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Osmium(VIII) Catalyzed Oxidation of DL-Ornithine Monohydrochloride by a New Oxidant, Diperiodatoargentate(III) in Aqueous Alkaline Medium

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Osmium(VIII) Catalyzed Oxidation of DL-Ornithine Monohydrochloride by a New Oxidant, Diperiodatoargentate(III) in Aqueous Alkaline Medium

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The kinetics of osmium(VIII) (Os(VIII)) catalyzed oxidation of DL-ornithine monohydrochloride (OMH) by diperiodatoargentate(III) (DPA) in alkaline medium at 298 K and a constant ionic strength of 0.10 mol dm⁻³ was studied spectrophotometrically. The stoichiometry is, i.e., [OMH]:[DPA] = 1:2. The main products were identified by spot tests, IR, ¹H NMR, GC-MS spectral studies. A suitable mechanism is proposed. 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. The active species of catalyst and oxidant have been identified.

Keywords DL-Ornithine monohydrochloride, diperiodatoargentate (III), kinetics, Os(VIII) catalysis, oxidation

1. INTRODUCTION

Amino acids act not only as the building blocks in protein syntheses but they also play a significant role in metabolism and have been oxidized by a variety of oxidizing agents.^[1] The study of the oxidation of amino acids is of interest because of their biological significance and selectivity towards the oxidant to yield the different products.^[2] DL-Ornithine monohydrochloride $[(\pm)-2, 5$ -Diaminopentanoic acid monohydrochloride] (OMH) is the most potent amino acid studied for stimulating the production of release of growth hormone in the body from the pituitary gland, which in turn helps with fat metabolism. It is further required for a properly functioning immune system and liver, and assists in ammonia detoxification and liver rejuvenation. It is also of use in healing and repairing skin and tissue, and is found in both these body parts. Ornithine has the ability to regenerate the thymus gland, liver, and heart tissue, enhance muscle growth, and increase immune system function.^[3]

Diperiodatoargentate(III) (DPA) is a powerful oxidizing agent in alkaline medium with the reduction potential,^[4]1.74 V. It is widely used as a volumetric reagent for the determination of various organic and inorganic species.^[5,6] Jayaprakash Rao et al.^[7,8] have used DPA as an oxidizing agent for the kinetics of oxidation of various substrates. They normally found that order with respect to both oxidant and substrate was unity and 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; on the other hand, they proposed mechanisms by generalizing the DPA as $[Ag(HL)L]^{(x+1)-}$. However, Kumar et al.^[9-11] put in an effort to give evidence for the reactive form of DPA in the large scale of alkaline pH. When the Ag(III) species are involved, it would be interesting to know which of the species is the active oxidant. In the present investigation, we have obtained the evidence for the reactive species for the DPA in alkaline medium. The DPA is a metal complex with Ag in 3+ oxidation state like Cu³⁺ in DPC and Fe³⁺ in hemoglobin.

Transition metals are known to catalyze many oxidationreduction reactions since they involve multiple oxidation states. In recent years, the use of transition metal ions such as osmium, ruthenium, palladium, chromium and iridium either alone, as binary mixtures, or as catalysts in various redox processes has attracted considerable interest.^[12] The role of osmium(VIII) as a catalyst in some redox reactions has been reviewed.^[13] Although the mechanism of catalysis depends on the nature of the substrate, oxidant and on experimental conditions, it has been shown [14] 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. In an earlier report,^[15] it has been observed that Os(VIII) forms a complex substrate, which gets oxidized by the oxidant to form a Os(VII) intermediate followed by the rapid reaction of Os(VII) with one more mole of oxidant to regenerate Os(VIII). In another report,^[16] it has been observed that oxidantsubstrate complex reacts with Os(VIII) to form Os(VI), which reacts with oxidant in a fast step to regenerate Os(VIII). In some other reports,^[17] it is observed that Os(VIII) forms complex with substrate, which gets oxidized by the oxidant with the regeneration of Os(VIII). Hence, understanding the role of Os(VIII)

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in catalyzed reactions is important. Osmium(VIII) catalysis in redox reactions involves several complexes, different oxidation states of osmium, etc. We have observed that osmium(VIII) catalyzes the oxidation of DL-ornithine monohydrochloride by DPA in alkaline medium in micro amounts.

Literature survey reveals that there is no report on osmium(VIII) catalyzed oxidation of DL-ornithine monohydrochloride by DPA in alkaline medium. In earlier reports of DPA oxidation,^[18] the order in [OH⁻] was found to be less than unity and periodate had a retarding effect in most of the reactions, and monoperiodatoargentate(III) (MPA) was considered to be active species. However, in the present study, we have observed entirely different kinetic observations, and diperiodatoargentate(III) (DPA) itself is found to be an active form of oxidant. In order to understand the active species of oxidant and catalyst, to compute the activity of the catalyst and to propose the appropriate mechanism, the title reaction is investigated in detail. An understanding of the mechanism allows the chemistry to be interpreted, understood and predicted.

2. EXPERIMENTAL

2.1. Materials and Reagents

All reagents used were of analytical reagent grade, and millipore water was used throughout the work. A solution of DLornithine monohydrochloride (HiMedia Laboratories) was prepared by dissolving an appropriate amount of recrystallised sample in millipore water. The purity of DL-ornithine monohydrochloride sample was checked by comparing its melting point, 232° C with literature data [literature melting point = 233°C]. The required concentration of OMH was obtained from its stock solution. The osmium(VIII) solution was prepared by dissolving OsO₄ (Johnson Matthey) in 0.50 mol dm⁻³ NaOH. The concentration was ascertained ^[19] by determining the unreacted $[Fe(CN)_6]^{4-}$ with standard Ce(IV) solution in an acidic medium. A stock standard solution of IO₄⁻ was prepared by dissolving a known weight of KIO₄ (S.D. fine) in hot water, and used after keeping for 24 h to complete the equilibrium. Its concentration was ascertained by iodometrically ^[20] at neutral pH maintained using phosphate buffer. The pH of the medium in the solution was measured by Elico model (LI 120) pH meter. KNO₃ (AR) and KOH (BDH) were used to maintain ionic strength and alkalinity of the reaction, respectively. Aqueous solution of AgNO₃ was used to study the product effect, Ag(I). t-Butyl alcohol (S.D. Fine Chem.) was used to study the dielectric constant of the reaction medium.

2.2. Preparation of DPA

DPA was prepared by oxidizing Ag(I) in presence of KIO_4 as described elsewhere.^[21] The mixture of 28 g of KOH and 23 g of KIO_4 in 100 cm³ of water along with 8.5 g AgNO₃ was heated just to boiling and 20 g of $K_2S_2O_8$ was added in several lots with stirring and 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 and washed three to four times with cold water. The pure crystals were dissolved in 50 cm³ water and warmed to 80° 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 recrystallized from water.

The complex was characterized from its UV spectrum, which exhibited three peaks at 216, 255 and 362 nm. These spectral features were identical to those reported earlier for DPA.^[20] The magnetic moment study revealed that the complex is diamagnetic. The compound prepared was analyzed ^[21] 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 of KI was added to the filtrate for IO_4^- . The stock solution of DPA was used for the required [DPA] solution in the reaction mixture.

2.3. Instruments Used

- (i) For kinetic measurements, a Peltier accessory (temperature control) attached to Varian CARY 50 Bio UV-visible 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.
- (iii) For pH measurements ELICO pH meter model LI 120 was used.

2.4. Kinetic Measurements

The kinetic measurements were performed on a Varian CARY 50 Bio UV-visible spectrophotometer. The kinetics was followed under pseudo first-order condition where [OMH] > [DPA] at $25 \pm 0.1^{\circ}$ C, unless specified. The reaction was initiated by mixing the DPA to DL-ornithine monohydrochloride solution, which also contained required concentrations of KNO₃, KOH, catalyst Os(VIII) and KIO₄. The progress of reaction was followed spectrophotometrically at 360 nm by monitoring decrease in absorbance due to DPA with the molar absorbancy index, ' ε ' to be 13900 \pm 100 dm³ mol⁻¹ cm⁻¹. The spectral changes during the chemical reaction for the standard condition at 298 K are shown in Figure 1.

It is evident from the figure that the concentration of DPA decreases at 360 nm. 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, $k_{\rm C}$, were determined from the log (absorbance) *versus* time plots. The plots were linear up to 85% completion of reaction under the range of



FIG. 1. Spectroscopic changes occurring in the oxidation of DL-ornithine monohydrochloride by alkaline DPA at 25 °C, $[DPA] = 5.0 \times 10^{-5}$, $[OMH] = 5.0 \times 10^{-4}$, $[OH^-] = 0.08$, $[IO_4^-] = 5.0 \times 10^{-5}$, $[Os] = 5.0 \times 10^{-6}$ and I = 0.10 mol dm⁻³ with scanning time of: (1) 1.0, (2) 2.0, (3) 3.0, (4) 4.0, (5) 5.0 and (6) 6.0 min

[OH⁻] used. The orders for various species were determined from the slopes of plots of log $k_{\rm C}$ versus respective concentration of species except for [DPA] in which non-variation of ' $k_{\rm C}$ ' was observed as expected to the reaction condition. During the kinetics a constant concentration, viz. 5.0×10^{-5} mol dm⁻³ of KIO₄ was used throughout the study unless otherwise stated. Since periodate is present in excess in DPA, the possibility of oxidation of DL-ornithine monohydrochloride by periodate in alkaline medium at 25°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 DL-ornithine monohydrochloride. The total periodate concentration was calculated by considering the periodate present in the DPA solution and that was 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 did 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 of-fice Excel—2003 program.

3. RESULTS

3.1. Stoichiometry and Product Analysis

Different sets of reaction mixtures containing varying ratios of DPA to DL-ornithine monohydrochloride in presence of constant amount of OH^- , Os(VIII) and KNO_3 , were kept for 3 hours in a closed vessel under nitrogen atmosphere. The remaining concentration of DPA was estimated spectrophotometrically at 360 nm. The results indicated 1:2 stoichiometry (OMH:DPA), as given in Scheme 1.

The main oxidation product was identified as 4-aminobutyric acid. The product was extracted with ether and recrystallized from aqueous alcohol. It was characterized by FT-IR, GC-MS and ¹H NMR spectral studies.

The presence of carboxylic acid was confirmed by IR spectroscopy,^[22] which showed >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 N-H stretching at 3427 cm⁻¹ indicating the presence of -NH₂ group in the product. 4-aminobutyric acid was further characterized by ¹H NMR spectrum (CDCl₃) two triplet at 2.31 δ (a) and 2.69 δ (c) and 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 were vanished on adding D₂O.

Further, the product was subjected to GC-MS spectral analysis. GC-MS data was obtained on a QP-2010S Shimadzu gas chromatograph mass spectrometer. The mass spectrum showed a molecular ion peak at 103 amu confirming 4-aminobutyric acid product (Figure 2).

All other peaks observed in GC-MS can be interpreted in accordance with the observed structure of the 4-aminobutyric acid.

The by-products were identified as ammonia by Nessler's reagent ^[23] and the CO_2 was qualitatively detected by bubbling nitrogen gas through the acidified reaction mixture and passing the liberated gas through the tube containing limewater. The formation of free Ag⁺ in solution was detected by adding KCl solution to the reaction mixture, which produced white turbidity due to the formation of AgCl. It was observed that 4-aminobutyric acid does not undergo further oxidation under the present kinetic conditions.

$$NH_{2} \xrightarrow{COO^{-} + 2 [Ag(H_{3}IO_{6})_{2}]^{-} + 3[OH^{-}]} \xrightarrow{Os(VIII)} NH_{2} \xrightarrow{b} + NH_{3} + 2Ag(I) + 4H_{3}IO_{6}^{2^{-}} + CO_{2} + H_{2}O_{1} + H_{2}O_{1}$$

SCH. 1. Stoichiometry of Os(VIII) catalyzed oxidation of DL-ornithine monohydrochloride by alkaline diperiodatoargentate(III).



FIG. 2. GC-mass spectrum of 4-aminobutyric acid with its molecular ion peak at 103 m/z.

3.2. Reaction Orders

As the diperiodatoargentate(III) oxidation of DL-ornithine monohydrochloride 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 $(k_{\rm T})$ is equal to the sum 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 $\log k_{\rm C}$ versus \log (concentration) plots by varying the concentrations of OMH, IO_4^- , OH⁻ and Os(VIII), in turn, while keeping others constant. The uncatalyzed reaction was followed under the condition, $[DPA] = 5.0 \times 10^{-5}$, $[OMH] = 5.0 \times 10^{-4}$, $[OH^{-}] = 0.08$, $[IO_{4}^{-}] = 5.0 \times 10^{-5}$, $I = 0.10 / \text{ mol dm}^{-3}$. The rate constant of uncatalyzed reaction $(k_{\rm U})$ was obtained by the plot of log (absorbance) versus time by following the progress of the reaction spectrophotometrically at 360 nm.

3.3. Effect of [diperiodatoargentate(III)]

The DPA concentration was varied in the range of 1.0×10^{-5} to 1.0×10^{-4} mol dm⁻³ and the linearity of the plots of log (absorbance) *versus* time up to 85% completion of the reaction ($r \ge 0.9858$, $S \le 0.016$) indicates a reaction order of unity in [DPA]. This is also confirmed by varying of [DPA], which did not result in any change in the pseudo first-order rate constants, $k_{\rm C}$ (Table 1).

3.4. Effect of [DL-ornithine monohydrochloride]

The DL-ornithine monohydrochloride concentration was varied in the range of 7.0×10^{-5} to 7.0×10^{-4} mol dm⁻³ at 25°C while keeping other reactant concentrations and conditions constant. The $k_{\rm C}$ values increased with the increase in concentration of DL-ornithine monohydrochloride indicating an apparent less than unit order dependence on [OMH]

($r \ge 0.9996$, $S \le 0.009$) under the concentrations studied (Table 1). This is also confirmed in the plots of $k_{\rm C}$ versus [OMH]^{0.79} which is linear rather than the direct plot of $k_{\rm C}$ versus [OMH] (Figure 3).

3.5. Effect of [Alkali]

The effect of alkali on the reaction has been studied in the range of 0.01 to 0.10 mol dm⁻³ at constant concentrations of OMH, DPA, Os(VIII) and a constant ionic strength of 0.10 mol dm⁻³. The rate constants decreased with increasing [alkali] and the order was found to be negative fractional order i.e., -0.33 (Table 1) (r \ge 0.9948, $S \le$ 0.007).



FIG. 3. Plot of $k_{\rm C}$ versus [OMH]^{0.79} and $k_{\rm C}$ versus [OMH] (conditions as in Table 1).

TABLE 1

Effect of variation of [DPA], [OMH], [OH⁻], $[IO_4^-]$ and [Os(VIII)] on the osmium(VIII) catalyzed oxidation of DL-ornithine monohydrochloride by diperiodatoargentate(III) in aqueous alkaline medium at 25°C and I = 0.10 mol dm⁻³

$\overline{\text{[DPA]} \times 10^5}$ (mol dm ⁻³)	$\begin{array}{c} [\text{OMH}] \times 10^4 \\ (\text{mol dm}^{-3}) \end{array}$	$\begin{array}{c} [OH^-]\times 10^1 \\ (mol \ dm^{-3}) \end{array}$	$[IO_4^-] \times 10^5$ (mol dm ⁻³)	$\begin{array}{c} [Os(VIII)] \times 10^6 \\ (mol \ dm^{-3}) \end{array}$	$\frac{k_{\rm T} \times 10^2}{({\rm s}^{-1})}$	$\frac{k_{\rm U} \times 10^3}{({\rm s}^{-1})}$	$k_{\rm C} \times$ Found	$10^{2}(s^{-1})$ Calculated
1.0	5.0	0.8	5.0	3.0	1.85	2.04	1.65	1.75
3.0	5.0	0.8	5.0	3.0	1.82	1.97	1.63	1.75
5.0	5.0	0.8	5.0	3.0	2.06	2.19	1.84	1.75
7.0	5.0	0.8	5.0	3.0	1.99	2.23	1.77	1.75
10.0	5.0	0.8	5.0	3.0	1.94	2.16	1.72	1.75
5.0	0.7	0.8	5.0	3.0	0.39	0.41	0.35	0.35
5.0	1.0	0.8	5.0	3.0	0.54	0.57	0.48	0.48
5.0	3.0	0.8	5.0	3.0	1.36	1.49	1.22	1.22
5.0	5.0	0.8	5.0	3.0	2.06	2.19	1.84	1.75
5.0	7.0	0.8	5.0	3.0	2.29	2.57	2.04	2.15
5.0	5.0	0.1	5.0	3.0	3.86	4.11	3.45	3.27
5.0	5.0	0.2	5.0	3.0	3.36	3.58	3.00	2.91
5.0	5.0	0.4	5.0	3.0	2.65	2.82	2.37	2.38
5.0	5.0	0.8	5.0	3.0	2.06	2.19	1.84	1.75
5.0	5.0	1.0	5.0	3.0	1.83	1.99	1.68	1.54
5.0	5.0	0.8	1.0	3.0	2.09	2.25	1.87	1.75
5.0	5.0	0.8	3.0	3.0	1.83	1.94	1.63	1.75
5.0	5.0	0.8	5.0	3.0	2.06	2.19	1.84	1.75
5.0	5.0	0.8	7.0	3.0	2.09	2.22	1.86	1.75
5.0	5.0	0.8	10.0	3.0	2.06	2.12	1.85	1.75
5.0	5.0	0.8	5.0	1.0	0.56	2.19	0.34	0.35
5.0	5.0	0.8	5.0	3.0	1.23	2.19	1.01	1.05
5.0	5.0	0.8	5.0	5.0	2.06	2.19	1.84	1.75
5.0	5.0	0.8	5.0	8.0	3.15	2.19	2.93	2.79
5.0	5.0	0.8	5.0	10.0	3.89	2.19	3.67	3.49

3.6. Effect of [Periodate]

Periodate concentration was varied from 1.0×10^{-5} to 1.0×10^{-4} at constant [DPA], [OMH], [OH⁻], [Os(VIII)] and ionic strength. It was observed that the added periodate had no effect on the reaction (Table 1).

3.7. Effect of [Os(VIII)]

The [Os(VIII)] concentration was varied from 1.0×10^{-6} to 1.0×10^{-5} mol dm⁻³ range, at constant concentrations of diperiodatoargentate(III), DL-ornithine monohydrochloride, al-kali and ionic strength. The order in [Os(VIII)] was found to be unity from the linearity of the plot of $k_{\rm C}$ versus [Os(VIII)] (Table 1) (Figure 4) ($r \ge 0.9994$, $S \le 0.019$).

3.8. Effect of Ionic Strength (1) and Dielectric Constant of the Medium (D)

The addition of KNO₃ at constant [DPA], [Os(VIII)], [OMH], $[OH^-]$ and $[IO_4^-]$ was found that increasing ionic strength had no significant effect on the rate of the reaction.







SCH. 2. Detailed scheme for the Os(VIII) catalyzed oxidation of DL-ornithine monohydrochloride by alkaline diperiodatoargentate(III)

Varying the t-butyl alcohol and water percentage varied dielectric constant of the medium, 'D'. The D values were calculated from the equation $D = D_w V_w + D_B V_B$, where D_w and D_B are dielectric constants of pure water and t-butyl alcohol, respectively, and V_w and V_B are the volume fractions of components water and t-butyl alcohol, respectively, in the total mixture. There was no effect of dielectric constant on the rate of reaction.

3.9. Effect of Initially Added Products

Initially added products, Ag(I), 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 =
$$k_{\rm C}$$
 [DPA]^{1.0} [OMH]^{0.79} [OH⁻]^{-0.33} [Os(VIII)]^{1.0}

3.10. 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 hour. Upon diluting the reaction mixture with methanol, precipitate resulted, suggesting there is participation of free radicals in the reaction. The blank experiments of either DPA or DL-ornithine alone with acrylonitrile did not induce any polymerization under the same condition 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.^[24]

3.11. Effect of Temperature (T)

The influence of temperature on the rate of reaction was studied at 15, 25, 35 and 45°C. The rate constants (*k*), of the slow step of Scheme 2 were obtained from the slopes and the intercept of the plots of $[Os(VIII)]/k_C$ versus 1/[OMH] and $[Os(VIII)]/k_C$ versus $[OH^-]$ 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.

3.12. Catalytic Activity

It has been pointed out by Moelwyn- Hughes ^[25] that in presence of the catalyst, the uncatalyzed and catalyzed reactions proceed simultaneously, so that

$$k_{\rm T} = k_{\rm U} + K_{\rm C} \, [\text{catalyst}]^{\times}$$
[1]

Here $k_{\rm T}$ is the observed pseudo first-order rate constant in the presence Os(VIII) catalyst, $k_{\rm U}$ the pseudo first-order rate constant for the uncatalyzed reaction, $K_{\rm C}$ the catalytic constant and 'x' the order of the reaction with respect to [Os(VIII)]. In the

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TABLE 2

Activation parameters and thermodynamic quantities for the osmium(VIII) catalyzed oxidation of DL-ornithine monohydrochloride by diperiodatoargentate(III) in aqueous alkaline medium with respect to the slow step of Scheme 2: (A) Effect of temperature, (B) Activation parameters (Scheme 2), (C) Effect of temperature to calculate K_1 and K_2 for the Os(VIII) catalyzed oxidation of DL-ornithine monohydrochloride by diperiodatoargentate(III) in alkaline medium, (D) Thermodynamic quantities using K_1 and K_2

(A) Temperature (K)	$k \times 10^{-4} (\mathrm{dm^3 \ mol^{-1} s^{-1}})$			
288	1.33			
298	2.18			
308	3.98			
318	4.95			
(B) Parameters	Values			
$E_a(\text{k J mol}^{-1})$	34.6			
$\Delta H^{\#}$ (k J mol ⁻¹)	32.2			
$\Delta S^{\#}(J \text{ K}^{-1} \text{ mol}^{-1})$	-53.8			
$\Delta G^{\#}$ (k J mol ⁻¹)	48.2			
$\log A$	10.4			
(C) Temperature (K)	$K_1 x \ 10^1 (\text{mol dm}^{-3})$	$K_2 \times 10^{-3} (\mathrm{dm^3 \ mol^{-1}})$		
288	1.25	0.59		
298	0.68	1.07		
308	0.51	1.49		
318	0.45	2.36		
(D) Thermodynamic quantities	Values from K_1	Values from K_2		
$\Delta H \text{ (k J mol}^{-1})$	-25.6	33.9		
$\Delta S (\mathrm{J} \mathrm{K}^{-1} \mathrm{mol}^{-1})$	-108.4	171.6		
$\Delta G_{298} \text{ (k J mol}^{-1})$	6.6	-17.3		

 $[DPA] = 5.0 \times 10^{-5}, [OMH] = 5.0 \times 10^{-4}, [OH^{-}] = 0.08, [IO_{4}^{-}] = 5.0 \times 10^{-5}, [Os(VIII)] = 5.0 \times 10^{-6}, I = 0.10 / mol dm^{-3}.$

present investigations, × values for the standard run were found to be unity for Os(VIII). Then the value of $K_{\rm C}$ is calculated using the equation,

$$K_{\rm C} = \frac{k_{\rm T} - k_{\rm U}}{[\text{Catalyst}]^{\times}} = \frac{k_{\rm C}}{[\text{Catalyst}]^{\times}} \text{ (where } k_{\rm T} - k_{\rm U} = k_{\rm C} \text{) } [2]$$

The values of $K_{\rm C}$ were evaluated at different temperatures and found to vary at different temperatures. Further, plots of log $K_{\rm C}$ 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. The value of $K_{\rm C}$ at 25 °C is 3.7 × 10³.

4. DISCUSSION

In the later period of the 20th century, the kinetics of oxidation of some organic and inorganic substrates have been studied by Ag(III) species, which may be due to its strong versatile

 TABLE 3

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

_	-
Temperature (K)	$K_{\rm C} \times 10^{-4}$
288	0.19
298	0.37
308	0.69
318	1.03
$Ea(k J mol^{-1})$	43.2
$\Delta H^{\#}$ (k J mol ⁻¹)	40.7
$\Delta S^{\#}(J \text{ K}^{-1} \text{mol}^{-1})$	-39.9
$\Delta G^{\#}$ (k J mol ⁻¹)	52.6
log A	11.1

 $[DPA] = 5.0 \times 10^{-5}, [OMH] = 5.0 \times 10^{-4}, [OH^{-1}] = 0.08, [IO_4^{-1}] = 5.0 \times 10^{-5}, [Os(VIII)] = 5.0 \times 10^{-6}, I = 0.10 / mol dm^{-3}.$

nature of two electrons oxidant. Among the various species of Ag(III), Ag(OH)₄⁻, diperiodatoargentate(III) and ethylenebis (biguanide), (EBS), silver(III) are of maximum attention to the researchers due to their relative stability.^[26] The stability of Ag(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) ^[27] are considerably stable; the DPA is used in highly alkaline medium and EBS is used in highly acidic medium.

The literature survey ^[21] reveals that the water soluble diperiodatoargentate(III) (DPA) has a formula $[Ag(IO_6)_2]^{7-}$ with dsp² 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 unlikely to exist as $[Ag(IO_6)_2]^{7-}$ as periodate is known to be in various protonated forms ^[28] depending on pH of the solution as given in following multiple equilibria (3)–(5).

$$H_5IO_6 \iff H_4IO_6^- + H^+$$
 [3]

$$H_4IO_6^- \iff H_3IO_6^{2-} + H^+$$
 [4]

$$H_3IO_6^{2-} \longrightarrow H_2IO_6^{3-} + H^+$$
 [5]

Periodic acid exists as H_5IO_6 in acid medium and as $H_4IO_6^$ near pH 7. Hence, under alkaline conditions as employed in this study, the main species are expected to be $H_3IO_6^{2-}$ and $H_2IO_6^{3-}$. At higher concentrations, periodate also tends to dimerise.^[4] However, formation of this species is negligible under conditions employed for kinetic study. On contrary, the authors^[7,8] in their recent studies have proposed the DPA species as $[Ag(HL)_2]^{X-}$ 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 ^[28] of IO_4^- at pH > 7, which is in the form $H_3IO_6^{2-}$ or $H_2IO_6^{3-}$. Hence, DPA could be as $[Ag(H_3IO_6)_2]^$ or $[Ag(H_2IO_6)_2]^{3-}$ in alkaline medium. Therefore, under the present condition, diperiodatoargentate(III), may be depicted as $[Ag(H_3IO_6)_2]^-$. The similar speciation of periodate in alkali was proposed^[29] for diperiodatonickelate(IV).

It is known that DL-ornithine exists in the form of zwitterion 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,^[30] as



4.1. Mechanism

Osmium(VIII) is known to form different complexes at different $OH^{-(17)}$ 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 decreased with increase in $[OH^-]$, it is reasonable that $[OsO_4(OH)_2]^{2-}$ was operative and its formation is important in the reaction. In earlier reports,^[15] it has been observed that in Os(VIII) catalyzed reaction, in view of less than unit order in substrate, unit order in Os(VIII) and oxidant, Os(VIII) is regenerated through formation of Os(VII). In another case,^[16] Os(VIII) is regenerated by Os(VI) intervention in view of unit order each in osmium, substrate and oxidant. In some other reports,^[17] it is observed that Os(VIII) forms a complex with substrate, which is oxidized by the oxidant with regeneration of the catalyst. Hence, the study of behavior of Os(VIII) in catalyzed reaction becomes significant. To explain all the observed orders, Scheme 2 is proposed for osmium(VIII) catalyzed reaction.

In the prior equilibrium step 1, the hydroxyl ion concentration with fractional order in OH^- concentration, the main oxidant species is likely to be $[Ag(H_3IO_6)_2]^-$ and its formation by the above equilibrium is important in the present study. The less than unit order in [OMH] presumably results from the formation of a complex (C) between the Os(VIII) species and DL-ornithine monohydrochloride. This complex (C) reacts with one mole of DPA in a slow step to give the free radical species of OMH, Ag(II) with the regeneration of catalyst, Os(VIII). Further this free radical species of OMH reacts with Ag(II) in a fast step to form 4-aminobutyraldehyde intermediate. This intermediate reacts with one mole of DPA in a further fast step to form the products such as 4-aminobutyric acid, Ag(I) and periodate as given in Scheme 2.

The probable structure of the complex (C) is given as,



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) $(5.0 \times 10^{-6}, [OH^-] = 0.08 \text{ mol dm}^{-3})$ and a mixture of both. A bathochromic shift of 4 nm from 364 nm to 368 nm in the spectra of Os(VIII) to the mixture of Os(VIII) and OMH was observed. Attempts to separate and isolate the complex were not successful. 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.^[17] The rate law (7) for the Scheme 2

could be derived as,

$$rate = \frac{-d[DPA]}{dt}$$

= $\frac{kK_1K_2[OMH][Os(VIII)][DPA]}{K_1 + K_1K_2[OMH] + [OH^-] + K_2[OMH][OH^-]}$ [6
 $\frac{rate}{[DPA]} = k_C = k_T - k_U$
= $\frac{kK_1K_2[OMH][Os(VIII)]}{K_1 + K_1K_2[OMH] + [OH^-] + K_2[OMH][OH^-]}$ [7

This explains all the observed kinetic orders of different species. The rate law (7) can be rearranged to be equation (8), which is suitable for verification.

$$\frac{[Os(VIII)]}{k_{C}} = \frac{[OH^{-}]}{kK_{1}K_{2}[OMH]} + \frac{[OH]}{kK_{1}} + \frac{1}{K_{1}K_{2}[OMH]} + \frac{1}{k}$$
[8]

According to Equation (8), other conditions being constant, the plots of $[Os(VIII)]/k_C$ versus $[OH^-]$ and $[Os(VIII)]/k_C$ versus 1/[OMH] should be linear and found to be so (Figure 5). From the intercepts and slopes of such plots, the reaction constants K_1 , K_2 and k were calculated as $(6.8 \pm 0.1) \times 10^{-2}$ mol dm⁻³, $(1.07 \pm 0.03) \times 10^3$ dm³ mol⁻¹, $(2.2 \pm 0.2) \times 10^4$ dm³ mol⁻¹ s⁻¹, respectively. The value K_1 obtained is in good agreement with previously reported value.^[31] 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 Scheme 2.

The thermodynamic quantities for the different equilibrium steps, in Scheme 2 can be evaluated as follows. The DL-ornithine monohydrochloride and hydroxide ion concentrations (Table 1) were varied at different temperatures. The plots of $[Os(VIII)]/k_C$ versus 1/[OMH] ($r \ge 0.9996$, $S \le 0.00133$), [Os(VIII)]/ $k_{\rm C}$ *versus* $[OH^{-}]$ (r > 0.9948, S < 0.00142) should be linear as shown in Figure 5. From the slopes and intercepts, the values of K_1 are calculated at different temperatures. A vant Hoff's plot was made for the variation of K_1 with temperature [i.e., log K_1 versus 1/T ($r \ge 0.9213$, $S \le 0.1034$)] and the values of the enthalpy of reaction ΔH , entropy of reaction ΔS and free energy of reaction ΔG , were calculated. These values are also given in Table 2. A comparison of the ΔH value of second step (33.9 k J mol⁻¹) of Scheme 2 with that of $\Delta H^{\#}$ (32.2 k J mol $^{-1}$) 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 slow and involves high activation energy.^[18] In the same manner, K_2 values were calculated at different temperatures and the corresponding values of thermodynamic quantities are given in Table 2.

The negligible effect of ionic strength and dielectric constant in the reaction might be due to the presence of various ions in



FIG. 5. Verification of rate law (7) for the Os(VIII) catalyzed oxidation of DL-ornithine monohydrochloride by diperiodatoargentate(III). Plots of (A) $[Os(VIII)]/k_C vs 1/[OMH]$, (B) $[Os(VIII)/k_C vs [OH^-]$, at six different temperatures (conditions as given in Table 1).

reaction (Scheme 2). The moderate $\Delta H^{\#}$ and $\Delta S^{\#}$ values are favorable for electron transfer reaction. The value of $\Delta H^{\#}$ was due to energy of solution changes in the transition state. The negative value of $\Delta S^{\#}$ (-53.8 J K⁻¹ mol⁻¹) suggests that the intermediate complex (C) is more ordered than the reactants.^[32] 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.^[33] The activation parameters evaluated for the reaction explain the catalytic effect on the reaction. The catalyst Os(VIII) forms 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.

5. CONCLUSIONS

The Os(VIII) catalyzed oxidation of DL-ornithine monohydrochloride by diperiodatoargentate(III) was studied. Oxidation products were identified. Among the various species of Ag(III) in alkaline medium, in earlier reports the monoperiodatoargentate(III) was the active species, whereas diperiodatoargentate(III) itself is considered to be the active species for the title reaction. Active species of Os(VIII) is $[OsO_4(OH)_2]^{2-}$ 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.

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APPENDIX

According to Scheme 2

rate =
$$k[C][Ag(H_3IO_6)_2]^- = \frac{kK_1K_2[OMH][Os(VIII)][DPA]}{[OH^-]}$$
[1]

The total concentration of DPA is given by (where T and F stand for total and free)

$$[DPA]_{T} = [DPA]_{F} + [Ag(H_{3}IO_{6})2]^{-}$$

= $[DPA]_{F} \left[\frac{[OH^{-}] + K_{2}}{[OH^{-}]} \right]$

Therefore,

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$$[DPA]_{F} = \left[\frac{[DPA]_{T}[OH^{-}]}{[OH^{-}] + K_{1}}\right]$$
[2]

Similarly,

$$[OMH]_{T} = [OMH]_{F} + [C]$$

=
$$[OMH]_{F} + K_{2}[OMH]_{F}[Os(VIII)]$$

=
$$[OMH]_{F}(1 + K_{2}[Os(VIII)])$$

In view of low concentration of Os(VIII) used,

$$[OMH]_{T} = [OMH]_{F}$$
[3]

$$[OH^{-}]_{T} = [OH^{-}]_{F}$$
 [4]

$$[Os(VIII)]_{T} = [Os(VIII)]_{F} + [C]$$

= [Os(VIII)]_{F} + K_2[OMH][Os(VIII)]_{F}

$$[Os(VIII)]_{F}\left[\frac{[Os(VIII)]_{T}}{\{1 + K_{2}[OMH]\}}\right]$$
[5]

Substituting equations (2)–(5) in equation (1) and omitting the subscripts T and F, we get

$$\frac{\text{rate}}{[\text{DPA}]} = k_{\text{C}} = k_{\text{T}} - k_{U}$$
$$= \frac{kK_1K_2[\text{OMH}][\text{Os}(\text{VIII})]}{K_1 + K_1K_2[\text{OMH}] + [\text{OH}^-] + K_2[\text{OMH}][\text{OH}^-]}$$