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Mechanism of Uncatalyzed and Osmium(VIII) Catalyzed Oxidation of L-alanine by Copper(III) Periodate Complex in Aqueous Alkaline Medium

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The kinetics of oxidation of the L-alanine (L-ala) by diperiodatocuprate(III) (DPC) was carried both in the absence and presence of osmium(VIII) catalyst in alkaline medium at constant ionic strength of 0.01 mol dm^{-3} spectrophotometrically. The involvement of free radicals was observed in both the reactions. The oxidation products in both the cases were acetaldehyde and Cu(II), identified by spot test and spectroscopic studies. The stoichiometry is the same in both cases; that is, [L-ala]:[DPC] = 1:2. The reaction was first order in [DPC] and has negative fractional order in [OH$^-$] in both the catalyzed and uncatalyzed cases. The order in [osmium(VIII)] was unity. A mechanism involving the formation of a complex between L-ala and DPC in case of uncatalyzed reaction and a mechanism involving the formation of a complex between L-alanine and osmium(VIII) in case of catalyzed reaction were proposed. The reaction constants involved in the different steps of the mechanisms were calculated for both reactions. The catalytic constant (Kc) was also calculated for catalyzed reaction at different temperatures. The activation parameters with respect to slow step of the mechanisms were computed and discussed for both the cases. The thermodynamic quantities were also determined for uncatalyzed and catalyzed reactions.

Keywords diperiodatocuprate(III), kinetics, L-alanine, Os(VIII) catalysis, oxidation

INTRODUCTION

In recent years, the study of highest oxidation state transition metals has intrigued many researchers. Transition metals in a higher oxidation state can be stabilized by chelation with suitable polydentate ligands. Metal chelates, such as diperiodatocuprate(III),[1] diperiodatoargentate(III),[2] and diperiodatonickelate(IV)[3] are good oxidants in a medium with an appropriate pH value. Periodate and tellurate complexes of copper in its trivalent state have been extensively used in the analysis of several organic compounds.[4] The kinetics of self-decomposition of these complexes was studied in some detail.[5] Copper(III) is an intermediate in the copper(II) catalyzed oxidation of amino acids by peroxydisulphate.[6] The oxidation reaction usually involves the copper(II)-copper(I) couple, and such aspects are detailed in different reviews.[7,8] The use of diperiodatocuprate(III) (DPC) as an oxidant in alkaline medium is new and restricted to a few cases due to its limited solubility and stability in aqueous medium. DPC is a versatile one-electron oxidant for various organic compounds in alkaline medium and its use as an analytical reagent is now well recognized.[9] Copper complexes have occupied a major place in oxidation chemistry due to their abundance and relevance in biological chemistry.[10] When the copper(III) periodate complex is the oxidant, and multiple equilibria between different copper(III) species are involved, it would be interesting to know which of the species is the active oxidant.

Enzymatic dehydrogenation of amino acids by flavoenzymes has attracted considerable attention in recent years. Amino acids have been oxidized by a variety of oxidizing agents.[11] The oxidation of amino acids is of interest as the oxidation products differ for different oxidants.[12,13] The study of amino acids becomes important because of their biological significance and selectivity towards the oxidant to yield different products. L-alanine [L-ala] chemically is (2S)-2-aminopropanoic acid. It is found primarily in poultry, beef, pork, and fish. Almost all animal based protein sources are rich in L-ala. The contraction of muscle results in increased L-ala levels within the body. As an amino acid, L-ala is used by the body as a building block of protein. L-ala plays a major role in transferring nitrogen from tissue sites in the body, to the liver. It is also used by the body to draw upon blood sugar as an energy source.[14]

Transition metals are known to catalyze many oxidation-reduction reactions since they involve multiple oxidation states. The use of transition metal ions, such as osmium, ruthenium, and irridium, either alone or as binary mixtures, as catalysts in various redox processes has attracted considerable interest.[15] The role of osmium(VIII) as a catalyst in some redox reactions has been reviewed.[16] Although the mechanism of catalysis depends on the nature of the substrate, the oxidant, and experimental conditions, it has been shown[17] that metal ions act as catalysts by one of these different paths such as the formation

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of complexes with reactants, 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 authors have observed that osmium(VIII) catalyzes the oxidation of L-ala by DPC in alkaline medium in micro amounts. In order to understand the active species of oxidant and catalyst, and to propose the appropriate mechanisms, the title reaction is investigated in detail in view of various mechanistic possibilities. An understanding of mechanism allows chemistry to be interpreted and hence understood and predicted.

EXPERIMENTAL

Materials and Reagents

All chemicals were of reagent grade, and double distilled water was used throughout the work. A solution of L-alanine (S.D Fine Chem.) was prepared by dissolving an appropriate amount of recrystallised sample in double distilled water. The purity of the L-ala sample was checked with its m.p. 312°C (Lit. m.p. 314°C). The required concentration of L-ala was made from its stock solution. The osmium(VIII) solution was prepared by dissolving OsO_4oxide (Johnson Matthey) in 0.50 mol dm^{-3} NaOH. The concentration was ascertained[18] by determining the unreacted $[Fe(CN)_6{}^{4-}$ with standard Ce(IV) solution in an acidic medium. KNO_3 and KOH (BDH) were used to maintain ionic strength and alkalinity of the reaction, respectively. The copper(III) periodate complex was prepared by standard procedure.[19] The aqueous solution of copper(III) was standardized by iodometric titration and gravimetrically by thiocyanate method.[20] The copper(II) solutions were prepared by dissolving a known amount of copper sulphate (BDH) in distilled water. Periodate solution was prepared by weighing out the required amount of sample in hot water and used after keeping it for 24 h. Its concentration was ascertained iodometrically[21] at neutral pH maintained using phosphate buffer. Since periodate is present in excess in DPC, the possibility of oxidation of L-ala by periodate in alkaline medium at 25°C was tested. The progress of the reaction was followed iodometrically. There was no significant reaction under the experimental conditions employed compared to the DPC oxidation of L-ala. The pH of the medium in the solution was measured by (ELICO (LI613) pH meter.

Kinetics

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-ala] > [DPC] both in uncatalyzed and catalyzed reaction at $25 \pm 0.1°C$, unless specified. In the absence of catalyst, the reaction was initiated by mixing the DPC to L-ala solution, which also contained required concentration of KNO_3, KOH, and KIO_4. The reaction in the presence of catalyst was initiated by mixing DPC to L-ala solution, which also contained required concentration of KNO_3, KOH, KIO_4, and Os(VIII) catalyst. The progress of reaction was followed spectrophotometrically at 415 nm by monitoring the decrease in absorbance due to DPC with the molar absorbency index, 'ε' taken as 6230 ± 100 dm^3 mol^{-1} cm^{-1} in both catalyzed and uncatalyzed reactions. It was verified that there is a negligible interference from other species present in the reaction mixture at this wavelength. The spectroscopic changes during the reaction are shown in Figure 1. It is evident from the figure that the concentration of DPC in terms of absorbance of DPC decreases at 415 nm.

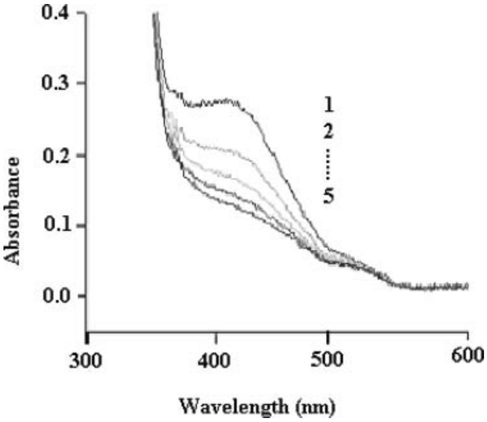


FIG. 1. Spectroscopic changes occurring in the oxidation of L-alanine by diperiodatocuprate(III) at 25°C, $[DPC] = 5.0 \times 10^{-5}$, $[L\text{-}ala] = 4.0 \times 10^{-4}$, $[OH^-] = 0.004$ and $I = 0.01$ mol $dm^{-3}$with scanningtime interval of: (1) 0.5, (2) 1.0, (3) 1.5, (4) 2.0, and (5) 2.5 minutes.

The pseudo first-order rate constants, ('k_U or k_C'), in both the cases were determined from the log (absorbance) versus time plots. The plots were linear up to 80% completion of reaction (for uncatalyzed and catalyzed) in Figure 2. The orders for various species were determined from the slopes of plots of log (k_U or k_C) versus respective concentration of species except for [DPC] in which non-variation of 'k_U or k_C' was observed as

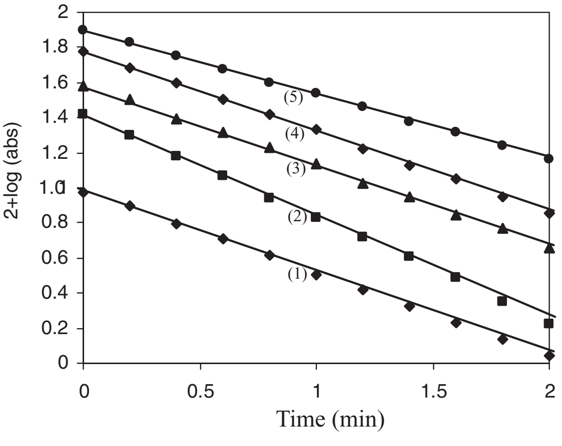


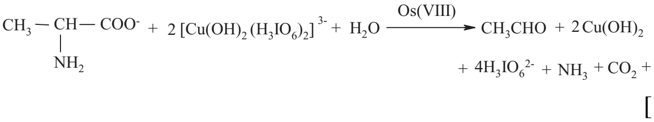
FIG. 2. First order plots for the oxidation of Os(VIII) catalyzed L-alanine by diperiodatocuprate(III) in aqueous alkaline medium. [diperiodatocuprate(III)] $\times 10^5$(mol dm^{-3}): 1) 1.0, 2) 3.0, 3) 5.0, 4) 8.0, and 5) 10.0.

expected to the reaction condition. The rate constants were reproducible to within ±5%. Regression analysis of experimental data to obtain regression coefficient r and the standard deviation s, of points from the regression line, was performed with the Microsoft office Excel-2003 program.

RESULTS AND DISCUSSION

Stoichiometry and Product Analysis

Different sets of reaction mixtures containing varying ratios of DPC to L-ala in the presence of constant amount of OH^-, KNO_3 and KIO_4 in uncatalyzed reaction and a constant amount Os(VIII) in catalyzed reaction were kept for 2 h in a closed vessel under nitrogen atmosphere. The remaining concentration of DPC was estimated by spectrophotometrically at 415 nm. The results indicate that 1:2 stoichiometry, as given in Eq. (1).



$$CH_3-CH(NH_2)-COO^- + 2\,[Cu(OH)_2(H_3IO_6)_2]^{3-} + H_2O \xrightarrow{Os(VIII)} CH_3CHO + 2\,Cu(OH)_2 + 4H_3IO_6^{2-} + NH_3 + CO_2 + H^+$$

[1]

The stoichiometric ratio in both the cases suggests that the main product was acetaldehyde, which was identified by spot test[22] and confirmed by its IR(KBr) spectrum showing a carbonyl stretching at 1729 cm^{-1} and -CH stretching at 2928 cm^{-1}. Ammonia was identified by Nessler's reagent.[20] CO_2 was qualitatively detected by bubbling N_2 gas through the acidified reaction mixture and passing a liberated gas through a tube containing limewater. The aldehyde was confirmed by preparing its 2, 4-DNP derivative.[23] The metal product Cu(II) was identified by UV-vis spectra. The reaction product did not undergo further oxidation under the present kinetic conditions.

Reaction Orders

As the diperiodatocuprate(III) oxidation of L-alanine in alkaline medium proceeds with a measurable rate in the absence of Os(VIII), the catalyzed reaction is understood to occur in parallel paths with contributions from both the catalyzed and uncatalyzed paths. Thus, the total rate constant (k_T) is equal to the sum of the rate constants of the catalyzed (k_C) and uncatalyzed (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 (concentration) plots by varying the concentrations of L-ala, alkali, periodate, and Os(VIII) catalyst in turn while keeping all other concentrations and conditions constant. The order in DPC was unity between the concentrations was varied in the range of 1.0×10^{-5} to 1.0×10^{-4} mol dm^{-3} at fixed L-ala, KOH and KNO_3 in both the cases uncatalyzed and catalyzed reactions. Linearity of the plots of log [absorbance] versus time up to 80% completion of the reaction indicates a reaction order of unity in [DPC]. This was also confirmed by varying [DPC], and did not result in any change in rate constants, k_U (Table 1) and k_C (Table 3). The effect of L-ala on the rate of reaction was studied at constant concentrations of alkali, DPC, and periodate at a constant ionic strength of 0.01 mol dm^{-3} in both the cases of catalyzed and uncatalyzed reaction. In case of catalyzed and uncatalyzed reaction, the L-ala concentration was varied in the range of 1.0×10^{-4} to 1.0×10^{-3} mol dm^{-3} at 25°C while keeping other reactant concentrations and conditions constant. The k_C and k_U values increased with the increase in concentration of L-ala indicating an apparent less than unit order dependence on [L-ala] (Table 1 and 3). The effect of alkali on the reaction has been studied for both the cases in the range of 0.001 to 0.01 mol dm^{-3} at constant concentrations of L-ala, DPC and periodate at a constant ionic strength of 0.01 mol dm^{-3} in uncatalyzed reaction and at concentration of Os(VIII) in catalyzed reaction. The rate constants decreased with increase in alkali concentration (Table 1 and 3), indicating negative fractional order dependence of rate on alkali concentration.

TABLE 1
Effect of [DPC], [L-ala], $[IO_4^-]$ and $[OH^-]$ on the oxidation of L-alanine by diperiodatocuprate(III) in alkaline medium at 25°C, I = 0.01 mol dm^{-3}

(A) Effect of temperature

Temperature (K)	$10^2 k_1$ (s^{-1})	$10^2 K_1$ (mol dm^{-3})	$10^{-2} K_2$ ($dm^3 mol^{-1}$)
298	4.2	1.2	2.7
303	5.4	1.1	3.3
308	6.0	0.9	3.5
313	7.6	0.5	4.4

(B) Thermodynamic activation parameter for the oxidation of L-alanine by diperiodatocuprate(III) in aqueous alkaline medium

Activation parameters using k_1	Values
$\Delta H^{\#}$ (kJ mol^{-1})	25 ± 2
$\Delta S^{\#}$(JK^{-1} mol^{-1})	−184 ± 20
$\Delta G^{\#}$ (kJ mol^{-1})	80 ± 3
log A	4.6 ± 0.2

(C) Thermodynamic quantities using K_1 and K_2

Thermodynamic quantities	Values from K_1	Values from K_2
ΔH (kJ mol^{-1})	−42.4 ± 2.0	20.3 ± 0.8
ΔS (JK^{-1} mol^{-1})	−178 ± 10	114 ± 5
ΔG_{298} (kJ mol^{-1})	12 ± 0.3	−14.8 ± 0.8

Effect of Periodate

The effect of increasing concentration of periodate was studied by varying the periodate concentration from 1.0×10^{-5} to 1.0×10^{-4} mol dm^{-3} keeping all other reactant concentrations constant. The added periodate had no effect on

TABLE 2
Effect of temperature on k_1, K_1 and K_2 for the oxidation of L-alanine by diperiodatocuprate(III) in aqueous alkaline medium

				10^3 $k_U(s^{-1})$	
10^5 [DPC] (mol dm^{-3})	10^4 [L-ala] (mol dm^{-3})	10^5 [IO_4^-] (mol dm^{-3})	10^2 [OH^-] (mol dm^{-3})	Found	Calculated
1.0	4.0	5.0	0.4	3.5	3.2
3.0	4.0	5.0	0.4	3.4	3.2
5.0	4.0	5.0	0.4	3.2	3.2
7.0	4.0	5.0	0.4	3.3	3.2
10.0	4.0	5.0	0.4	3.4	3.2
5.0	1.0	5.0	0.4	0.89	0.86
5.0	2.0	5.0	0.4	1.6	1.7
5.0	4.0	5.0	0.4	3.2	3.2
5.0	6.0	5.0	0.4	5.0	4.8
5.0	10.0	5.0	0.4	6.7	6.8
5.0	4.0	1.0	0.4	3.4	3.2
5.0	4.0	3.0	0.4	3.5	3.2
5.0	4.0	5.0	0.4	3.2	3.2
5.0	4.0	8.0	0.4	3.4	3.2
5.0	4.0	10.0	0.4	3.2	3.2
5.0	4.0	5.0	0.1	4.2	3.9
5.0	4.0	5.0	0.2	3.5	3.7
5.0	4.0	5.0	0.4	3.2	3.2
5.0	4.0	5.0	0.8	2.8	2.9
5.0	4.0	5.0	1.0	2.4	2.4

the rate of reaction (Table 1 and 3) in catalyzed and uncatalyzed reactions.

Effect of 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 cases.

Effect of Ionic Strength (I) and Dielectric Constant (D)

It was found that ionic strength (using KNO_3) and dielectric constant of the medium (using t-butyl alcohol and H_2O) had no significant effect on the rate of reaction in both the cases of uncatalyzed and catalyzed reactions.

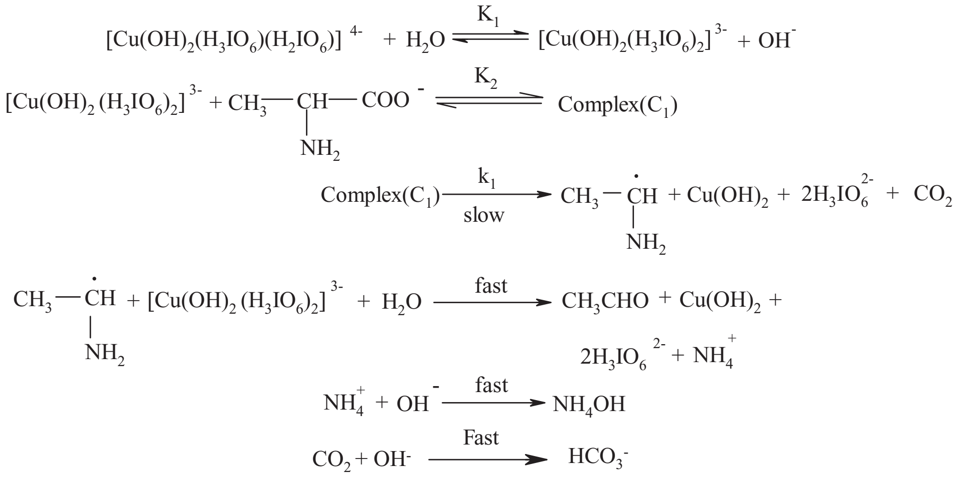
Test for Free Radicals (Polymerization Study)

The involvement of free radicals, for both uncatalyzed and catalyzed reactions was tested. The reaction mixture was mixed with acrylonitrile monomer initially added, and was kept for 2 h in an inert atmosphere. On diluting the reaction mixture with methanol, a white precipitate was formed, indicating the involvement of free radicals in both catalyzed and uncatalyzed reactions. The blank experiments of either DPC or L-ala alone with acrylonitrile did not induce any polymerization under the same conditions. Initially added acrylonitrile decreased the rate of reaction, indicating free radical participation.

Effect of Temperature

The influence of temperature on the rate of reaction was studied for uncatalyzed reaction at 25, 30, 35, and 40°C. The rate constants, (k_1), of the slow step of Scheme 1 were obtained from the slopes and the intercepts of the plots of $1/k_u$ versus 1/[L-ala] plots at four different temperatures. The values are given in Table 1 and were used to calculate the activation parameters. The energy of activation corresponding to these constants was evaluated from the Arrhenius plot of log k_1 versus 1/T ($r \geq 0.9997$, $S \leq 0.011$) and other activation parameters obtained are tabulated in Table 2.

The influence of temperature on the rate of reaction was studied for catalyzed reaction at 25, 30, 35, and 40°C. The rate constants, (k_2), of the slow step of Scheme 2 were obtained from the slopes and the intercepts of the plots of [Os(VIII)]/k_C versus 1/[L-ala] plots at four different temperatures. The values are given in Table 3. The activation parameters for the rate



SCH. 1. Detailed scheme for the oxidation of L-alanine by alkaline diperiodatocuprate(III).

determining step were obtained by the least square method of plot of log k_2 versus 1/T and are presented in Table 4.

Effect of [Os(VIII)]

The [Os(VIII)] concentration was varied from 5.0×10^{-7} to 5.0×10^{-6} mol dm^{-3} range, at constant concentration of diperiodatocuprate(III), L-ala, alkali, and ionic strength. The order in [Os(VIII)] was found to be unity from the linearity of the plots of k_C versus [Os(VIII)].

Catalytic Activity

It has been pointed out by Moelwyn-Hughes[24] that in presence of the catalyst, the uncatalyzed and catalyzed reaction proceed simultaneously, so that

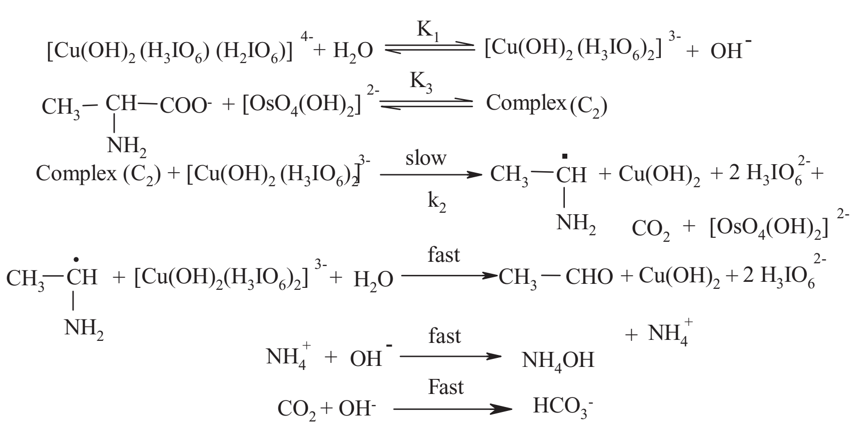
$$k_T = k_U + K_C[\mathrm{Os(VIII)}]^x \quad [2]$$

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 uncatalyzed 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. Then the value of K_C is calculated using the equation,

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

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 activation and other activation parameters with reference to catalyst were computed. These results are summarized in Table 5.

The water-soluble copper(III) periodate complex is reported[25] to be $[\mathrm{Cu(HIO_6)_2(OH)_2}]^{7-}$. However, in aqueous alkaline medium at high pH as employed in this study, periodate is unlikely to exist as $\mathrm{HIO_6}^{4-}$(as present in the complex) as is evident from its involvement in the multiple equilibria[26]



SCH. 2. Detailed scheme for the Os(VIII) catalyzed oxidation of L-alanine by alkaline diperiodatocuprate(III).

TABLE 3

Effect of [DPC], [L-ala], [IO$_4$], [OH$^-$], and [Os(VIII)] on the osmium(VIII) catalyzed oxidation of L-alanine by DPC in alkaline medium at 25°C, $I = 0.01$ mol dm^{-3}

10^5 [DPC] (mol dm^{-3})	10^4 [L-ala] (mol dm^{-3})	10^5 [IO$_4$] (mol dm^{-3})	10^2 [OH$^-$] (mol dm^{-3})	10^7 [Os(VIII)] (mol dm^{-3})	10^2 k_T (s^{-1})	10^3 k_U (s^{-1})	$10^2 k_C$ (s^{-1}) Found	$10^2 k_C$ (s^{-1}) Calculated
1.0	4.0	5.0	0.4	8.0	2.9	3.5	2.5	2.5
3.0	4.0	5.0	0.4	8.0	2.7	3.4	2.3	2.5
5.0	4.0	5.0	0.4	8.0	2.8	3.2	2.5	2.5
8.0	4.0	5.0	0.4	8.0	2.7	3.3	2.3	2.5
10.0	4.0	5.0	0.4	8.0	2.5	3.4	2.1	2.5
5.0	1.0	5.0	0.4	8.0	0.82	0.89	0.73	0.72
5.0	2.0	5.0	0.4	8.0	1.5	1.6	1.4	1.4
5.0	4.0	5.0	0.4	8.0	2.8	3.2	2.5	2.6
5.0	6.0	5.0	0.4	8.0	4.4	5.0	3.9	3.7
5.0	10.0	5.0	0.4	8.0	6.2	6.7	5.5	5.6
5.0	4.0	1.0	0.4	8.0	3.5	3.8	3.0	2.5
5.0	4.0	3.0	0.4	8.0	3.2	3.5	2.9	2.5
5.0	4.0	5.0	0.4	8.0	2.8	3.2	2.9	2.5
5.0	4.0	8.0	0.4	8.0	2.6	3.4	2.8	2.5
5.0	4.0	10.0	0.4	8.0	2.4	3.2	2.9	2.5
5.0	4.0	5.0	0.1	8.0	3.8	4.2	3.3	3.1
5.0	4.0	5.0	0.2	8.0	3.2	3.5	2.9	2.9
5.0	4.0	5.0	0.4	8.0	2.8	3.2	2.5	2.6
5.0	4.0	5.0	0.6	8.0	2.5	2.8	2.3	2.4
5.0	4.0	5.0	1.0	8.0	2.3	2.4	2.1	2.0
5.0	4.0	5.0	0.4	5.0	1.5	3.2	1.2	1.3
5.0	4.0	5.0	0.4	8.0	2.8	3.2	2.5	2.6
5.0	4.0	5.0	0.4	10.0	3.4	3.2	3.1	3.3
5.0	4.0	5.0	0.4	30.0	8.6	3.2	8.3	8.4
5.0	4.0	5.0	0.4	50.0	14.0	3.2	14.0	14.5

(4)–(6) depending on the pH of the solution.

$$H_5IO_6 \rightleftharpoons H_4IO_6{}^- + H^+ \qquad [4]$$

$$H_4IO_6^- \rightleftharpoons H_3IO_6{}^{2-} + H^+ \qquad [5]$$

$$H_3IO_6^{2-} \rightleftharpoons H_2IO_6{}^{3-} + H^+ \qquad [6]$$

Periodic acid exists as H_5IO_6 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.[27] However, formation of this species is negligible under the conditions employed for this study. Hence, at the pH employed in this study, the soluble copper(III) periodate complex exists as diperiodatocuprate(III), $[Cu(H_3IO_6)_2(OH)_2]^{2-}$, a conclusion also supported by earlier work.[28]

In most of the reports[1,28] on DPC oxidation, periodate retards and OH$^-$ increases the rate of the reaction. However, in the present kinetic study, entirely different kinetic observations have been obtained. In this study, OH$^-$ retards the rate of reaction and periodate shows no effect on the rate. The result of decrease in rate of reaction with increase in alkalinity (Table 1) can be explained in terms of a prevailing equilibrium of formation of $[Cu(OH)_2(H_3IO_6)_2)]^{3-}$ from $[Cu(OH)_2(H_3IO_6)(H_2IO_6)]^{4-}$ hydrolysis as given below.

$$[Cu(OH)_2(H_3IO_6)(H_2IO_6)]^{4-} + H_2O \overset{K_1}{\rightleftharpoons} [Cu(OH)_2(H_3IO_6)_2]^{3-} + OH^-$$

Because of this reaction and the observation that the k_U or k_C values are inversely related to the hydroxyl ion concentration with fractional order in OH concentration, the main oxidant species is likely to be $[Cu(OH)_2(H_3IO_6)_2]^{3-}$ and its formation by the above equilibrium is important in the present study.

It is known that L-ala exists in the form of Zwitterion[29] in aqueous medium. In highly acidic medium, it exists in the protonated form, whereas in highly basic medium it exists as

TABLE 4
Thermodynamic activation parameters for the osmium(VIII) catalyzed oxidation of L-alanine by DPC in aqueous alkaline medium with respect to the slow step of Scheme 2

(A) Temperature effect

Temperature (K)	$10^{-5}k_2$ ($dm^3\ mol^{-1}\ s^{-1}$)	10^2K_1 ($mol\ dm^{-3}$)	$10^{-2}K_3$ (dm^3mol^{-1})
298	3.3	1.6	3.4
303	3.8	1.4	3.9
308	4.7	0.8	5.8
313	5.7	0.5	6.6

(B) Activation parameters (Scheme 2)

Activation parameters using k_2	Values
$\Delta H^\#$ (kJ mol^{-1})	25.2 ± 0.4
$\Delta S^\#$(JK^{-1} mol^{-1})	−56.5 ± 5
$\Delta G^\#$ (kJ mol^{-1}0	42.5 ± 2
log A	10.3 ± 0.4

(C) Thermodynamic quantities using K_1 and K_3

Thermodynamic quantities	Values from K_1	Values from K_3
ΔH (kJ mol^{-1})	−55.0 ± 3.0	36.3 ± 2.0
ΔS (JK^{-1} mol^{-1})	−218 ± 20	170 ± 18
ΔG_{298} (kJ mol^{-1})	11.6 ± 0.1	−15.6 ± 0.9

the anionic form according to the following equilibria.

$$\mathrm{CH_3{-}CH(NH_2)COOH} \overset{\text{aqueous}}{\rightleftharpoons} \mathrm{CH_3{-}CH(NH_3^+)\,COO^-}$$

$$\mathrm{CH_3 - CH(NH_2)COOH + OH^-} \overset{\text{basic}}{\rightleftharpoons} \mathrm{CH_3 - CH(NH_2)COO^-_+H_2O}$$

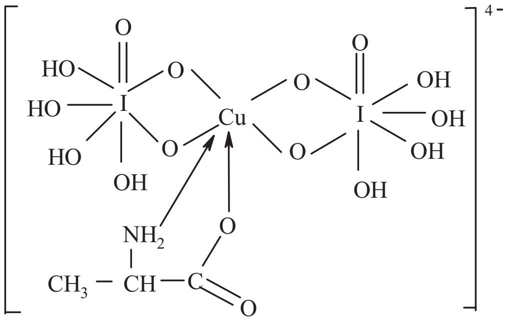
The less than unit order in [L-ala] presumably results from formation of a complex(C_1) between the DPC species and L-ala prior to the formation of the products. This complex(C_1) decomposes in a slow step to form a free radical derived from L-ala. This free radical species further reacts with another molecule of DPC in a fast step to form the products aldehyde, Cu(II) and periodate as given in Scheme 1.

Since Scheme 1 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. The free radical scavenging experiment revealed such a possibility (see infra). This type of radical intermediate has also been observed in earlier work.[30]

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

Temperature	10^{-2} K_C
298	2.5
303	3.5
308	4.3
313	5.3
Ea (kJ mol^{-1})	37.8
$\Delta H^\#$ (kJ mol^{-1})	35.2
$\Delta S^\#$ (kJ^{-1} mol^{-1})	−159.6
$\Delta G^\#$(kJ mol^{-1})	84.1
log A	5.0

The probable structure of the complex is given by



Spectroscopic evidence for the complex formation between oxidant and substrate was obtained from UV-vis spectra of L-ala = (4.0 × 10^{-4}), DPC = (5.0 × 10^{-5}), [OH$^-$] = 0.004 (mol dm^{-3}) and a mixture of both. A hypsochromic shift of about 8 nm from 247 nm of L-ala to 239 nm of mixture of DPC and L-ala and a hyperchromicity at 239 nm was observed. A Lineweaver-Burk plot also indicated the complex formation between DPC and L-ala, which explains the less than unit order dependence on [L-ala]. Such a type of complex between a substrate and an oxidant has been observed in other studies.[31]

The rate law for Scheme 1 could be derived as

$$\text{Rate} = \frac{-d[\text{DPC}]}{dt} = \frac{k_1K_1K_2[\text{L-ala}]}{[\text{OH}^-] + K_1 + K_1K_2[\text{L-ala}]} \qquad [7]$$

$$k_U = \frac{k_1K_1K_2[\text{L-ala}]}{[\text{OH}^-] + K_1 + K_1K_2[\text{L-ala}]} \qquad [8]$$

which explains all the observed kinetic orders of different species.

The rate law (8) can be rearranged to Eqn (9), which is suitable for verification.

$$\frac{1}{k_U} = \frac{[\text{OH}^-]}{k_1K_1K_2[\text{L-ala}]} + \frac{1}{K_1K_2[\text{L-ala}]} + \frac{1}{k_1} \qquad [9]$$

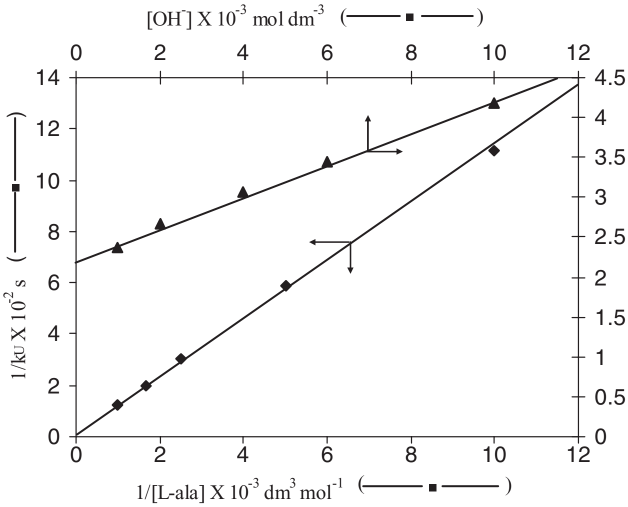


FIG. 3. Verification of rate law (8) in the form of (9) for the oxidation of L-alanine by diperiodatocuprate(III) at 25°C K.

According to equation (9), the plots of $1/k_U$ versus $[OH^-]$ (r $\geq$ 0.998, S $\leq$ 0.014) and $1/k_U$ versus 1/[L-ala] (r $\geq$ 0.997, S $\leq$ 0.016) should be linear, which is the case as given in Figure 3. From the slopes and intercepts of such plots, the reaction constants K_1, $K_2$and k_1 were calculated as $(1.2 \pm 0.04) \times 10^{-2}$ mol dm^3, $(2.7 \pm 0.1) \times 10^2$ dm^3 mol^{-1} and $(4.2 \pm 0.1) \times 10^{-2}$s^{-1} respectively. The value of K_1 is in good agreement with the literature.[32] Using these constants, the rate constants were calculated and the values agreed well with the experimental values (Table 1).

The thermodynamic quantities for the first and second equilibrium steps of Scheme 1 can be evaluated as follows. The [L-ala] and $[OH^-]$ (Table 1) were varied at four different temperatures. The plots of $1/k_U$ versus 1/[L-ala] and $1/k_U$ versus $[OH^-]$ should be linear (Figure 3). From the slopes and intercepts, the values of K_1 and K_2 were calculated at different temperatures and these values are given in Table 2. The vant Hoff's plots were made for variation of K_1 and K_2 with temperature (log K_1 versus 1/T (r $\geq$ 0.9604, S $\leq$ 0.006), log K_2 versus 1/T (r $\geq$ 0.996, s $\leq$ 0.007) and the values of enthalpy of reaction ΔH, entropy of reaction ΔS and free energy of reaction ΔG, were calculated for the first and second equilibrium steps. These values are given in Table 2. A comparison of ΔH value (20.3 $\pm$ 2) from K_2 with that of $\Delta H^{\#}$ (25.0 $\pm$ 2) of rate limiting step supports that the second step of Scheme 1 is fairly fast since it involves low activation energy.[33]

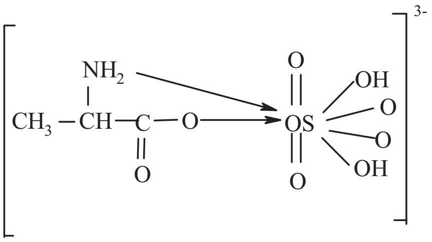
The moderate values of $\Delta H^{\#}$ and $\Delta S^{\#}$ were both favorable for electron transfer processes. The value of $\Delta S^{\#}$ within the range for a radical reaction has been ascribed[34] to the nature of electron pairing and unpairing processes and to the loss of degrees of freedom upon the formation of rigid transition state. The observed modest enthalpy of activation and a relatively low value of the entropy of activation, as well as a higher rate constant of the slow step, indicate that the oxidation presumably occurs via an inner-sphere mechanism. This conclusion is supported by earlier observations.[35,36] A high negative value of $\Delta S^{\#}$ (–184 JK^{-1}mol^{-1}) suggests that intermediate complex is more ordered than the reactants.[37]

Osmium(VIII) is known to form different complexes at different OH^-[38] concentrations, such as $[OsO_4(OH)_2]^{2-}$ and $[OsO_5(OH)]^{3-}$. At higher concentration of OH^-, $[OsO_5(OH)]^{3-}$is significant. At lower concentrations of OH^-, as employed in the present study, and since the rate of oxidation increased with increase in $[OH^-]$, it is reasonable that $[OsO_4(OH)_2]^{2-}$ was operative and its formation is important in the reaction. To explain the observed orders, the following Scheme 2 is proposed for osmium(VIII) catalyzed reaction.

The reaction between the diperiodatocuprate(III) complex and L-alanine in alkaline medium in the presence of osmium(VIII) catalyst has the stoichiometry 1:2 (L-ala:DPC) with a first order dependence on [DPC] and [Os(VIII)]. Based on these experimental results, a mechanism is proposed for which all the observed orders in each constituent such as [oxidant], [reductant], $[OH^-]$, [Os(VIII)] and $[H_3IO_6^{2-}]$ may be well accommodated.

Anionic form of L-ala reacts with Os(VIII) active species to form a complex (C_2), which further reacts with one mole of DPC in a slow step to give the free radical of L-ala, Cu(II) with regeneration of catalyst, osmium(VIII). Further, this free radical of L-ala reacts with one more molecule of DPC species in a fast step to yield the products, as given in Scheme 2.

The probable structure of the complex (C_2) is given below:



Spectroscopic evidence for the complex formation between catalyst and substrate was obtained from UV-Vis spectra of L-ala (4.0×10^{-4}), Os(VIII) (8.0×10^{-7}), $[OH^-] = 0.004$ mol dm^{-3}) and mixture of both. A hypsochromic shift of about 7 nm from 292 nm of L-alanine to 285 nm of mixture of Os(VIII) and L-ala and a hyperchromicity at 285 nm, was observed. The Lineweaver-Burk plot proved the complex formation between Os(VIII) and L-ala, which explains less than unit order in [L-ala]. The rate law for Scheme 2 could be derived as,

$$\text{Rate} = \frac{-d[DPC]}{dt} = \frac{k_2K_1K_3[DPC][L\text{-}ala][Os(VIII)]}{[OH^-] + K_1 + K_3[L\text{-}ala][OH^-] + K_1K_3[L\text{-}ala]} \qquad [10]$$

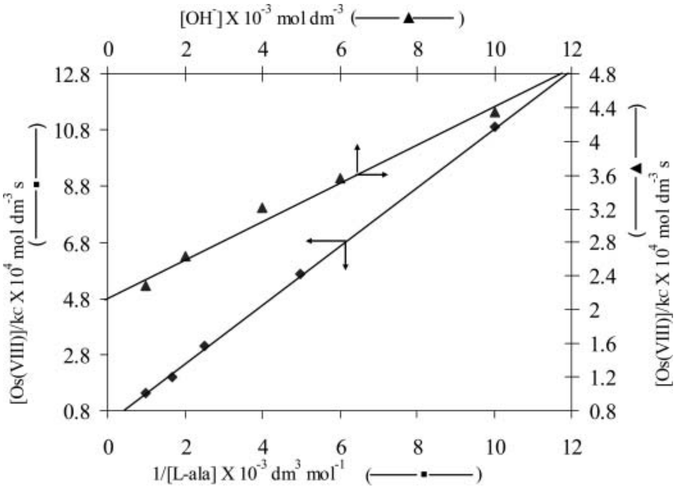


FIG. 4. Verification of rate law (11) in the form of (12) for the Os(VIII) catalyzed oxidation of L-alanine by diperiodatocuprate(III) at 25°C.

$$\frac{\text{Rate}}{[\text{DPC}]} = k_C = k_T - k_U = \frac{k_2 K_1 K_3 [L\text{-}ala][Os(VIII)]}{[OH^-] + K_1 + K_3[L\text{-}ala][OH^-] + K_1 K_3 [L\text{-}ala]} \qquad [11]$$

The rate law (11) can be rearranged to Eqn (12), which is suitable for verification

$$\frac{[\text{Os(VIII)}]}{k_C} = \frac{[\text{OH}^-]}{k_2 K_1 K_3 [\text{L-ala}]} + \frac{1}{k_2 K_3 [\text{l-ala}]} + \frac{[\text{OH}^-]}{k_2 K_1} + \frac{1}{k_2} \qquad [12]$$

According to Eq (12), the plots of [Os(VIII)]/$k_C$versus 1/[L-ala] and [Os(VIII)]/$k_C$versus[OH^-] were linear (Figure 4). From the intercepts and slopes of such plots, the reaction constants K_1, K_3 and k_2 were calculated as $(1.6 \pm 0.02) \times 10^{-2}$ mol dm^{-3}, $(3.5 \pm 0.2) \times 10^2$ dm^3 mol^{-1} $(3.3 \pm 0.1) \times 10^5$ dm^3 mol^{-1} 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 Scheme 2.

The thermodynamic quantities for the different equilibrium steps in Scheme 2 can be evaluated as follows. The L-ala and hydroxide ion concentrations (Table 3) were varied at different temperatures. The plots of [Os(VIII)]/k_C versus 1/[L-ala] ($r \geq 0.9996, s \leq 0.00134$), [Os(VIII)]/$k_C$ versus [OH^-] ($r \geq 0.9994, s \leq 0.00086$), should be linear, as shown in Figure 4. 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 ($r \geq 0.9992$, $s \leq 0.1106$)], 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 4. In the same manner, K_3 values were calculated at different temperatures, and the corresponding values of thermodynamic quantities are given in Table 4. A comparison of ΔH value (36.3) from K_3 with that of $\Delta H^\#$ (25.2 ± 0.4) of rate limiting step, supports that the second step of Scheme 2 is fairly slow since it involves high activation energy.[33]

Negligible effect of ionic strength and dielectric constant in uncatalyzed and catalyzed reaction might be due to involvement of neutral species in the reaction (Schemes 1 and 2). The negative value of $\Delta S^\#$ suggests that the intermediate complex is more ordered than the reactants.[37] The observed modest enthalpy of activation and a higher rate constant for the slow step indicate that the oxidation presumably occurs via an inner-sphere mechanism. This conclusion is supported by an earlier observation.[36]

The activation parameters evaluated for the catalyzed and uncatalyzed reaction explain the catalytic effect on the reaction. The catalyst Os(VIII) forms the complex (C_2) with L-ala, 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 Os(VIII) catalyzed reaction, however, is reasonably fast in view of readiness of Os(VIII) to act across the –COO bond.

The activation parameters for the uncatalyzed and Os(VIII) catalyzed oxidation of some amino acids by DPC are summarized in Tables 6 and 7. The entropy of activation for the title reaction falls within the observed range. Variation in the rate

TABLE 6
Activation parameters for uncatalyzed reactions, oxidation of some amino acids (for isokinetic temperature)

Amino acids	10^2 k_1 (dm^3 mol^{-1} s^{-1}) at T = 298 K	10^2 k_1^1 (dm^3 mol^{-1} s^{-1}) at T = 303 K	$\Delta H^\#$ (J/K/mol)	$\Delta S^\#$ (kJ/mol)	References
Vanilline	3.7	4.2	13.1	−227	[31]
L-glutamic acid	0.98	1.12	13.1	−238	[42]
L-valine	1.20	1.62	38.0	−154	[43]
L-proline	2.7	3.16	29.0	−181	[44]
L-alanine	4.2	5.4	25.0	−184	Present work

TABLE 7
Activation parameters for Os(VIII) catalyzed reactions, oxidation of some amino acids (for isokinetic temperature)

Amino acids	10^2 k_1 (dm^3 mol^{-1} s^{-1}) at T = 298 K	10^2 k_1^1 (dm^3 mol^{-1} s^{-1}) at T = 303 K	$\Delta H^{\#}$ (J/K/mol)	Δ $S^{\#}$ (kJ/mol)	References
L-tryptophan	3.2	5.3	44.0	−30	[45]
L-lysine	2.8	3.08	15.5	−107	[46]
Vanilline	1.4	1.8	41.0	−25.7	[47]
L-alanine	3.3	3.8	25.2	−6.7	Present work

within the reaction series may be caused by change in the enthalpy or entropy of activation. Changes in rate are caused by changes in both $\Delta H^{\#}$ and $\Delta S^{\#}$, but these quantities vary extensively in a parallel fashion. A plot of $\Delta H^{\#}$ versus $\Delta S^{\#}$ is linear according to the following equation:

$$\Delta H^{\#} = \beta \Delta S^{\#} + \text{constant}$$

β is called the isokinetic temperature; it has been asserted that apparently linear correlations of $\Delta H^{\#}$ with $\Delta S^{\#}$ are sometimes misleading and the evaluation of β by means of the above equation lacks statistical validity.[39] Exner[40] advocates an alternative method for the treatment of experimental data. If the rates of several reactions in series have been measured at two temperatures and log k_2 (at T_2) is linearly related to log k_1 (at T_1), *i.e.*, log k_2 = a + b log k_1, he proposes that β can be evaluated from the equation:

$$\beta = T_1 T_2(b - 1)/(T_2 b - T_1)$$

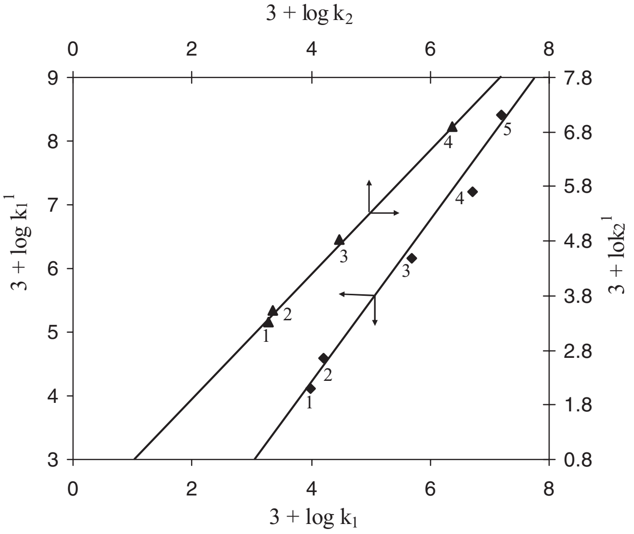


FIG. 5. Plot of log k_1^1at 303 K versus log k_1 at 298 K and plot of log k_2^1 at 303 K versus log k_2 at 298 K for the isokinetic temperature (Tables 6 and 7). For uncatalyzed (−■−): (1) L-glutamic acid; (2) L-valine; (3) L-proline; (4) Vanilline; (5) L-alanine. For catalyzed (−▼−): (1) L-lysine; (2) L-tryptophan; (3) Vanilline; (4) L-alanine.

We have calculated the isokinetic temperature for uncatalyzed and Os(VIII) catalyzed reaction. The values for β of uncatalyzed reaction to be 325.5 K by plotting log ${k_1}^1$at 303 K versus log k_1 at 298 K ($r \geq 0.9865$, $s \leq 0.007$) and isokinetic temperature for Os(VIII) catalyzed reaction to be 333.4 K by plotting log k_2^1 at 303 K versus log k_2 at 298 K ($r \geq 0.9788$, $s \leq 0.005$), as in (Figure 5). The values of β for uncatalyzed (325.5 K) and catalyzed (333.4 K) are higher than experimental temperature (298 K). This indicates that the rate is governed by enthalpy of activation[41] in both the cases. The linearity and the slope of the plot obtained may confirm that the kinetics of these reactions follow a similar mechanism, as previously suggested.

CONCLUSION

The comparative study of uncatalyzed and osmium(VIII) catalyzed oxidation of L-ala by diperiodatocuprate(III) was studied. Oxidation products were identified. Among the various species of Cu(III) in alkaline medium, protonated DPC is considered to be the active species for the title reaction. Active species of Os(VIII) is found to be $[OsO_4(OH)_2]^{2-}$. Activation parameters were evaluated for both uncatalyzed and catalyzed reactions with respect to slow step of reaction schemes. Catalytic constants and activation parameters with respect to catalyst were also computed. Isokinetic temperature for both uncatalyzed and catalyzed reactions was also determined.

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APPENDIX

According to Scheme 2,

$$\text{Rate} = \frac{-\text{d[DPC]}}{\text{dt}} = \text{k}_2\text{[C]}\,[\text{Cu(OH)}_2(\text{H}_3\text{IO}_6)_2]^{3-} \qquad \text{[A-1]}$$

$$= \frac{\text{k}_2\text{K}_1\text{K}_3\text{[L-ala]}\,[\text{DPC}]_\text{f}[\text{Os(VIII)}]}{[\text{OH}^-]} \qquad \text{[A-2]}$$

$$[\text{DPC}]_\text{T} = [\text{DPC}]_\text{f} + [\text{Cu(OH)}_2(\text{H}_3\text{IO}_6)_2]^{3-} \qquad \text{[A-3]}$$

$$[\text{DPC}]_T = [\text{DPC}]_\text{f} + \frac{\text{K}_1[\text{DPC}]}{[\text{OH}^-]} = [\text{DPC}]_\text{f}\left[\frac{[\text{OH}^-] + \text{K}_1]}{[\text{OH}^-]}\right] \qquad \text{[A-4]}$$

Where $[\text{DPC}]_\text{T}$ and [DPC] refer to total and free DPC concentrations, respectively. The free DPC is given by

$$[\text{DPC}]_\text{f} = \frac{[\text{DPC}]_\text{T}[\text{OH}^-]}{[\text{OH}^-] + \text{K}_1} \qquad \text{[A-5]}$$

Similarly total $[\text{OH}^-]$ can be calculated by

$$\begin{aligned}[\text{OH}^-]_\text{T} &= [\text{OH}^-]_\text{f} + [\text{Cu(OH)}_2(\text{H}_3\text{IO}_6)_2]^{3-}\\ &= [\text{OH}^-]_\text{f} + \frac{K_1[\text{DPC}]}{[\text{OH}^-]}\end{aligned}$$

In view of low concentration of DPC used,

$$[\text{OH}^-]_\text{T} = [\text{OH}^-]_\text{f} \qquad \text{[A-6]}$$

Similarly

$$\begin{aligned}[\text{L-ala}]_\text{T} &= [\text{L-ala}]_\text{f} + [\text{C}]\\ &= [\text{L-ala}]_\text{f} + \text{K}_3[\text{L-ala}]\,[\text{Os(VIII)}]\end{aligned}$$

In view of low concentration of [Os(VIII)] is used,

$$\begin{aligned}[\text{L-ala}]_\text{f} &= [\text{L-ala}]_\text{T} && \text{[A-7]}\\ [\text{Os(VIII)}]_\text{T} &= [\text{Os(VIII)}_\text{f} + [\text{C}]\\ &= [\text{Os(VIII)}_\text{f} + \text{K}_3[\text{L-ala}]\,[\text{Os(VIII)}]\\ &= [\text{Os(VIII)}]_\text{f}\,\{1 + \text{K}_3[\text{L-ala}]\}\\ [\text{Os(VIII)}]_\text{f} &= \frac{[\text{Os(VIII)}]_\text{T}}{1 + \text{K}_3[\text{L-ala}]} && \text{[A-8]}\end{aligned}$$

Substituting eqn (A-5), (A-6), (A-7) and (A-8) in eqn (A-2) and omitting the T and f subscript s, we get

$$\begin{aligned}\text{Rate} &= \frac{-\text{d[DPC]}}{\text{dt}}\\ &= \frac{\text{k}_2\,\text{K}_1\,\text{K}_3[\text{DPC}]\,[\text{L-ala}]\,[\text{Os (VIII)}]}{[\text{OH}^-] + \text{K}_1 + \text{K}_3[\text{L-ala}][\text{OH}^-] + \text{K}_1\text{K}_3[\text{L-ala}]}\end{aligned} \qquad \text{[A-9]}$$

Similarly rate equation for uncatalyzed reaction can be derived.