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

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Received: 16-04-2009

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 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 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 and on the other hand they proposed mechanisms by generalizing the DPA as [Ag(HL)L]$(x+1)^-$.$^8$ However, Anil Kumar et al.$^9$ 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 °C with literature data [Lit. mp. 296 °C]. The required concentration of L-valine was obtained from its stock solution. A stock solution of 613) pH meter. KNO₃ (AR) and KOH (BDH) were used.

2.2. Preparation of DPA

DPA was prepared by oxidizing Ag(I) in presence of KIO₄ as described elsewhere.³ the mixture of 28 g of KOH and 23 g of KIO₄ in 100 cm² of water along with 8.5 g AgNO₃ was heated just to boiling and 20 g of K₂S₂O₈ 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 cm² 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 U.V. spectrum, which exhibited three peaks at 216, 255 and 362 nm. These spectral features were identical to those reported earlier for DPA.³ 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, recovering and weighing the AgCl for Ag and titrating the iodine liberated when excess of KI was added to the filtrate for IO₄⁻.

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 KNO₃, KOH and KIO₄. 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 dm³ mol⁻¹ cm⁻¹. It was verified that there was 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 (kobs). 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 KIO₄ 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 KIO₄ 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 N₂ 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 N₂ 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 polyethylene/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⁻, KNO₃ 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.
The main reaction product was identified as isobutyraldehyde by spot test. 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 \(\delta\) 9.2 ppm due to –CHO group, multiplet at \(\delta\) 1.8 ppm due to 1H of –CH, a doublet at \(\delta\) 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, 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 \(k_{\text{obs}}\) 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 \([\text{Diperiodatoargentate(III)}]\)

The oxidant DPA concentration was varied in the range of \(1.0 \times 10^{-5}\) to \(1.0 \times 10^{-4}\) mol dm\(^{-3}\) and the fairly constant \(k_{\text{obs}}\) 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 (\(r \geq 0.998\), \(S \leq 0.02\)) 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 \(1.0 \times 10^{-4}\) to \(1.0 \times 10^{-3}\) mol dm\(^{-3}\). The \(k_{\text{obs}}\) 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) (\(r \geq 0.994\), \(S \leq 0.004\)). This was also confirmed by the plots of \(k_{\text{obs}}\) versus [L-val]\(^{0.78}\) which is linear rather than the direct plot of \(k_{\text{obs}}\) versus [L-val] (Fig. 2).
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 ($r \geq 0.964, S \leq 0.003$), 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 $1.0 \times 10^{-5}$ to $1.0 \times 10^{-4}$ 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).

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/kobs versus 1/[L-val] and 1/kobs 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 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)5−, 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)5− 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;3–14, 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(IO6)2]2− with dsp2 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 unlikely to be existed as [Ag(IO6)2]2− as periodate is known to be in various protonated forms depending on pH of the solution as H2IO6− and H3IO6− in pH ≤ 7; H4IO6− and H2IO63− in pH > 7 and dimeric form,22 H5IO6− in alkaline medium with highly concentrated solution. However, H2IO6−, H3IO6− and H4IO6+ may be neglected as the reaction medium is alkaline and low [IO42−] used in the study. Hence, the IO42− is existed as either H2IO6− and H3IO63− or both. Therefore, under the present condition, diperiodatoargentate(III), may be depicted as [Ag(H3IO6)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]3+ in which ‘L’ is a periodate with uncertain number of protons or ‘HL’ is a protonated periodate of uncertain number of protons.3 This can be ruled out by considering the alternative form of IO42− at pH > 7 which is in the form H2IO6− in the pH range 7–12 and H2IO63− of pH ≥ 12.22 Hence, DPA could be as [Ag(H3IO6)2]− or [Ag(H2IO6)]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 [IO42−] may be well accommodated.

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.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>ΔH° (kJ mol⁻¹)</td>
<td>52 ± 2</td>
</tr>
<tr>
<td>ΔS° (J K⁻¹ mol⁻¹)</td>
<td>-106 ± 4</td>
</tr>
</tbody>
</table>

Table 3. Thermodynamic quantities using K1 and K2.

<table>
<thead>
<tr>
<th>Thermodynamic quantities</th>
<th>Values from K1</th>
<th>Values from K2</th>
</tr>
</thead>
<tbody>
<tr>
<td>ΔH (kJ mol⁻¹)</td>
<td>43.4 ± 2</td>
<td>-42 ± 2</td>
</tr>
<tr>
<td>ΔS (J K⁻¹ mol⁻¹)</td>
<td>67 ± 3</td>
<td>-59 ± 3</td>
</tr>
</tbody>
</table>
It is interesting to note that in most of the reports of DPA oxidation, 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$_3$IO$_6$)$_2$]$^-$ from [Ag(H$_2$IO$_6$)(H$_3$IO$_6$)]$^{2-}$ hydrolysis as given in the following equation.

\[
\frac{[\text{Ag}(\text{H}_2\text{IO}_6)(\text{H}_3\text{IO}_6)]^{2-} + \text{H}_2\text{O}}{K_1} \rightarrow [\text{Ag}(\text{H}_3\text{IO}_6)_2]^+ + \text{OH}^-
\]  

(1)

Such type of equilibrium (1) has been well noticed in literature. 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$_2$IO$_6$)$_2$]$^-$ 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 isobutyraldehyde, 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).](image)

Spectroscopic evidence for the complex formation between oxidant and substrate was obtained from UV-vis spectra of [L-val] ($5 \times 10^{-4}$ mol dm$^{-3}$), [DPA] ($5.0 \times 10^{-5}$ 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.

![Scheme 2. Detailed Scheme for the oxidation of L-valine by alkaline diperiodatoargentate (III).](image)
Scheme 2 leads to the rate law (3)

$$\text{rate} = -\frac{d [\text{DPA}]}{dt} = \frac{k K_1 K_2 [\text{L-val}] [\text{DPA}]}{[\text{OH}^-] + K_1 + K_1 K_2 [\text{L-val}]}$$  \hspace{1cm} (2)

$$k_{\text{obs}} = \frac{\text{rate}}{[\text{DPA}]} = \frac{k K_1 K_2 [\text{L-val}]}{[\text{OH}^-] + K_1 + K_1 K_2 [\text{L-val}]}$$  \hspace{1cm} (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.

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

According to equation (4), other conditions being constant, plots of $1/k_{\text{obs}}$ versus $[\text{OH}^-]$ ($r \geq 0.999, S \leq 0.014$) and $1/k_{\text{obs}}$ versus $1/[\text{L-val}]$ ($r \geq 0.999, S \leq 0.016$) should be linear and found to be so (Fig. 5). The slopes and intercepts of such plots lead to 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 $1/T$ ($r \geq 0.9982, S \leq 0.006$) and $\log K_2$ versus $1/T$ ($r \geq 0.9971, S \leq 0.007$) and the values of enthalpy of reaction $\Delta H$, entropy of reaction $\Delta S$ and free energy of reaction $\Delta G$, were calculated for the first and second equilibrium steps. These values are given in Table 2. A comparison of $\Delta H$ 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.$^{27}$

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 between two negatively charged ions, as seen in Scheme 2. Amis has shown that a plot of $\log k_{\text{obs}}$ 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.$^{26}$
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.

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

\( \beta \) 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 \( \beta \) 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 \( \beta \) can be evaluated from the equation.

\[
\beta = \frac{T_1 T_2 (b-1)}{(T_2 - T_1)}
\]

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 \( \beta \) (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., \([\text{Ag(H}_3\text{IO}_6]^-\) 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.

### 5. Appendix

According to Scheme 2

\[
\text{rate} = -\frac{d[DPA]}{dt} = k [C] = k \frac{K_1 K_2 [\text{L-val}]}{[\text{H}_3\text{IO}_6]^- [\text{Ag(H}_2\text{IO}_6] \text{[H}_2\text{IO}_6]^-)}
\]

Where \( T \) and \( f \) refer to total and free concentrations.

\[
[DPA]_f = [DPA]_t \left[ 1 + \frac{K_1}{[\text{OH}]} + \frac{K_1 K_2 [\text{L-val}]}{[\text{OH}]^2} \right]
\]
In view of low concentrations of DPA used, the second term of above eqn. is neglected. Therefore,

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

Similarly,

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

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

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

5. References

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 oksidan-ta 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).