

Review

# Osmium(VIII) catalysed oxidation of L-leucine by a new oxidant, diperiodatoargentate(III) in aqueous alkaline medium

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## Abstract

The kinetics of Os(VIII) catalysed oxidation of L-leucine by diperiodatoargentate(III) (DPA) in alkaline medium at 298 K and a constant ionic strength of  $0.60 \text{ mol dm}^{-3}$  was studied spectrophotometrically. The oxidation products in both the cases are pentanoic acid and Ag(I). The stoichiometry is, i.e., [L-leucine]:[DPA] = 1:2. The reaction is of first order in Os(VIII) and [DPA] and has less than unit order in both [L-leu] and [alkali]. The oxidation reaction in alkaline medium has been shown to proceed via a Os(VIII)–L-leucine complex, which further reacts with one molecule of MPA in a rate determining step followed by other fast steps to give the products. The main products were identified by spot test and spectral studies. The reaction constants involved in the different steps of the mechanism are calculated. The catalytic constant ( $K_C$ ) was also calculated for Os(VIII) catalysis at different temperatures. From the plots of  $\log K_C$  versus  $1/T$ , values of activation parameters with respect to the catalyst have been evaluated. The activation parameters with respect to slow step of the mechanism are computed and discussed and thermodynamic quantities are also determined. The active species of catalyst and oxidant have been identified.

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**Keywords:** L-leucine; Os(VIII) catalysis; Diperiodatoargentate(III); Oxidation; Kinetics

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## 1. Introduction

Amino acids act not only as the building blocks in protein synthesis but they also play a significant role in metabolism. Amino acids can undergo many types of reaction depending on whether a particular amino acid contains non-polar groups or polar substituents. The oxidation of amino acids is of interest as the oxidation products differ for different oxidants [1,2]. Thus, the study of amino acids becomes important because of their biological significance and selectivity towards the oxidant. L-leucine is an essential amino acid. It forms active sites of enzymes and helps in maintaining their proper conformation by keeping them in proper ionic states. So oxidation of L-leucine may help in understanding some aspects of enzyme kinetics.

Diperiodatoargentate(III) (DPA) is a powerful oxidizing agent in alkaline medium with the reduction potential [3a] 1.74 V. It is widely used as a volumetric reagent for the determination of various organic and inorganic species [4]. Jayaprakash Rao et al. [5] have used DPA as an oxidizing agent for the kinetics of oxidation of various organic substrates. They normally found that order with respect to both oxidant and substrate was unity and  $[\text{OH}^-]$  was found to enhance the rate of reaction. It was also observed that they did not arrive the possible active species of DPA in alkali and on the other hand they proposed mechanisms by generalizing the DPA as  $[\text{Ag}(\text{HL})\text{L}]^{(\alpha+1)-}$ . However, Kumar et al. [6] put an effort to give an evidence for the reactive form of DPA in the large scale of alkaline pH. In the present investigation, we have obtained the evidence for the reactive species for DPA in alkaline medium.

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 [7]. The role of osmium(VIII) as a catalyst in some redox reactions has been reviewed [8]. Although the mechanism of catalysis depends on the nature of the substrate, the oxidant and experimental conditions, it has been shown [9] 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 several complexes, different oxidation states of osmium, etc. The uncatalysed reaction of oxidation of L-leucine by DPA has been studied [10]. We have observed that osmium(VIII) catalyze the oxidation of L-leucine by DPA in alkaline medium in micro amounts. In order to understand the active species of oxidant and catalyst, and to propose the appropriate mechanism, the title reaction is investigated in detail. An understanding of mechanism allows chemistry to be interpreted and hence understood and predicted.

## 2. Experimental

### 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-leucine

(Sisco, Chem Ltd.) was prepared by dissolving an appropriate amount of recrystallised sample in double distilled water. The required concentration of L-leucine was used from its aqueous stock solution. The osmium(VIII) solution was prepared by dissolving  $\text{OsO}_4$ (VIII) oxide (Johnson Matthey) in  $0.50 \text{ mol dm}^{-3}$  NaOH. The concentration was ascertained [11] by determining the unreacted  $[\text{Fe}(\text{CN})_6]^{4-}$  with standard Ce(IV) solution in an acidic medium.  $\text{KNO}_3$  and KOH (BDH) were used to maintain ionic strength and alkalinity of the reaction, respectively. Aqueous solution of  $\text{AgNO}_3$  was used to study the product effect, Ag(I). A stock standard solution of  $\text{IO}_4^-$  was prepared by dissolving a known weight of  $\text{KIO}_4$  (Riedel-de Haen) in hot water and used after keeping for 24 h. Its concentration was ascertained iodometrically [12] at neutral pH maintained using phosphate buffer. The pH of the medium in the solution was measured by [ELICO (LI613)] pH meter.

### 2.2. Preparation of DPA

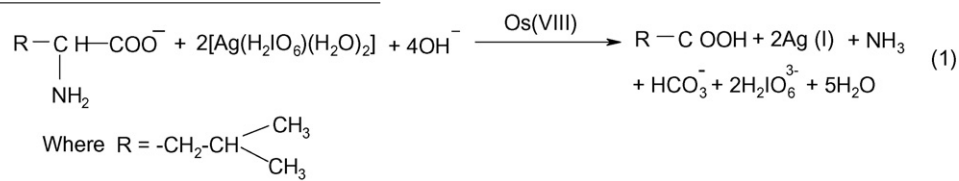
DPA was prepared by oxidizing Ag(I) in presence of  $\text{KIO}_4$  as described elsewhere [13]: the mixture of 28 g of KOH and 23 g of  $\text{KIO}_3$  in  $100 \text{ cm}^3$  of water along with 8.5 g  $\text{AgNO}_3$  was heated just to boiling and 20 g of  $\text{K}_2\text{S}_2\text{O}_8$  was added in several lots with stirring then allowed to cool. It was filtered through a medium porosity fritted glass filter and 40 g of NaOH was added slowly to the filtrate, whereupon a voluminous orange precipitate agglomerates. The precipitate is filtered as above and washed three to four times with cold water. The pure crystals were dissolved in  $50 \text{ cm}^3$  water and warmed to  $80^\circ\text{C}$  with constant stirring thereby some solid was dissolved to give a red solution. The resulting solution was filtered when it was hot and on cooling at room temperature, the orange crystals separated out and were recrystallised from water.

The complex was characterized from its UV spectrum, exhibited three peaks at 216, 255 and 362 nm. These spectral features were identical to those reported earlier for DPA [13]. The magnetic moment study revealed that the complex is diamagnetic. The compound prepared was analyzed [14] for silver and periodate by acidifying a solution of the material with HCl, recovering and weighing the AgCl for Ag and titrating the iodine liberated when excess KI was added to the filtrate for  $\text{IO}_4^-$ . The aqueous solution of DPA was used for the required [DPA] in the reaction mixture. During the kinetics a constant concentration, viz.  $1 \times 10^{-4} \text{ mol dm}^{-3}$  of  $\text{KIO}_4$  was used throughout the study unless otherwise stated. Thus, the possibility of oxidation of L-leucine by periodate was tested and found that there was no significant interference due to  $\text{KIO}_4$  under experimental condition. The effect of dissolved oxygen on the rate of reaction was checked by preparing the reaction mixture and following the reaction in an atmosphere of nitrogen. No significant difference between the results under nitrogen and in presence of air was observed.

### 2.3. Kinetic measurements

The kinetic measurements were performed on a Varian CARY 50 Bio UV-vis Spectrophotometer. The kinetics was followed

under pseudo first-order condition where  $[L\text{-leu}] > [DPA]$  at  $25 \pm 0.1^\circ\text{C}$ , unless specified. The reaction was initiated by mixing the DPA to L-leucine solution which also contained



required concentration of  $\text{KNO}_3$ ,  $\text{KOH}$ , catalyst  $\text{Os(VIII)}$  and  $\text{KIO}_4$ . The progress of reaction was followed spectrophotometrically at 360 nm by monitoring decrease in absorbance due to DPA with the molar absorptivity index, ' $\epsilon$ ' to be  $13,900 \pm 100 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ . It was verified that there is a negligible interference from other species present in the reaction mixture at this wavelength.

The pseudo first-order rate constants, ' $k_C$ ', were determined from the  $\log(\text{absorbance})$  versus time plots. The plots were linear up to 85% completion of reaction under the range of  $[\text{OH}^-]$  used. The orders for various species were determined from the slopes of plots of  $\log k_C$  versus respective concentration of species except for  $[\text{DPA}]$  in which non-variation of ' $k_C$ ' was observed as expected to the reaction condition. During the kinetics a constant concentration, viz.  $1.0 \times 10^{-4} \text{ mol dm}^{-3}$  of  $\text{KIO}_4$  was used throughout the study unless otherwise stated. Since periodate is present in excess in DPA, the possibility of oxidation of L-leucine by periodate in alkaline medium at  $25^\circ\text{C}$  was tested. The progress of the reaction was followed iodometrically. However, it was found that there was no significant reaction under the experimental conditions employed compared to the DPA oxidation of L-leucine. The total periodate concentration was calculated by considering the periodate present in the DPA solution and that additionally added.

In view of the modest concentration of alkali used in the reaction medium, attention was also directed to the effect of the reaction vessel surface on the kinetics. Use of polythene/acrylic wares and quartz or polyacrylate cells gave the same results, indicating that the surface does not have any significant effect on the reaction rates.

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, however fresh solutions were nevertheless used for carrying out each kinetic only.

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 programme.

### 3. Results and discussion

#### 3.1. Stoichiometry and product analysis

Different sets of reaction mixtures containing varying ratios of DPA to L-leucine in presence constant amount of  $\text{OH}^-$ ,  $\text{KNO}_3$  and  $\text{Os(VIII)}$ , were kept for 3 h in closed vessel under nitrogen atmosphere. The remaining concentration of DPA was estimated

by spectrophotometrically at 360 nm. The results indicate that two moles of DPA consumed one mole of L-leucine 2:1 stoichiometry as given in Eq. (1).

The main oxidation products were identified as pentanoic acid by spot test [15], ammonia by Nessler's reagent and the  $\text{CO}_2$  was qualitatively detected by bubbling nitrogen gas through the acidified reaction mixture and passing the liberated gas through tube containing limewater. The nature of the carboxylic acid was confirmed by the IR spectrum, which showed a carbonyl( $\text{C}=\text{O}$ ) stretch at  $1708 \text{ cm}^{-1}$  and a signal of  $3042 \text{ cm}^{-1}$  due to  $\text{O}-\text{H}$  stretching of the acid. The formation of free  $\text{Ag}^+$  in solution was detected by adding  $\text{KCl}$  solution to the reaction mixture, which produced white turbidity due to formation of  $\text{AgCl}$ . It was observed that pentanoic acid does not undergo further oxidation under the present kinetic conditions. The products obtained are similar to that obtained for the uncatalysed reaction.

#### 3.2. Reaction orders

As the diperiodatoargentate(III) oxidation of L-leucine in alkaline medium proceeds with a measurable rate in the absence of  $\text{Os(VIII)}$ , the catalysed reaction is understood to occur in parallel paths with contributions from both the catalysed and uncatalysed paths. Thus, the total rate constant ( $k_T$ ) is equal to the sum of the rate constants of the catalysed ( $k_C$ ) and uncatalysed ( $k_U$ ) reactions, so  $k_C = k_T - k_U$ . Hence the reaction orders have been determined from the slopes of  $\log k_C$  versus  $\log(\text{concentration})$  plots by varying the concentrations of L-leucine,  $\text{IO}_4^-$ ,  $\text{OH}^-$  and  $\text{Os(VIII)}$ , in turn, while keeping others constant. The DPA concentration was varied in the range of  $1.0 \times 10^{-5}$  to  $1.0 \times 10^{-4} \text{ mol dm}^{-3}$  and the linearity of the plots of  $\log(\text{absorbance})$  versus time up to 85% completion of the reaction indicates a reaction order of unity in  $[\text{DPA}]$ . This is also confirmed by varying of  $[\text{DPA}]$ , which did not result in any change in the pseudo first-order rate constants,  $k_C$  (Table 1  $\text{Os(VIII)}$ ). The L-leucine concentration was varied in the range  $5.0 \times 10^{-5}$  to  $5.0 \times 10^{-4} \text{ mol dm}^{-3}$  at  $25^\circ\text{C}$  while keeping other reactant concentrations and conditions constant. The  $k_C$  values increased with the increase in concentration of L-leucine indicating an apparent less than unit order dependence on  $[\text{L-leu}]$  (Table 1). The effect of alkali on the reaction has been studied in the range of  $0.04\text{--}0.40 \text{ mol dm}^{-3}$  at constant concentrations of L-leucine, DPA,  $\text{Os(VIII)}$  and a constant ionic strength of  $0.60 \text{ mol dm}^{-3}$ . The rate constants increased with increasing  $[\text{alkali}]$  and the order was found to be less than unity (Table 1).

#### 3.3. Effect of [periodate]

Periodate concentration was varied from  $8.0 \times 10^{-5}$  to  $8.0 \times 10^{-4}$  at constant  $[\text{DPA}]$ ,  $[\text{L-leu}]$ ,  $[\text{Os(VIII)}]$  and ionic

Table 1  
Effect of [DPA], [L-leu], [OH<sup>-</sup>] and [IO<sub>4</sub><sup>-</sup>] on the osmium(VIII) catalysed oxidation of L-leucine by DPA in alkaline medium at 25 °C, *I* = 0.60 mol dm<sup>-3</sup>

10 <sup>5</sup> [DPA] (mol dm <sup>-3</sup> )	10 <sup>4</sup> [L-leu] (mol dm <sup>-3</sup> )	[OH <sup>-</sup> ] (mol dm <sup>-3</sup> )	10 <sup>4</sup> [IO <sub>4</sub> <sup>-</sup> ] (mol dm <sup>-3</sup> )	10 <sup>6</sup> [Os(VIII)] (mol dm <sup>-3</sup> )	10 <sup>3</sup> <i>k</i> <sub>T</sub> (s <sup>-1</sup> )	10 <sup>4</sup> <i>k</i> <sub>U</sub> (s <sup>-1</sup> )	10 <sup>3</sup> <i>k</i> <sub>C</sub> (s <sup>-1</sup> )	
							Found	Calculated
1.0	2.0	0.2	1.0	5.0	8.7	8.8	7.8	7.6
3.0	2.0	0.2	1.0	5.0	8.5	8.9	7.6	7.6
5.0	2.0	0.2	1.0	5.0	8.6	8.9	7.7	7.6
8.0	2.0	0.2	1.0	5.0	8.5	8.8	7.7	7.6
10.0	2.0	0.2	1.0	5.0	8.6	8.7	7.7	7.6
3.0	0.5	0.2	1.0	5.0	4.1	1.4	4.0	3.8
3.0	1.0	0.2	1.0	5.0	6.3	5.6	5.7	5.7
3.0	2.0	0.2	1.0	5.0	8.6	8.9	7.7	7.6
3.0	3.0	0.2	1.0	5.0	10.0	11.1	8.9	8.5
3.0	5.0	0.2	1.0	5.0	11.0	15.2	9.4	9.4
3.0	2.0	0.04	1.0	5.0	3.5	2.1	3.3	3.3
3.0	2.0	0.1	1.0	5.0	6.0	5.2	5.5	5.6
3.0	2.0	0.2	1.0	5.0	8.6	8.9	7.7	7.6
3.0	2.0	0.3	1.0	5.0	9.0	10.2	8.0	8.2
3.0	2.0	0.4	1.0	5.0	10.4	14.8	8.9	8.7
3.0	2.0	0.2	0.8	5.0	10.0	8.7	9.1	9.1
3.0	2.0	0.2	1.0	5.0	8.6	8.9	7.7	7.6
3.0	2.0	0.2	3.0	5.0	6.6	8.4	5.7	5.6
3.0	2.0	0.2	6.0	5.0	4.7	8.1	3.6	3.5
3.0	2.0	0.2	8.0	5.0	4.0	7.7	3.1	3.2
3.0	2.0	0.2	1.0	1.0	2.1	8.9	1.2	1.1
3.0	2.0	0.2	1.0	3.0	5.4	8.9	4.5	4.5
3.0	2.0	0.2	1.0	5.0	8.6	8.9	7.7	7.6
3.0	2.0	0.2	1.0	8.0	9.8	8.9	8.9	8.8
3.0	2.0	0.2	1.0	10.1	13.0	8.9	12.1	12.0

strength. It was observed that the rate constants decreased by increasing [IO<sub>4</sub><sup>-</sup>] (Table 1).

### 3.4. Effect of added products

Initially added products, Ag(I), and pentanoic acid did not affect the rate of reaction.

### 3.5. Effect of ionic strength (*I*) and dielectric constant of the medium (*D*)

The addition of KNO<sub>3</sub>, to increase the ionic strength of the reaction, increased the rate of reaction at constant [DPA], [L-leu], [OH<sup>-</sup>], [IO<sub>4</sub><sup>-</sup>] and [Os(VIII)]; the plot of log *k*<sub>C</sub> versus  $\sqrt{I}$  was found to be linear with positive slope (Fig. 1).

Dielectric constant of the medium, '*D*' was varied by varying the *t*-butyl alcohol and water percentage. The decrease in dielectric constant of the reaction medium, increases the rate and the plot of log *k*<sub>C</sub> versus 1/*D* was linear with positive slope (Fig. 1).

### 3.6. Effect of temperature

The influence of temperature on the rate of reaction were studied at 25, 30, 35 and 40 °C. The rate constants (*k*), of the slow step of Scheme 1 were obtained from the slopes and the intercept of the plots of [Os(VIII)]/*k*<sub>C</sub> versus 1/[L-leu], [Os(VIII)]/*k*<sub>C</sub> versus 1/[OH] and [Os(VIII)]/*k*<sub>C</sub> versus [H<sub>3</sub>IO<sub>6</sub><sup>2-</sup>] at four different temperatures. The values are given in Table 2. 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 presented in Table 2.

### 3.7. Test for free radicals (polymerization study)

The intervention of free radicals was examined as follows, the reaction mixture, to which a known quantity of acrylonitrile scavenger has been added initially, was kept in an inert atmosphere for 1 h. Upon diluting the reaction mixture with methanol, precipitate resulted, suggesting there is participation of free radicals in the reaction.

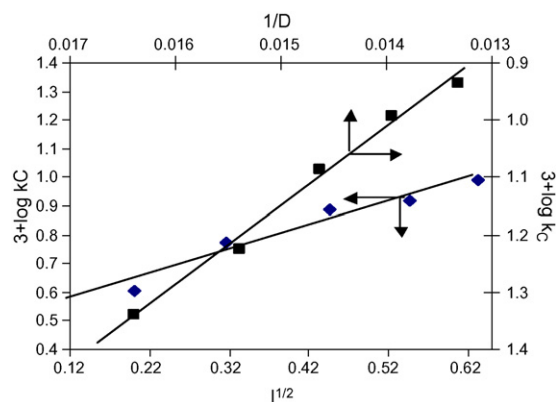
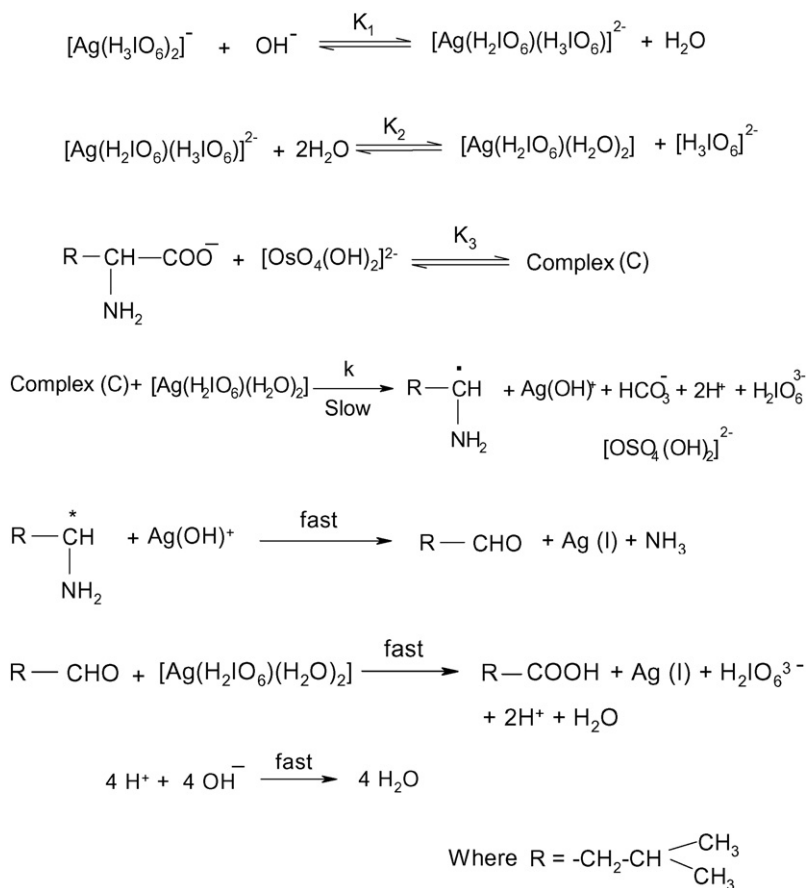


Fig. 1. Effect of ionic strength and dielectric constant of the medium on Os(VIII) catalyzed oxidation of L-leucine by diperiodatoargentate(III) at 25 °C.



Scheme 1. Detailed Scheme for the Os(VIII) catalysed oxidation of L-leucine by alkaline diperiodatoargentate(III).

### 3.8. Effect of [Os(VIII)]

The [Os(VIII)] concentrations was varied from  $1.0 \times 10^{-6}$  to  $1.0 \times 10^{-5} \text{ mol dm}^{-3}$  range, at constant concentration of diperiodatoargentate(III), L-leucine, alkali and ionic strength. The order in [Os(VIII)] was found to be unity from the linearity of the plot of  $\log k_C$  versus  $\log[\text{Os(VIII)}]$ .

### 3.9. Catalytic activity

It has been pointed out by Moelwyn-Hughes [16] that in presence of the catalyst, the uncatalysed and catalysed reactions proceed simultaneously, so that

$$k_T = k_U + K_C[\text{catalyst}]^x \quad (2)$$

Here  $k_T$  is the observed pseudo first-order rate constant in the presence [Os(VIII)] catalyst,  $k_U$  the pseudo first-order rate constant for the uncatalysed reaction,  $K_C$  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 for Os(VIII). Then the value of  $K_C$  is calculated using the equation,

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

The values of  $K_C$  were evaluated for Os(VIII) catalyst 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 3.

In the later period of 20th Century the kinetics of oxidation of various organic and inorganic substrates have been studied by Ag(III) species which may be due to its strong versatile nature of two electrons oxidant. Among the various species of Ag(III),  $\text{Ag}(\text{OH})_4^-$ , diperiodatoargentate(III) and ethylenebis (biguanide) (EBS), silver(III) are of maximum attention to the researchers due to their relative stability [17]. The stability of  $\text{Ag}(\text{OH})_4^-$  is very sensitive towards traces of dissolved oxygen and other impurities in the reaction medium whereupon it had not drawn much attention. However, the other two forms of Ag(III) [5,6,18] are considerably stable; the DPA is used in highly alkaline medium and EBS is used in highly acidic medium.

The literature survey [13] reveals that the water soluble diperiodatoargentate(III) (DPA) has a formula  $[\text{Ag}(\text{IO}_6)_2]^{7-}$  with  $dsp^2$  configuration of square planar structure, similar to diperiodatocopper(III) complex with two bidentate ligands, periodate to form a planar molecule. When the same molecule is used in alkaline medium, it is unlike to be existed as  $[\text{Ag}(\text{IO}_6)_2]^{7-}$  as periodate is known to be in various protonated forms [19]



Table 2  
Thermodynamic activation parameters for the osmium(VIII) catalysed oxidation of L-leucine by DPA in aqueous alkaline medium with respect to the slow step of Scheme 1

(A) Effect of temperature		(B) Activation Parameters (Scheme 1)	
Temperature (K)	$10^{-3}k$ ( $s^{-1}$ )	Parameters	Values
298	1.85	$E_a$ ( $\text{kJ mol}^{-1}$ )	$11.7 \pm 0.53$
303	1.93	$\Delta H^\ddagger$ ( $\text{kJ mol}^{-1}$ )	$9.2 \pm 0.42$
308	2.15	$\Delta S^\ddagger$ ( $\text{J K}^{-1} \text{mol}^{-1}$ )	$-151.1 \pm 7.0$
313	2.38	$\Delta G^\ddagger$ ( $\text{kJ mol}^{-1}$ )	$54.2 \pm 2.3$
		$\log A$	$5.3 \pm 0.22$

[DPA] =  $3.0 \times 10^{-5}$ ; [L-leu] =  $2.0 \times 10^{-4}$ ; [OH<sup>-</sup>] = 0.20; [Os(VIII)] =  $5.0 \times 10^{-6}$  mol dm<sup>-3</sup>; [IO<sub>4</sub><sup>-</sup>] =  $1.0 \times 10^{-4}$  mol dm<sup>-3</sup>

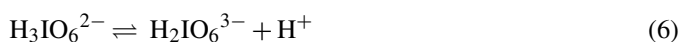
(C) Effect of temperature to calculate  $K_1$ ,  $K_2$  and  $K_3$  for the Os(VIII) catalyzed oxidation of L-leucine by diperiodatoargentate (III) in alkaline medium

Temperature (K)	$K_1$ ( $\text{dm}^3 \text{mol}^{-1}$ )	$K_2 \times 10^4$ ( $\text{mol dm}^{-3}$ )	$K_3 \times 10^{-3}$ ( $\text{dm}^3 \text{mol}^{-1}$ )
298	$0.13 \pm 0.006$	$2.8 \pm 0.12$	$1.39 \pm 0.05$
303	$0.28 \pm 0.01$	$2.1 \pm 0.10$	$2.47 \pm 0.10$
308	$0.45 \pm 0.02$	$1.6 \pm 0.06$	$3.79 \pm 0.14$
313	$0.58 \pm 0.025$	$1.0 \pm 0.04$	$4.97 \pm 0.20$

(D) Thermodynamic quantities using  $K_1$ ,  $K_2$  and  $K_3$

Thermodynamic quantities	Values from $K_1$	Values from $K_2$	Values from $K_3$
$\Delta H$ ( $\text{kJ mol}^{-1}$ )	$74.4 \pm 3.4$	$-50.7 \pm 2.2$	$65.8 \pm 2.0$
$\Delta S$ ( $\text{J K}^{-1} \text{mol}^{-1}$ )	$234.5 \pm 11.0$	$-239.9 \pm 11.2$	$301.5 \pm 12$
$\Delta G_{298}$ ( $\text{kJ mol}^{-1}$ )	$4.88 \pm 0.20$	$20.2 \pm 0.8$	$-23.6 \pm 1.0$

depending on pH of the solution as given in following multiple equilibria (4)–(6).



Periodic acid exists as  $\text{H}_5\text{IO}_6$  in acid medium and as  $\text{H}_4\text{IO}_6^-$  at pH 7. Thus, under the present alkaline conditions, the main species are expected to be  $\text{H}_3\text{IO}_6^{2-}$  and  $\text{H}_2\text{IO}_6^{3-}$ . At higher concentrations, periodate also tends to dimerise [3b]. On contrary, the authors [5] in their recent past studies have proposed the DPA as  $[\text{Ag}(\text{HL})_2]^{x-}$  in which 'L' is a periodate with uncertain

number of protons and 'HL' is a protonated periodate of uncertain number of protons. This can be ruled out by considering the alternative form [19] of  $\text{IO}_4^-$  at pH > 7 which is in the form  $\text{H}_3\text{IO}_6^{2-}$  or  $\text{H}_2\text{IO}_6^{3-}$ . Hence, DPA could be as  $[\text{Ag}(\text{H}_3\text{IO}_6)_2]^-$  or  $[\text{Ag}(\text{H}_2\text{IO}_6)_2]^{3-}$  in alkaline medium. Therefore, under the present condition, diperiodatoargentate(III), may be depicted as  $[\text{Ag}(\text{H}_3\text{IO}_6)_2]^-$ . The similar speciation of periodate in alkali was proposed [20] for diperiodatonickelate(IV).

### 3.10. Mechanism

Osmium(VIII) is known to form different complexes at different OH<sup>-</sup> [21] concentrations  $[\text{OsO}_4(\text{OH})_2]^{2-}$  and  $[\text{OsO}_5(\text{OH})]^{3-}$ . At higher concentration of OH<sup>-</sup>,  $[\text{OsO}_5(\text{OH})]^{3-}$  is significant. At lower concentrations of OH<sup>-</sup>, as employed in the present study, and since the rate of oxidation increased with increase in [OH<sup>-</sup>], it is reasonable that  $[\text{OsO}_4(\text{OH})_2]^{2-}$  was operative and its formation is important in the reaction. To explain the observed orders the following Scheme 1 is proposed for osmium(VIII) catalysed reaction.

In the prior equilibrium step 1, the [OH<sup>-</sup>] deprotonates the DPA to give a deprotonated diperiodatoargentate(III); in the second step displacement of a ligand, periodate takes place to give free periodate which is evidenced by decrease in the rate with increase in [periodate] (Table 1). It may be expected that lower Ag(III) periodate species such as MPA is more important in the reaction than the DPA. The inverse fractional order in  $[\text{H}_3\text{IO}_6]^{2-}$  might also be due to this reason. In the pre rate determining stage, the Os(VIII) species combines with a molecule of anionic species of L-leu to give an intermediate complex (C), which further reacts with one mole of MPA in a rate determining step

Table 3  
Values of catalytic constant ( $K_C$ ) at different temperatures and activation parameters calculated using  $K_C$  values

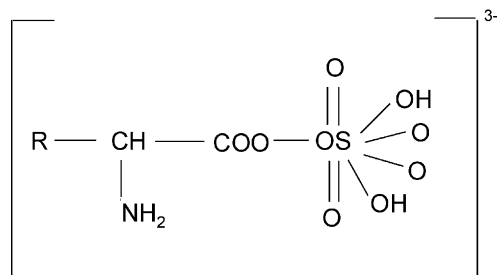
Temperature (K)	$10^{-2}K_C$ Ru(III) <sup>a</sup>	$10^{-2}K_C$ Os(VIII)
298	3.64	12.1
303	4.12	13.0
308	4.61	13.9
313	5.19	14.6
$E_a$ ( $\text{kJ mol}^{-1}$ )	18.1	9.64
$\Delta H^\ddagger$ ( $\text{kJ mol}^{-1}$ )	15.7	7.16
$\Delta S^\ddagger$ ( $\text{J K}^{-1} \text{mol}^{-1}$ )	-143.0	-161.7
$\Delta G^\ddagger$ ( $\text{kJ mol}^{-1}$ )	58.3	55.3
$\log A$	5.75	4.77

[DPA] =  $3.0 \times 10^{-5}$ ; [L-leu] =  $2.0 \times 10^{-4}$ ; [OH<sup>-</sup>] = 0.20 mol dm<sup>-3</sup>; [IO<sub>4</sub><sup>-</sup>] =  $1.0 \times 10^{-4}$  mol dm<sup>-3</sup>;  $I = 0.60$  mol dm<sup>-3</sup>; [Os(VIII)] =  $5.0 \times 10^{-6}$  mol dm<sup>-3</sup>; [Ru(III)] =  $5.0 \times 10^{-6}$  mol dm<sup>-3</sup>.

<sup>a</sup> From ref. [26].

to give free radical derived from L-leucine and regeneration of catalyst, osmium(VIII). This free radical derived from L-leucine further reacts with another molecule of MPA species in further fast step to give the products as given in Scheme 1.

The probable structure of the complex (C) is given below:



Spectroscopic evidence for the complex formation between catalyst and substrate was obtained from UV–vis spectra of L-leucine ( $2.0 \times 10^{-4}$ ), Os(VIII) ( $5.0 \times 10^{-6}$ ,  $[\text{OH}^-] = 0.2 \text{ mol dm}^{-3}$ ) and mixture of both. A bathochromic shift of about 4 nm from 436 to 440 nm in the spectra of Os(VIII) was observed. However, the Michelis–Menten plot proved the complex formation between catalyst and reductant, which explains less than unit order in [L-leu]. The rate law (8) for Scheme 1 could be derived as,

$$\text{rate} = \frac{-d[\text{DPA}]}{dt} = \frac{kK_1K_2K_3[\text{DPA}][\text{L-leu}][\text{OH}^-][\text{Os(VIII)}]}{[\text{H}_3\text{IO}_6^{2-}] + K_1[\text{OH}^-][\text{H}_3\text{IO}_6^{2-}] + K_1K_2[\text{OH}^-] + K_1K_2K_3[\text{OH}^-][\text{L-leu}] + K_3[\text{H}_3\text{IO}_6^{2-}][\text{L-leu}] + K_1K_3[\text{L-leu}][\text{OH}^-][\text{H}_3\text{IO}_6^{2-}]} \quad (7)$$

The terms  $K_3[\text{H}_3\text{IO}_6^{2-}][\text{L-leu}]$  and  $K_1K_3[\text{L-leu}][\text{OH}^-][\text{H}_3\text{IO}_6^{2-}]$  of denominator of Eq. (7) can be neglected in the view of low concentrations of L-leucine and Periodate used in study. Therefore, Eq. (7) becomes

$$\frac{\text{rate}}{[\text{DPA}]} = k_C = k_T - k_U = \frac{kK_1K_2K_3[\text{L-leu}][\text{OH}^-][\text{Os(VIII)}]}{[\text{H}_3\text{IO}_6^{2-}] + K_1[\text{OH}^-][\text{H}_3\text{IO}_6^{2-}] + K_1K_2[\text{OH}^-] + K_1K_2K_3[\text{OH}^-][\text{L-leu}]} \quad (8)$$

Eq. (8) can be rearranged to Eq. (9), which is suitable for verification.

$$\frac{[\text{Os(VIII)}]}{k_C} = \frac{[\text{H}_3\text{IO}_6^{2-}]}{kK_1K_2K_3[\text{L-leu}][\text{OH}^-]} + \frac{[\text{H}_3\text{IO}_6^{2-}]}{kK_2K_3[\text{L-leu}]} + \frac{1}{kK_3[\text{L-leu}]} + \frac{1}{k} \quad (9)$$

According to Eq (9), the plots of  $[\text{Os(VIII)}]/k_C$  versus  $[\text{H}_3\text{IO}_6^{2-}]$ ,  $[\text{Os(VIII)}]/k_C$  versus  $1/[\text{OH}^-]$  and  $[\text{Os(VIII)}]/k_C$  versus  $1/[\text{L-leu}]$  were linear (Fig. 2). From the intercepts and slopes of such plots, the reaction constants  $K_1$ ,  $K_2$ ,  $K_3$  and  $k$  were calculated as  $(0.13 \pm 0.006) \text{ dm}^3 \text{ mol}^{-1}$ ,  $(2.8 \pm 0.10) \times 10^{-4} \text{ mol dm}^{-3}$ ,  $(1.39 \pm 0.05) \times 10^3 \text{ dm}^3 \text{ mol}^{-1}$ ,  $(1.85 \pm 0.08) \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ , respectively. These constants were used to calculate the rate constants and compared with the experimental  $k_C$  values and found to be in reasonable agreement with each other, which fortifies the Scheme 1. The equilibrium constant  $K_1$  is far greater than  $K_2$  which may be

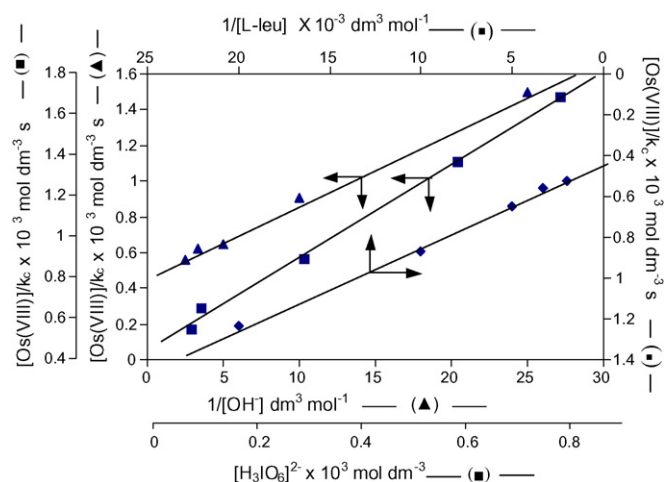


Fig. 2. Verification of rate law (9) of Os(VIII) catalyzed oxidation of L-leucine by diperioatoargentate(III) at 25 °C.

attributed to the greater tendency of DPA to under go deprotonation compared to the formation of hydrolysed species in alkaline medium.

The thermodynamic quantities for the different equilibrium steps, in Scheme 1 can be evaluated as follows. The L-leucine and hydroxide ion concentrations (Table 1) were varied at different temperatures. The plots of  $[\text{Os(VIII)}]/k_C$  versus  $1/[\text{L-leu}]$  ( $r \geq 0.9988$ ,  $S \leq 0.00132$ ),  $[\text{Os(VIII)}]/k_C$  ver-

sus  $[\text{H}_3\text{IO}_6^{2-}]$  ( $r \geq 0.9993$ ,  $S \leq 0.00122$ ),  $[\text{Os(VIII)}]/k_C$  versus  $1/[\text{OH}^-]$  ( $r \geq 0.9996$ ,  $S \leq 0.00087$ ) should be linear as shown in Fig. 2. From the slopes and intercepts, the values of  $K_1$  are calculated at different temperatures. A van't Hoff's plot was made for the variation of  $K_1$  with temperature [i.e.,  $\log K_1$  versus  $1/T$  ( $r \geq 0.9984$ ,  $S \leq 0.1105$ )] and the values of the enthalpy of reaction  $\Delta H$ , entropy of reaction  $\Delta S$  and free energy of reaction  $\Delta G$ , were calculated. These values are also given in Table 2. 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 the rate determining step is fairly slow and involves a high activation energy [22]. In the same manner,  $K_2$  and  $K_3$  values were calculated at different temperatures and the corresponding values of thermodynamic quantities are given in Table 2.

The increase in the rate, with increasing ionic strength, is in the favor of a reaction between opposite charged species of

reactants, as presented in Scheme 1 of the proposed mechanism. The effect of solvent on the reaction rate is described in detail in the literature [23]. For the limiting case of a zero angle approach between two dipoles or anion-dipole system, Amis [23] has shown that a plot of  $\log k_C$  versus  $1/D$  gives a straight line, with a negative slope for a reaction between a negative ion and a dipole or two dipoles and with appositive slope for positive ion and dipole interaction. In the present study, the plot observed had a negative slope, which is in the right direction as shown in Scheme 1.

The negative value of  $\Delta S^\ddagger$  suggests that the intermediate complex is more ordered than the reactants [24]. 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 [25]. The activation parameters evaluated for the catalysed and uncatalysed reaction explain the catalytic effect on the reaction. The catalyst Os(VIII) form the complex (C) with substrate which enhances the reducing property of the substrate than that without catalyst. Further, the catalyst Os(VIII) modifies the reaction path by lowering the energy of activation.

The activation parameters for Ru(III) catalysed oxidation L-leucine by DPA is reported earlier [26]. The values of  $\Delta H^\ddagger$ ,  $\Delta S^\ddagger$ ,  $\Delta G^\ddagger$  and rate constant ( $k$ ) indicate the order of reactivity of the catalysts as Ru(III) < Os(VIII) for the oxidation of L-leucine by DPA. The Os(VIII) catalysed reaction, however, is reasonably fast in view of readiness of Os(VIII) to act across the –COO group and the Ru(III) catalysed reaction is slower probably owing to the less ability of the Ru(III) to act across the –COO group.

#### 4. Conclusion

The Os(VIII) catalysed oxidation of L-leucine by diperiodatoargentate(III) was studied. Oxidation products were identified. Among the various species of Ag(III) in alkaline medium, in earlier reports the diperiodatoargentate(III) was the active species, whereas monoperiodatoargentate(III) itself is considered to be the active species for the title reaction. Active species of Os(VIII) is  $[\text{OsO}_4(\text{OH})_2]^{2-}$ . Activation parameters were evaluated for both catalysed and uncatalysed reactions. Catalytic constants and the activation parameters with reference to catalyst were also computed. Catalytic efficiency is Os(VIII) > Ru(III).

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