^{-1})	15.5	9.8
$\Delta H^{\#}$ (kJ mol^{-1})	13	7.3
$\Delta S^{\#}$ (JK^{-1} mol^{-1})	−120	−134
$\Delta G^{\#}$ (kJ mol^{-1})	49	47
log A	6.9	6.2

[DPC] = 5.0×10^{-5}; [L-lys] = 5.0×10^{-4}; [OH^-] = 0.06 mol dm^{-3}; [Os(VIII)] = 5.0×10^{-6} mol dm^{-3}; [Ru(III)] = 5.0×10^{-6} mol dm^{-3}

given in Tables 2 and 4. A comparison of the latter values with those obtained for the slow step of the reaction shows that these values mainly refer to the rate limiting step, supporting the fact that the reaction before rate determining step is fairly fast and involves low activation energy [27]. In the same manner K_2 and K_3 values were calculated at different temperatures and their corresponding values of the thermodynamic quantities are given in the Table 4.

The activation parameters evaluated for the catalysed and uncatalysed reaction explain the catalytic effect on the reaction. The catalyst Ru(III) or Os(VIII) forms the complex (C) with the substrate, which enhances the reducing property of the substrate over that without catalyst (Ru(III) or Os(VIII)). Further, the catalyst Ru(III) or Os(VIII) modifies the reaction path by lowering the energy of activation. The negative value of $\Delta S^{\#}$ suggests that the intermediate complex is more ordered than the reactants [28]. The observed modest enthalpy of activation and a higher rate constant for the slow step indicates that the oxidation presumably occurs via an inner-sphere mechanism. This conclusion is supported by earlier observations [29]. The value of $\Delta S^{\#}$ within the range for radical reaction has been ascribed [30] 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.

The values of $\Delta S^{\#}$, $\Delta G^{\#}$ and the rate constant (k) indicate that the order of reactivity of the catalysts is Ru(III) < Os(VIII) for the oxidation of L-lysine by DPC. The Os(VIII)-catalysed reaction, however, is reasonably fast in view of readiness of Os(VIII) to act across the double bond and the Ru(III) catalysed reaction is slower, probably owing to the less ability of the Ru(III) to act across the double bond.

5 Conclusion

The comparative study of Ru(III) and Os(VIII) catalysed oxidation of L-lysine by diperiodatocuprate(III) was studied. Oxidation products were identified. Among various species of Cu(III) in alkaline medium, monoperiodatocuprate (III) is considered to be the active species for the title reaction. The active species of Ru(III) is found to be $[Ru(H_2O)_5OH]^{2+}$ and that for Os(VIII) as $[OsO_4(OH)_2]^{2-}$. Activation parameters were evaluated for both catalysed and uncatalysed reactions. Catalytic constants and the activation parameters with reference to the catalyst were also computed. The catalytic efficiency is Ru(III) $<$ Os(VIII).

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Appendix A

According to Scheme 2

$$\begin{aligned}\text{Rate} &= k[C][Cu(H_3IO_6)(OH)_2]^- \\ &= \frac{kK_1K_2K_3[DPC][Ru(III)][OH^-][\text{L}-Lys]}{[H_3IO_6^{2-}]}\end{aligned} \tag{I}$$

The total concentration of DPC is given by (Where T and f stands for total and free)

$$\begin{aligned}[DPC]_T &= [DPC]_f + [Cu(OH)_2(H_3IO_6)(H_2IO_6)]^{4-} + [Cu(H_3IO_6)(OH)_2]^- \\ &= [DPC]_f\left\{\frac{[H_3IO_6^{2-}] + K_1[OH^-][H_3IO_6^{2-}] + K_1K_2[OH^-]}{[H_3IO_6^{2-}]}\right\}\end{aligned}$$

Therefore,

$$[DPC]_f = \frac{[DPC]_T[H_2IO_6^{3-}]}{[H_3IO_6^{2-}] + K_1[OH^-][H_3IO_6^{2-}] + K_1K_2[OH^-]} \tag{II}$$

Similarly,

$$\begin{aligned}[OH]_T &= [OH]_f + [Cu(OH)_2(H_3IO_6)(H_2IO_6)]^{4-} \\ &\quad + [Cu(H_3IO_6)(OH)_2]^- \\ &= [OH]_f + K_1[DPC][OH^-] + \frac{K_1K_2[PDC][OH^-]}{[H_3IO_6^{2-}]}\end{aligned}$$

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

$$[OH]_T = [OH]^f \tag{III}$$

Similarly,

$$\begin{aligned}[\text{L-lys}]_T &= [\text{L-lys}]_f + [C] \\ &= [\text{L-lys}](1 + K_3[Ru(III)])\end{aligned}$$

In view of the low concentration of [Ru(III)]) used,

$$[\text{L-lys}]_T = [\text{L-lys}]_f \tag{IV}$$

$$\begin{aligned}[Ru(III)]_T &= [Ru(III)]_f + C \\ &= [Ru(III)]_f\{1 + K_3[\text{L-lys}]\}\end{aligned}$$

$$[Ru(III)]_f \frac{[Ru(III)]_T}{1 + K_3[\text{L-Lys}]} \tag{V}$$

Substituting (II), (III), (IV) and (V) in (I) and omitting the subscripts T and f, we get

$$\frac{\text{Rate}}{[DPC]} = K_C = k_T - k_U = \frac{kK_1K_2K_3[\text{L}-Lys][OH^-][Ru(III)]}{[H_3IO_6^{2-}] + K_1[OH^-][H_3IO_6^{2-}] + K_1K_2[OH^-] + K_1K_2K_3[OH^-][\text{L-Lys}]}$$

Similarly for Os(VIII) catalysis, the rate law can be derived.

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