Mechanistic Investigations on the Oxidation of L-valine by Ag(III) Periodate Complex in Alkali Media: a Kinetic Approach

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Abstract

The oxidation of an amino acid, L-valine (L-val) by diperiodatoargentate(III) (DPA) in alkaline medium at a constant ionic strength of 0.006 mol dm^{-3} was studied spectrophotometrically. The reaction between DPA and L-val in alkaline medium exhibits 1:1 stoichiometry (L-val:DPA). Intervention of free radicals was observed in the reaction. Based on the observed orders and experimental evidences, a mechanism involving the protonated diperiodatoargentate(III) (DPA) as the reactive species of oxidant has been proposed. The products were identified by spot test and characterized by spectral studies. The reaction constants involved in the different steps of the mechanism were calculated. The activation parameters with respect to slow step of the mechanism were computed and discussed. The thermodynamic quantities were determined for different equilibrium steps. Isokinetic temperature was also calculated and found to be 188.9 K.

Keywords: Kinetics, mechanism, oxidation, l-valine, diperiodatoargentate(III).

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.[2–4] L-valine is an essential amino acid with hydrocarbon side chains amino acid. It is usually found in the interior of proteins. It has an antagonistic property with structurally similar leucine and isoleucine, and imbalance among these three items results in suspension of growth. Particular symptoms of valine deficiency include loss of balance during locomotion, changes in the ventral horn and susceptibility to irritation allergens. Some of valine derivatives have antibiotic action.

Diperiodatoargentate(III) (DPA) is a powerful oxidizing agent in alkaline medium with the reduction potential,[5] 1.74 V. It is widely used as a volumetric reagent for the determination of various organic and inorganic species.[6, 7] Jaya Prakash Rao *et al.*[8] have used DPA as an oxi-

dizing 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 and on the other hand they proposed mechanisms by generalizing the DPA as [Ag(HL)L]$^{(x+1)-}$. However, Anil Kumar *et al.*[9, 10] 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 the DPA in alkaline medium. The DPA is a metal complex with Ag in 3+ oxidation state like Cu^{3+} in DPC and Fe^{3+} in hemoglobin. However, former is a single equivalent oxidant, having a structural similarity with DPA and DPC; and latter has structural dissimilarity with DPN.[11] Since multiple equilibria between different Ag(III) species are involved, it would be interesting to know which of the species is the active oxidant.

Literature survey reveals that there is no report on the oxidative mechanism of L-val by diperiodatoargentate(III). Hence, it was important and interesting for the detailed investigation of oxidation of L-valine by DPA in aqueous alkaline medium. The present study deals with

the title reaction to investigate the redox chemistry of DPA in alkaline media, to compute the thermodynamic quantities of various steps of Scheme 1 and to arrive at a suitable mechanism.

2. Experimental

2. 1. Materials and Reagents

All chemicals used were of reagent grade and millipore water was used throughout the work. A solution of L-valine (S. D. Fine Chem.) was prepared by dissolving an appropriate amount of recrystallised sample in millipore water. The purity of L-valine sample was checked by comparing its melting point 294 ^{o}C with literature data [Lit. mp. 296 °C]. The required concentration of L-valine was obtained from its stock solution. A stock solution of IO_4^- was prepared by dissolving a known weight of KIO_4 (S. D. Fine Chem.) in hot water. The stock solution was used after keeping for 24 hours to complete the equilibrium. Its concentration was ascertained iodometrically at neutral pH maintained by phosphate buffer.[12] The pH of the medium in the solution was measured by ELICO (LI 613) pH meter. KNO_3 (AR) and KOH (BDH) were used to maintain ionic strength and alkalinity of the reaction respectively. Aqueous solution of $AgNO_3$ was used to study the product effect, Ag(I).

2. 2. Preparation of DPA

DPA was prepared by oxidizing Ag(I) in presence of KIO_4 as described elsewhere:[13] the mixture of 28 g of KOH and 23 g of KIO_4 in 100 cm^3 of water along with 8.5 g $AgNO_3$ 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 as above and washed three to four times with cold water. The pure crystals were dissolved in 50 cm^3 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 recrystallised from water.

The complex was characterized from its U.V. spectrum, which 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 for silver and periodate by acidifying a solution of the material with HCl,[14] 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. Kinetic Measurements

Kinetic measurements were performed on a Varian CARY Bio-50 UV-visible spectrophotometer. The kinetics was followed under pseudo-first order condition where [L-val] > [DPA] at 25 ± 0.1 °C, unless specified. The reaction was initiated by mixing the DPA to L-val solution, which also contained required concentrations of KNO_3, KOH and KIO_4. The progress of reaction was followed spectrophotometrically at 360 nm by monitoring the decrease in absorbance due to DPA with the molar absorbancy index, 'ε' to be 13900 ± 100 dm^3 mol^{-1} cm^{-1}. It was verified that there is a negligible interference from other species present in the reaction mixture at this wavelength.

The reaction was followed to more than 90% completion of the reaction. Plots of log (absorbance) versus time lead to the first order rate constants (k_{obs}). The plots were linear up to 80% completion of reaction and rate constants were reproducible within ±5%. During the kinetics a constant concentration *viz.* 5.0×10^{-5} mol dm^{-3} of KIO_4 was used throughout the study unless otherwise stated. Thus, the possibility of oxidation of L-val by periodate was tested and found that there was no significant interference due to KIO_4 under experimental condition. The total concentration of OH$^-$ was calculated by considering the amount present in the DPA solution and that additionally added. Kinetics runs were also carried out in N_2 atmosphere in order to understand the effect of dissolved oxygen on the rate of reaction. No significant difference in the results was obtained under a N_2 atmosphere and in the presence of air. In view of the ubiquitous contamination of carbonate in the basic medium, the effect of carbonate was also studied. Added carbonate had no effect on the reaction rates.

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.

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-val in presence of constant amount of OH$^-$, KNO_3 were kept for 4 hours in a closed vessel under nitrogen atmosphere. The remaining concentration of DPA was estimated spectrophotometrically at 360 nm. The results indicated a 1:1 stoichiometry as given in Scheme 1.
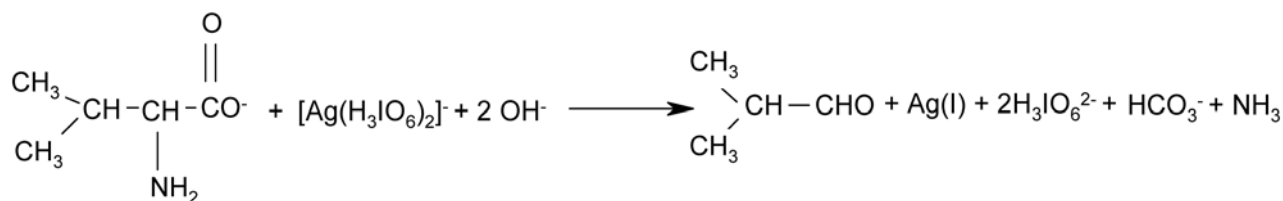
Scheme 1. Stoichiometry of the reaction

The main reaction product was identified as isobutyraldehyde by spot test.[15] The nature of aldehyde was confirmed by its IR spectrum, which showed a carbonyl stretch at 1,719 cm^{-1} and a band at 2,938 cm^{-1} due to aldehydic C–H stretch and characterized by its ^{1}H NMR spectrum (singlet at δ 9.2 ppm due to 1H of –CHO group, multiplet at δ 1.8 ppm due to 1H of –CH, a doublet at δ 1.0 ppm due to 6H of two equivalent –CH$_3$ group), thus confirming the presence of isobutyraldehyde. It was further observed that the aldehyde does not undergo further oxidation under the present kinetic conditions. A test for corresponding acid proved negative.

The by-products were identified as ammonia by Nessler's reagent,[16] the CO$_2$ was qualitatively detected by bubbling nitrogen gas through the acidified reaction mixture and passing the liberated gas through tube containing lime water. 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.

3. 2. Reaction Orders

The reaction orders were determined from the slope of log k$_{obs}$ versus log (concentration) plots by varying the concentrations of L-val, alkali in turn while keeping all other concentrations and conditions constant.

3. 3. Effect of [Diperiodatoargentate(III)]

The oxidant DPA concentration was varied in the range of 1.0×10^{-5} to 1.0×10^{-4} mol dm^{-3} and the fairly constant k$_{obs}$ values indicate that order with respect to [DPA] was unity (Table 1). This was also confirmed by linearity of the plots of log (Absorbance) versus time (r ≥ 0.998, S ≤ 0.02) up to 80% completion of the reaction (Fig. 1).

3. 4. Effect of [L-valine]

The effect of L-valine on the rate of reaction was studied at constant concentrations of alkali, DPA and periodate at a constant ionic strength of 0.006 mol dm^{-3}. The substrate, L-val was varied in the range of 1.0×10^{-4} to 1.0×10^{-3} mol dm^{-3}. The k$_{obs}$ values increased with increase in concentration of L-val. The order with respect to [L-val] was found to be less than unity (Table 1) (r ≥

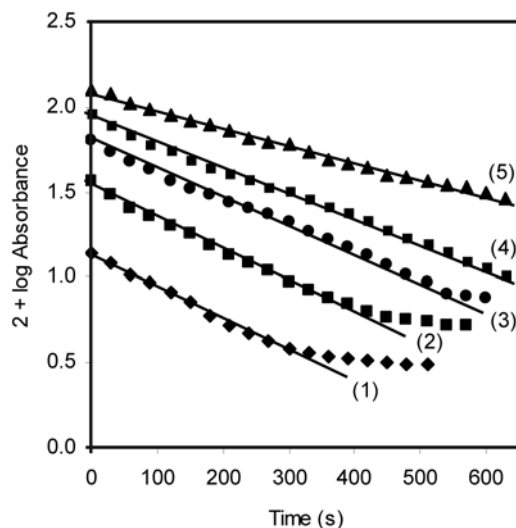**Figure 1.** First order plots for the oxidation of L-valine by DPA in aqueous alkaline medium at 25 °C [DPA]; (1) 1.0×10^{-5} (mol dm^{-3}); (2) 3.0×10^{-5} (mol dm^{-3}); (3) 5.0×10^{-5} (mol dm^{-3}); (4) 7.0×10^{-5} (mol dm^{-3}); (5) 10.0×10^{-5} (mol dm^{-3}).

0.994, S ≤ 0.004). This was also confirmed by the plots of k$_{obs}$ versus [L-val]$^{0.78}$ which is linear rather than the direct plot of k$_{obs}$ versus [L-val] (Fig. 2).

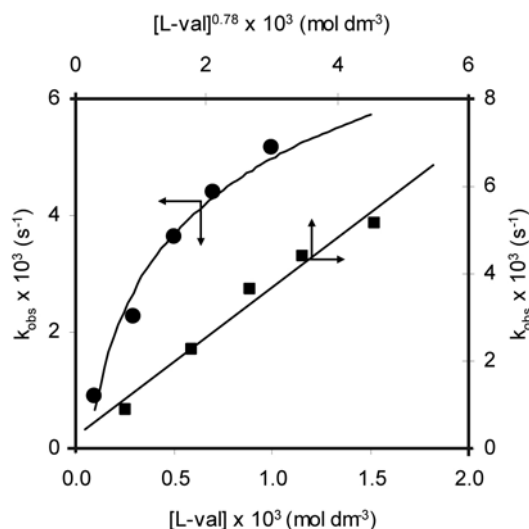**Figure 2.** Plots of k$_{obs}$ versus [L-val]$^{0.78}$ and k$_{obs}$ versus [L-val] (conditions as given in Table 1).

Table 1. Effect of variation of [DPA], [L-val], [IO_4^-] and [OH⁻] on the oxidation of L-valine by diperioda-toargentate(III) in alkaline medium at T = 298 K, *I* = 0.006 mol dm⁻³.

10^5 [DPA] (mol dm⁻³)	10^4 [L–val] (mol dm⁻³)	10^5 [IO_4^-] (mol dm⁻³)	10^3 [OH⁻] (mol dm⁻³)	10^3 k (s⁻¹) Found	10^3 k (s⁻¹) Calculated
1.0	5.0	5.0	2.0	4.23	3.42
3.0	5.0	5.0	2.0	3.80	3.42
5.0	5.0	5.0	2.0	3.63	3.42
7.0	5.0	5.0	2.0	3.74	3.42
10.0	5.0	5.0	2.0	3.44	3.42
5.0	1.0	5.0	2.0	0.89	0.88
5.0	3.0	5.0	2.0	2.26	2.31
5.0	5.0	5.0	2.0	3.63	3.42
5.0	7.0	5.0	2.0	4.39	4.31
5.0	10.0	5.0	2.0	5.15	5.34
5.0	5.0	1.0	2.0	3.63	3.42
5.0	5.0	3.0	2.0	3.79	3.42
5.0	5.0	5.0	2.0	3.56	3.42
5.0	5.0	7.0	2.0	3.48	3.42
5.0	5.0	10.0	2.0	3.33	3.42
5.0	5.0	5.0	0.2	8.00	8.87
5.0	5.0	5.0	0.5	6.96	7.01
5.0	5.0	5.0	1.0	5.35	5.19
5.0	5.0	5.0	2.0	3.63	3.42
5.0	5.0	5.0	4.0	1.99	2.03
5.0	5.0	5.0	6.0	1.45	1.45

3. 5. Effect of [Alkali]

The effect of increase in concentration of alkali on the reaction was studied at constant concentrations of L-valine, DPA and periodate at a constant ionic strength of 0.006 mol dm⁻³ at 25 °C. The rate constants decreased with increase in alkali concentration (Table 1), indicating negative fractional order dependence of rate on alkali concentration (r ≥ 0.964, S ≤ 0.003), which is rarely observed in DPA oxidation.
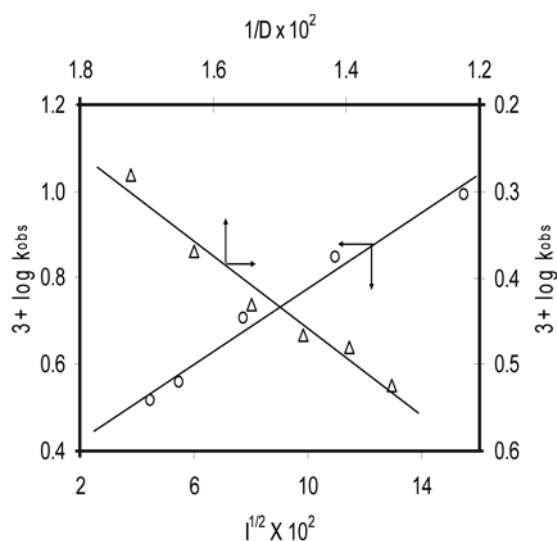
3. 6. Effect of [Periodate]

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. It was found that the added periodate had negligible effect on the rate of reaction.

3. 7. Effect of Ionic Strength (I) and Dielectric Constant of the Medium (D)

The addition of KNO_3 at constant [DPA], [L-val], [OH⁻] and [IO_4^-] was found that increasing ionic strength of the reaction medium increases the rate of the reaction (Fig. 3). 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. The decrease in dielectric constant of the reaction medium decreased the rate of reaction (Fig. 3).

Figure 3. Effect of ionic strength and dielectric constant of the medium on oxidation of L-valine by diperiodatoargentate(III) reaction at 25 °C.

3. 8. Effect of Initially Added Products

The externally added products, Ag(I) ($AgNO_3$) and isobutyraldehyde did not have any significant effect on the rate of the reaction.

3. 9. Polymerization Study

The intervention of free radicals in the reaction was examined as follows. The reaction mixture, to which a known quantity of acrylonitrile monomer was initially added, was kept for 2 hours in an inert atmosphere. On diluting the reaction mixture with methanol, a white precipitate was formed, which indicated the intervention of free radicals in the reaction.[17]

3. 10. Effect of Temperature

The kinetics was studied at six different temperatures (15, 20, 25, 30, 35 and 40 °C) under varying concentrations of L-valine and alkali keeping other conditions constant. The rate constants were found to increase with increase in temperature. The rate constants (k) of the slow step of the reaction mechanism were obtained from the slopes and intercepts of $1/k_{obs}$ versus $1/[L\text{-val}]$ and $1/k_{obs}$ versus $[OH^-]$ plots at six different temperatures and were used to calculate the activation parameters. The energy of activation corresponding to these constants was evaluated

Table 2. Thermodynamic activation parameters for the oxidation of L-valine by DPA in aqueous alkaline medium with respect to the slow step of Scheme 2.

(A) Effect of Temperature

Temperature	10^2 k (s^{-1})
288	0.61
293	0.89
298	1.22
303	1.83
308	2.75
313	3.66

(B) Activation Parameters (Scheme 2)

Parameters	Values
$\Delta H^{\#}$ (k J mol^{-1})	52 ± 2
$\Delta S^{\#}$ (J K mol^{-1})	–106 ± 4

(C) Effect of temperature to calculate K_1 and K_2 for the oxidation of L–valine by diperiodatoargentate(III) in alkaline medium.

Temperature (K)	10^4 K_1 (mol dm^{-3})	10^{-4} K_2 (dm^3 mol^{-1})
288	0.60	2.70
293	0.87	1.96
298	1.06	1.55
303	1.42	1.22
308	1.72	0.83
313	2.87	0.66

(D) Thermodynamic quantities using K_1 and K_2

Thermodynamic quantities	Values from K_1	Values from K_2
ΔH (k J mol^{-1})	43.4 ± 2.0	–42 ± 2
ΔS (J K^{-1} mol^{-1})	67 ± 3	–59 ± 3

from the Arrhenius plot of log k versus 1/T (r ≥ 0.9988, S ≤ 0.011) and other activation parameters obtained are tabulated in Table 2.

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), Ag(OH)$_4^-$, diperiodatoargentate(III) and ethylenebis (biguanide), (EBS), silver(III) are of maximum attention to the researcher due to their relative stability.[18] 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) are considerably stable;[8–14, 19, 20] the DPA is used in highly alkaline medium and EBS is used in highly acidic medium.

It is known that L-val exists in zwitterionic form in aqueous medium.[21] In highly acidic medium, it exists in the protonated form, whereas in highly basic medium it is in the fully deprotonated form.[21]

The literature survey reveals that the water soluble diperiodatoargentate(III) has a formula $[Ag(IO_6)_2]^{7-}$ with dsp^2 configuration of square planar structure, similar to diperiodatocopper(III) complex with two bidentate ligands, periodate to form a planar molecule.[13] When the same molecule is used in alkaline medium, it is unlike to be existed as $[Ag(IO_6)_2]^{7-}$ as periodate is known to be in various protonated forms depending on pH of the solution as H_5IO_6 and $H_4IO_6^-$ in pH ≤ 7; $H_3IO_6^{2-}$ and $H_2IO_6^{3-}$ in pH > 7 and dimeric form,[22] $H_2I_2O_{10}^{4-}$ in alkaline medium with highly concentrated solution. However, H_5IO_6, $H_4IO_6^-$ and $H_2I_2O_{10}^{4-}$ may be neglected as the reaction medium is alkaline and low $[IO_4^-]$ used in the study. Hence, the IO_4^- is existed as either $H_3IO_6^{2-}$ and $H_2IO_6^{3-}$ or both. 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 for diperiodatonickelate(IV).[23] On contrary, the authors in their recent past studies have proposed the DPA as $[Ag(HL)_2]^{x-}$ in which 'L' is a periodate with uncertain number of protons or 'HL' is a protonated periodate of uncertain number of protons.[8] This can be ruled out by considering the alternative form of IO_4^- at pH > 7 which is in the form $H_3IO_6^{2-}$ in the pH range 7–12 and $H_2IO_6^{3-}$ of pH ≥ 12.[22] Hence, DPA could be as $[Ag(H_3IO_6)_2]^-$ or $[Ag(H_2IO_6)]^{3-}$ depending on pH of the reaction medium.

The reaction between diperiodatoargentate(III) complex and L-valine in alkaline medium has the stoichiometry 1:1 (DPA:L-val) with a first order dependence on [DPA] and an apparent less than unit order in [substrate], a negative fractional order dependence on [alkali]. No effect of added products was observed. Based on the experimental results, a mechanism is proposed for which all the observed orders in each constituent such as [oxidant], [reductant], $[OH]^-$ and $[IO_4]^-$ may be well accommodated.

It is interesting to note that in most of the reports of DPA oxidation,[24] OH⁻ had an increasing effect on the rate of the reaction, periodate retarded the rate of reaction, MPA was considered as active species of DPA and free radical intervention was observed. However, in the present kinetic study, different kinetic results have been obtained. In this study, increasing the concentration of OH⁻ decreases the rate of the reaction and negligible effect of periodate on rate of reaction; free radical intervention was observed in the reaction and DPA itself was the active species of the reaction. The result of decrease in rate of reaction with increase in alkalinity (Table 1) can be explained in terms of prevailing equilibrium of formation of $[Ag(H_3IO_6)_2]^-$ from $[Ag(H_2IO_6)(H_3IO_6)]^{2-}$ hydrolysis as given in the following equation.

$$[Ag(H_2IO_6)(H_3IO_6)]^{2-} + H_2O$$
$$\underset{\xrightarrow{\hspace{2cm}}}{\overset{K_1}{}} [Ag(H_3IO_6)_2]^- + OH^- \qquad (1)$$
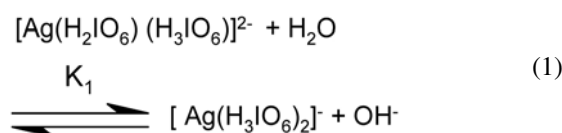
Such type of equilibrium (1) has been well noticed in literature.[24] Because of this reaction and the fact that k_{obs} values are inverse function of hydroxyl ion concentration with fractional order in OH⁻ concentration, the main oxidant species is likely to be $[Ag(H_3IO_6)_2]^-$ and its formation by the above equilibrium is important in the present study. The less than unit order in [L-val] presumably results from formation of a complex (C) between the DPA species and L-val prior to the formation of the products. This complex (C) decomposes in a slow step, to form iso-butyraldehyde, Ag(I) and periodate as given in Scheme 2.

The direct plot of k_{obs} versus [L-val] was drawn to know the parallel reaction if any along with interaction of oxidant and reductant. However, the plot of k_{obs} versus

[L-val] was not linear. Thus, in Scheme 2, the parallel reaction and involvement of two molecules of L-valine in the complex are excluded. The probable structure of the complex (C) is given in Scheme 3.
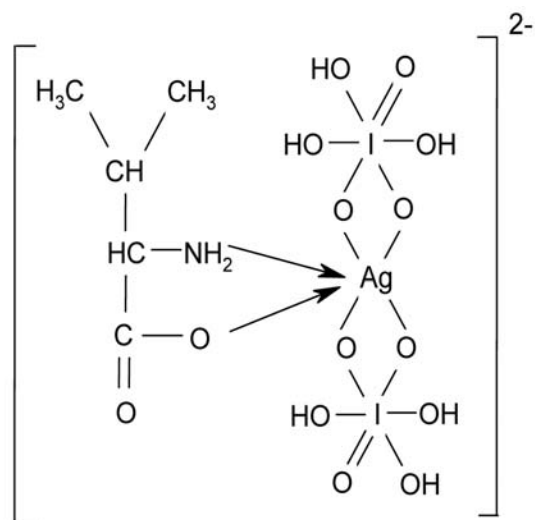

Scheme 3. The probable structure of the complex (C).

Spectroscopic evidence for the complex formation between oxidant and substrate was obtained from UV-vis spectra of [L-val] (5×10^{-4} mol dm⁻³), [DPA] (5.0×10^{-5} mol dm⁻³), [OH⁻] (0.002 mol dm⁻³) and mixture of DPA and L-val. A bathochromic shift of about 6 nm from 256 to 262 nm in the spectra of DPA was observed (Fig. 4).

However, the Michaelis-Menten plot proved the complex formation between DPA and L-val, which explains the less than unit order dependence on [L-val]. Such complex between an oxidant and substrate has also been observed in other studies.[25]
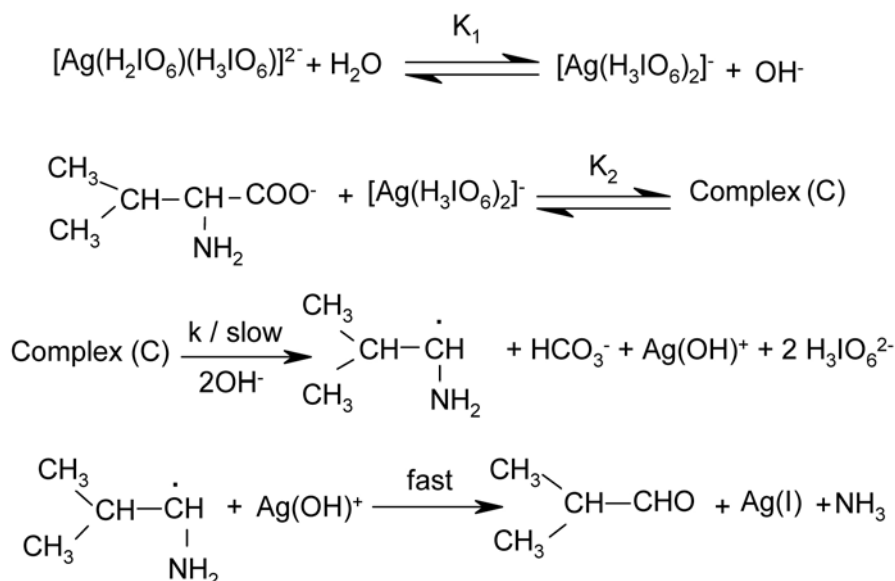
Scheme 2. Detailed Scheme for the oxidation of L-valine by alkaline diperiodatoargentate (III).
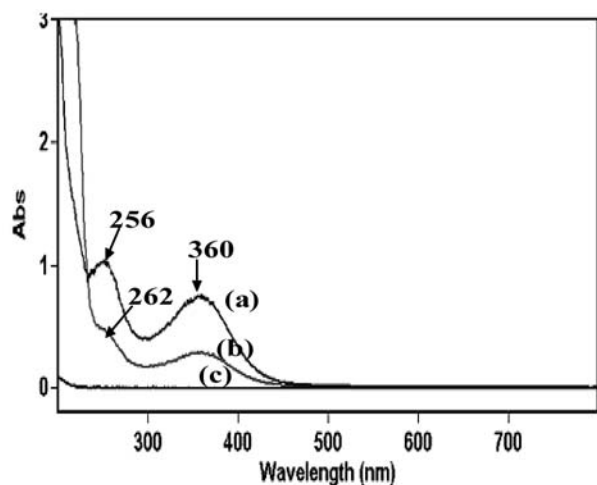
Figure 4. Spectroscopic evidence for the complex formation between DPA and L-val. (a) UV-vis spectra of DPA complex (360 nm and 256); (b) UV-vis spectra of mixture of L-val and DPA (360 nm and 262 nm); (c) UV-vis spectra of L-val;

Scheme 2 leads to the rate law (3)

$$\text{rate} = -\frac{d\,[DPA]}{dt} = \frac{k\,K_1\,K_2\,[\text{L-val}]\,[DPA]}{[OH]^- + K_1 + K_1\,K_2\,[\text{L-val}]} \quad (2)$$

$$k_{obs} = \frac{\text{rate}}{[DPA]} = \frac{k\,K_1\,K_2\,[\text{L-val}]}{[OH]^- + K_1 + K_1\,K_2\,[\text{L-val}]} \quad (3)$$

This explains all the observed kinetic orders of different species. The rate law (3) can be rearranged in the following form, which is suitable for verification.

$$\frac{1}{k_{obs}} = \frac{[OH]^-}{k\,K_1\,K_2\,[\text{L-val}]} + \frac{1}{k\,K_2\,[\text{L-val}]} + \frac{1}{k} \quad (4)$$

According to equation (4), other conditions being constant, plots of $1/k_{obs}$ versus $[OH^-]$ (r $\geq$ 0.999, S $\leq$ 0.014) and $1/k_{obs}$ versus $1/[\text{L-val}]$ (r $\geq$ 0.999, S $\leq$ 0.016) should be linear and are found to be so (Fig. 5). The slopes and intercepts of such plots lead to the values of K_1, K_2 and k as $(0.10 \pm 0.01) \times 10^{-4}$ mol dm^{-3}, $(1.5 \pm 0.03) \times 10^{+4}$ dm^3 mol^{-1}, and $(1.22 \pm 0.05) \times 10^{-2}$ s^{-1} respectively. These constants were used to calculate the rate constants and compared with the experimental k_{obs} values and found to be in reasonable agreement with each other, which fortifies Scheme 2. The effect of increasing ionic strength on the rate explains qualitatively the reac-

tion between two negatively charged ions, as seen in Scheme 2. Amis has shown that a plot of log k_{obs} versus 1/D is linear with a negative slope for a reaction between a negative ion and a dipole or two dipoles, and with a positive slope for a positive ion-dipole interaction.[26] However, in the present study, an increase in the content of t-butyl alcohol in the reaction medium leads to the increase in the reaction rate, which is in agreement with Amis theory.[26]

The thermodynamic quantities for the first and second equilibrium steps of Scheme 2 can be evaluated as follows. [L-val] and [OH$^-$] (as in Table 1) were varied at six different temperatures. The plots of $1/k_{obs}$ versus [OH$^-$] and $1/k_{obs}$ versus 1/[L-val] should be linear (Fig. 5). 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 $\geq$ 0.9882, S $\leq$ 0.006) and log K_2 versus 1/T (r $\geq$ 0.9971, 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 (43.4 $\pm$ 2.0) from K_1 with that of $\Delta H^{\#}$ (52 $\pm$ 2) of rate determining step supports that the first step of Scheme 2 is fairly fast since it involves low activation energy.[27]
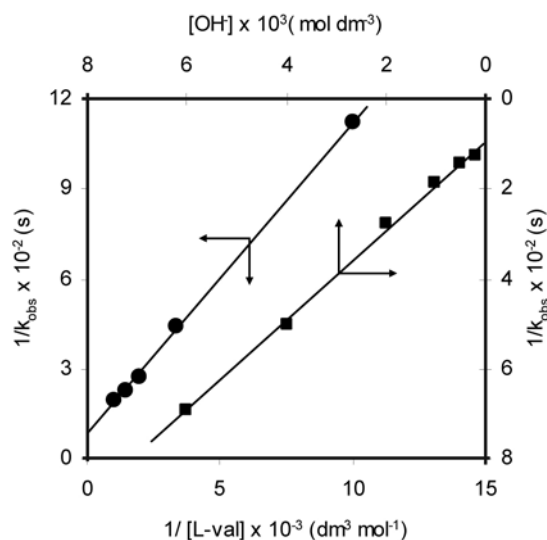
Figure 5. Verification of rate law (4) of oxidation of L-valine by DPA at 25 °C.

The values of $\Delta H^{\#}$ and $\Delta S^{\#}$ were both favourable for electron transfer processes. The favourable enthalpy was due to release of energy on solutions changes in the transition state. The negative value of $\Delta S^{\#}$ suggests that the intermediate complex is more ordered than the reactants.[28] The observed modest enthalpy of activation and a higher rate constant for the slow step indicates that the oxidation

presumably occurs via an inner-sphere mechanism. This conclusion is supported by earlier observations.[29]

The activation parameters for the oxidations of some amino acids by DPA are summarized in Table 3. The entropy of the activation for the reaction falls within the observed range. Variation in the rate within a reaction series may be caused by change in the enthalpy or entropy of activation. Changes in the 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.[30] Exner advocates an alternative method for the treatment of experimental data.[31] If the rates of several reactions in a 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 proposed that β can be evaluated from the equation.
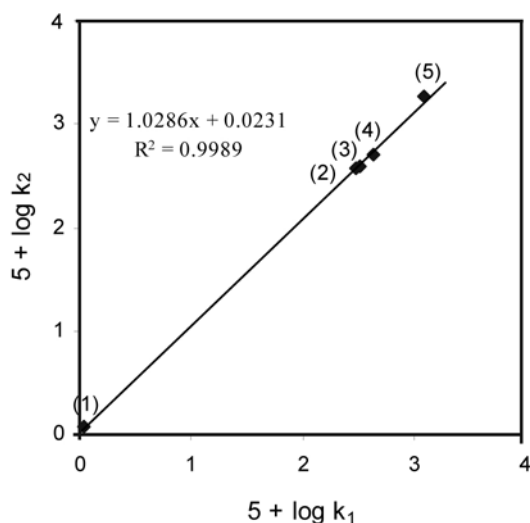
$$\beta = T_1 T_2 (b-1) / (T_2 b - T_1)$$

We have calculated the isokinetic temperature to be 188.9 K by plotting $\log k_2$ at 303 K versus $\log k_1$ at 298 K ($r \geq 0.9994$, $S \leq 0.006$) in Fig. 6. The value of β (188.9 K) is lower than experimental temperature (298 K). This indicates that the rate is governed by the entropy of activation.[32] The linearity and the slope of the plot obtained may confirm that the kinetics of these reactions follows a similar mechanism, as previously suggested.

4. Conclusion

Among various species of DPA in alkaline medium, protonated DPA i.e., $[Ag(H_3IO_6)_2]^-$ is considered as active species for the title reaction. The results indicate that, the role of pH in the reaction medium is crucial. Rate constant of slow step and other equilibrium constants involved in the mechanism are evaluated and activation parameters with respect to slow step of reaction were computed. The overall mechanistic sequence described here is consistent with product studies, mechanistic and kinetic studies.

Table 3. Activation parameters for oxidation of some amino acids (for isokinetic temperature)

Amino acids	$10^3 k_1$ (dm^3 mol^{-1} s^{-1}) at T=298 K	$10^3 k_2$ (dm^3 mol^{-1} s^{-1}) at T = 303 K	$\Delta H^{\#}$ (k J mol^{-1})	$\Delta H^{\#}$ (J K^{-1} mol^{-1})	$\Delta S^{\#}$ References
L-proline	3.3	3.84	25	–211	33
L-alanine	3.04	3.66	24	–212	33
L-isoleucine	0.011	0.012	14.9	–231	33
L-leucine	4.29	4.98	19.4	–225	33
L-valine	12.2	18.3	52.2	–106	Present work

5. Appendix

According to Scheme 2

$$\text{rate} = -\frac{d[DPA]}{dt} = k[C] = \qquad (I)$$

$$= \frac{k \, K_1 \, K_2 \, [L\text{-val}] \, [Ag(H_2IO_6)(H_3IO_6)]^{2-}}{[OH]^-}$$

Where T and f refer to total and free concentrations.

$$[DPA]_T = [DPA]_f \left[1 + \frac{K_1}{[OH]^-} + \frac{K_1 K_2 [L\text{-val}]}{[OH]^-} \right]$$

Figure 6. Plot of $\log k_2$ at 303 K versus $\log k_1$ at 298 K for isokinetic temperature (Table 3). (1) L-isoleucine; (2) L-alanine; (3) L-proline; (4) L-leucine; (5) L-valine.

y = 1.0286x + 0.0231
R² = 0.9989

$$[DPA]_f = \frac{[DPA]_T \, [OH]^-}{[OH]^- + K_1 + K_1 K_2 \, [L\text{-val}]}$$

$$[L\text{-val}]_T = [L\text{-val}]_f + [C] \tag{II}$$

$$[L\text{-val}]_f = [L\text{-val}]_T \left[\frac{[OH]^-}{[OH]^- + K_1 K_2 \, [DPA]_f} \right]$$

In view of low concentrations of DPA used, the second term of above eqn. is neglected. Therefore,

$$[L\text{-val}]_T = [L\text{-val}]_f \tag{III}$$

Similarly, $[OH]^-_T = [OH]^-_f \tag{IV}$

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

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

$$= \frac{k \, K_1 K_2 \, [L\text{-val}] \, [DPA]}{[OH]^- + K_1 + K_1 K_2 \, [L\text{-val}]} \tag{V}$$

5. References

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Povzetek

Z UV-Vis spektroskopijo smo raziskovali oksidacijo L-valina s srebrovo (III) soljo perjodove kisline (DPA) v alkalnem mediju pri konstantni ionski moči 0.006. Izkazalo se je, da reakcija med L-valinom in DPA poteče v stehiometričnem razmerju 1:1 ob sodelovanju prostih radikalov. Predpostavili smo mehanizem reakcije, ki kot reaktivno obliko oksidanta privzema protonirano obliko DPA. Produkte smo karakterizirali spektrofotometrično in s "spot" testi. Izračunali smo konstante reakcijske hitrosti za posamezne stopnje reakcije ter parametre aktivacije za posamezne stopnje. Za posamezna ravnotežja smo ocenili tudi termodinamske parametre ter izokinetično temperaturo (188.9 K).