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CHEMICAL KINETICS AND CATALYSIS

Oxidation of L-Phenylalanine by Diperiodatoargentate(III) in Aqueous Alkaline Medium. A Mechanistic Approach[1]

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Abstract—The kinetics of oxidation of L-phenylalanine (L-Phe) by diperiodatoargentate(III) (DPA) in alkaline medium at a constant ionic strength of 0.25 mol/dm^{-3} has been studied spectrophotometrically. The reaction between DPA and L-phenylalanine in alkaline medium exhibits 1 : 1 stoichiometry (L-phenylalanine : DPA). The reaction shows first order in [DPA] and has less than unit order dependence each in both [L-Phe] and [Alkali] and retarding effect of [IO_4^-] under the reaction conditions. The active species of DPA is understood to be as monoperiodatoargentate(III) (MPA). The reaction is shown to proceed via a MPA–L-Phe complex, which decomposes in a rate-determining step to give intermediates followed by a fast step to give the products. The products were identified by spot and spectroscopic studies. The reaction constants involved in the different steps of the mechanisms were calculated. The activation parameters with respect to slow step of the mechanism were computed and discussed. The thermodynamic quantities were also determined for the reaction.

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INTRODUCTION

Amino acids act not only as the building blocks in protein syntheses but they also play a significant role in metabolism. Amino acids can undergo many types of reaction depending on whether a particular amino acid contains non-polar groups or polar substituents. The oxidation of amino acids is of interest as the oxidation substrates differ for different oxidants [1, 2]. Thus, the study of amino acids becomes important because of their biological significance and selectivity towards the oxidants. Amino acids have been oxidized by variety of oxidizing agents [3].

L-Phenylalanine is an essential amino acid. It forms active sites of enzymes and helps in maintaining their proper conformation by keeping them in proper ionic states. So oxidation of L-phenylalanine may help in understanding some aspects of enzyme kinetics. L-phenylalanine, is part of almost all proteins, especially, those of animal origin. L-phenylalanine supplementation helps in the suppression of the pain and aid weight loss through the suppression of appetite. It is converted in to tyrosine, which is precursor to dopamine levels, have a definite function in sexual desire.

Diperiodatoargentate(III) DPA is a powerful oxidizing agent in alkaline medium with the reduction potential 1.74 V [4]. It is widely used as a volumetric reagent for the determination of various organic and inorganic species [5]. Jayapraksh Rao et al. [6], have used DPA as an oxidizing agent for the kinetics of oxidation of various organic substrates. They normally found that order with respect to both oxidant and substrate was unity and [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, Kumar et al. [7] put an effort to give an evidence for the reactive species form of DPA in the large scale of alkaline pH. When the silver(III) periodate complex is oxidant and multiple equilibria among different silver(III) species are involved, it would be interesting to know which is the active species of the oxidant. In the present investigation, we have obtained the evidence for the reactive species of DPA in alkaline medium. A literature survey reveals that there are no reports on the mechanistic studies of L-phenylalanine (L-Phe) oxidation by DPA. The present study is undertaken to deduce a suitable mechanism for oxidation of L-Phe by DPA on the basis of kinetic results and to understand the redox chemistry of DPA in alkaline medium.

EXPERIMENTAL

Materials and Reagents

All chemicals used were of reagent grade and double distilled water was used throughout the work. A solution of L-phenylalanine (Himedian Pvt. Ltd.,) was prepared by dissolving an appropriate amount of a recrystallised sample in double distilled water. Comparing its IR spectrum with literature data checked the

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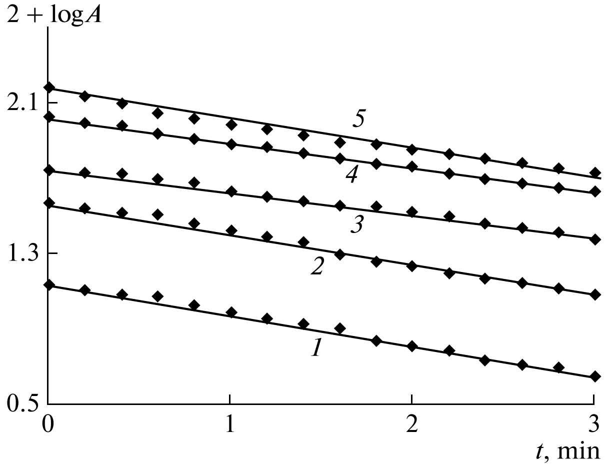


Fig. 1. First order plots for oxidation of L-phenylalanine by DPA in aqueous alkaline medium at 27°C; [DPA] × 10^5 (mol dm^3): (*1*) 1.0, (*2*) 3.0, (*3*) 5.0, (*4*) 8.0, (*5*) 10.0; *A* is absorbance.

purity of the L-Phe sample and with its m.p. 273°C (lit m.p 275°C). The required concentration of L-Phe was used from its aqueous stock solution. KNO_3 and KOH were used to maintain ionic strength and alkalinity of the reaction respectively. An aqueous solution of $AgNO_3$ was used to study the product effect, Ag(I). A stock standard solution of IO_4^- was prepared by dissolving a known weight of KIO_4 (Riedel-de Haen) in hot water and used after keeping 24 h to maintain the equilibrium. Its concentration was ascertained iodometrically [8] at neutral pH maintained using phosphate buffer. The pH of the medium in the solution was measured by ELICO LI613 pH meter.

Preparation of DPA

DPA was prepared by oxidizing Ag(I) in presence of KIO_4 as described elsewhere [9]: a mixture of 28 g of KOH and 23 g of KIO_4 in 100 cm^3 of water along with 8.5 g of $AgNO_3$ was heated just to boiling and 20 g of $K_2S_2O_8$ was added in several lots with stirring and then the mixture was allowed to cool. It was filtered through a medium porosity fritted glass filter and NaOH (40 g) was added slowly to the filtrate, whereupon a voluminous orange precipitate agglomerates. The precipitate was filtered as above and washed three to four times with cold water. The pure crystals were dissolved in water (50 cm^3) 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, orange crystals separated out and were recrystallised from water.

The complex was characterized from its UV spectrum, exhibited three peaks at 216, 255, and 362 nm. These spectral features were identical to those reported earlier for DPA [9]. The magnetic moment study reveled that the complex is diamagnetic. The compound prepared was analyzed [10] for silver and periodate by acidifying a solution of the material with HCl, recovering and weighing the AgCl for Ag and titrating the iodine liberated when excess KI was added to the filtrate for IO_4^-. The aqueous solution of DPA was used for the required in the reaction mixture. During the kinetics a constant concentration, viz. 1.0×10^{-5} mol dm^{-3} of KIO_4 was used throughout the study unless otherwise stated. Thus, the possibility of oxidation of L-Phe by periodate was tested and found that there was no significant interference due to KIO_4 under experimental conditions.

Kinetic Measurements

The kinetics was followed under pseudo first-order condition where [L-Phe] > [DPA] at 27 ± 0.1°C, unless otherwise specified. The reaction was initiated by mixing the DPA to L-Phe solution, which also contained the required concentration 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 pseudo first order rate constants, k_{obs}, were determined from the log*A* (*A* is absorbance) *vs* time plots. The plots were linear up to 80% (Fig. 1) completion of reaction under the range of $[OH^-]$ used.

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

Kinetics runs were also carried out under 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, however fresh solutions were nevertheless used for carrying out each kinetic only. The spectroscopic changes during the reaction are shown in Fig. 2. It is evident from the Fig. 2 that the concentration of DPA decreases at 360 nm.

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.

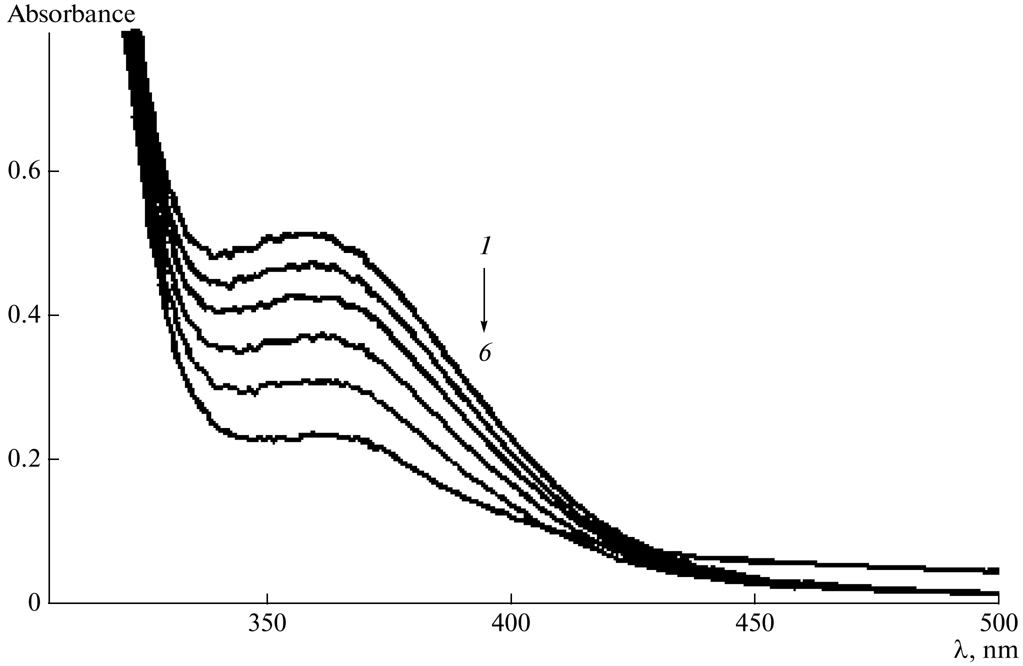
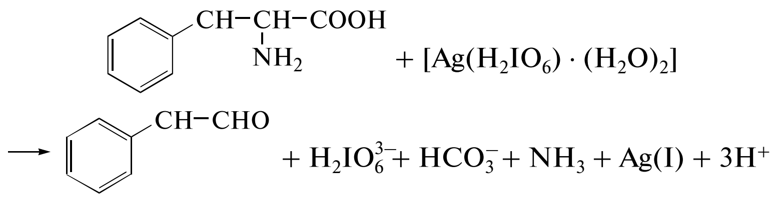


Fig. 2. Spectroscopic changes occurring in the oxidation of L-phenylalanine by [diperiodatoargentate(III)] at 27°C, [DPA] = 5.0×10^{-5}, [L-Phe] = 5.0×10^{-4}, [OH^-] = 0.05, and $I = 0.02$ mol/dm^3 with scanning time of: (*1*) 0.5, (*2*) 1.0, (*3*) 1.5, (*4*) 2.0, (*5*) 2.5, and (*6*) 3.0 min.

RESULTS

Stoichiometry and Product Analysis

Different sets of reaction mixtures containing varying ratios of DPA to L-phenylalanine in presence constant amount of OH^-, KNO_3, and KIO_4, were kept for 3 h in closed vessel under nitrogen atmosphere. The remaining concentration of DPA was estimated by spectrophotometrically at 360 nm. The results indicate that one mole of DPA consumed one mole of L-phenylalanine (1 : 1 stoichiometry) as given in equation:



(1)

The main oxidation products were identified as corresponding aldehyde (phenyl acetaldehyde) by spot test [11], ammonia by Nessler's reagent and 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. Preparing its 2.4-DNP derivative identified the corresponding aldehyde. Such products were also obtained in previous work [12]. The nature of phenyl acetaldehyde was confirmed by its IR spectrum which showed a C=O stretching at 1630 cm^{-1} indicating the presence of aldehydic C=O and C–H stretching at 2855 cm^{-1}. The formation of free Ag^+ in solution was detected by adding KCl solution to the reaction mixture, which produced white turbidity due to formation of AgCl. It was observed that phenyl acetaldehyde does not undergo further oxidation under the present kinetic conditions.

The reaction orders were determined from the slopes of $\log k_{obs}$ vs. $\log c$ (c is concentration) plots by varying the concentration of the reductant and alkali in turn while keeping other conditions constant. The DPA concentration was varied in the range of 1.0×10^{-5} to 1.0×10^{-4} mol dm^{-3} and the linearity of the plots of $\log A$ vs. time up to 80% completion of the reaction indicates a reaction order of unity in [DPA]. This is also confirmed by varying [DPA], which did not result in any change in the pseudo first order rate constants, k_{obs} (Table 1). The L-phenylalanine concentration was varied in the range of 3.0×10^{-4} to 3.0×10^{-3} mol dm^{-3} at 27°C while keeping other reactant concentrations

Table 1. Effect of [DPA], [L-Phe], [IO_4^-], and [OH^-] on diperiodatoargentate(III) oxidation of L-phenylalanine in alkaline medium at 27°C, $I = 0.25$ mol dm^{-3}

[DPA] × 10^5, mol dm^{-3}	[L-Phe] × 10^4, mol dm^{-3}	[OH^-], mol dm^{-3}	[IO_4^-] × 10^5, mol dm^{-3}	$k_{obs} \times 10^3$, s^{-1}	$k_{cal} \times 10^3$, s^{-1}
1.0	5.0	0.05	1.0	4.6	4.6
3.0	5.0	0.05	1.0	4.5	4.6
5.0	5.0	0.05	1.0	4.7	4.6
8.0	5.0	0.05	1.0	4.6	4.6
10.0	5.0	0.05	1.0	4.4	4.6
5.0	3.0	0.05	1.0	4.0	3.6
5.0	5.0	0.05	1.0	4.6	4.6
5.0	8.0	0.05	1.0	5.1	6.0
5.0	10.0	0.05	1.0	6.0	6.6
5.0	20.0	0.05	1.0	7.0	8.4
5.0	30.0	0.05	1.0	8.0	9.2
5.0	5.0	0.01	1.0	2.0	2.0
5.0	5.0	0.03	1.0	4.0	3.8
5.0	5.0	0.05	1.0	4.6	4.6
5.0	5.0	0.08	1.0	5.1	5.3
5.0	5.0	0.1	0.5	5.5	5.5
5.0	5.0	0.05	0.5	6.9	5.5
5.0	5.0	0.05	0.8	5.6	4.9
5.0	5.0	0.05	1.0	4.6	4.6
0.5	5.0	0.05	3.0	3.5	2.8
0.5	0.5	0.05	5.0	2.7	2.0

and conditions constant. The k_{obs} values increased with the increase in concentration of L-phenylalanine indicating an apparent less than unit order dependence on [L-Phe] (Table 1). The effect of alkali on the reaction has been studied in the range of 0.01 to 0.1 mol dm^{-3} at constant concentrations of L-phenylalanine, DPA and a constant ionic strength of 0.25 mol dm^{-3}. The rate constants increased with increasing [alkali] and the order was found to less than unity (Table 1).

Effect of [periodate]. Periodate concentration was varied from 5.0×10^{-6} to 5.0×10^{-5} mol dm^{-3} at constant [DPA], [L-Phe], and ionic strength. It was observed that the rate constants decreased by increasing [IO_4^-] (Table 1).

Table 2. Thermodynamic activation parameters for the oxidation of L-phenylalanine by DPA in aqueous medium with respect to the slow step of Scheme 1

T, K	$k \times 10^3$, s^{-1}	K_1, dm^3 mol^{-1}	$K_2 \times 10^4$, dm^3 mol	$K_3 \times 10^{-4}$, mol dm^{-3}
295	7.0	0.17 ± 0.007	1.35 ± 0.06	2.73 ± 0.11
300	8.0	0.25 ± 0.011	2.08 ± 0.08	1.34 ± 0.06
305	8.6	0.40 ± 0.018	2.44 ± 0.1	0.95 ± 0.04
310	10.3	0.64 ± 0.028	3.02 ± 0.13	0.52 ± 0.02

Effect of added products. Initially added products, Ag(I) and aldehyde did not have any significant effect on the rate of reaction.

Effect of ionic strength (*I*) and dielectric constant of the medium (*D*). It was found that ionic strength and dielectric constant of the medium had no significant effect on the rate of reaction.

Effect of temperature (*T*). The influence of temperature on the k_{obs} values were studied at 22, 27, 32, and 37°C. The rate constants, k, of the slow step of Scheme 1 were obtained from the slopes and the intercept of the plots of $1/k_{obs}$ vs. $1/[\mathrm{Phe}]$, $1/k_{obs}$ vs. $1/[OH^-]$, and $1/k_{obs}$ vs. [$H_3IO_6^{2-}$] at four different temperatures. The values are given in Table 2. The activation parameters for the rate determining step were obtained by the least square method of plot of $\log k$ vs. $1/T$: $E_a = 18.4 \pm 0.8$ kJ mol^{-1}, $\Delta H^{\#} = 15.9 \pm 0.7$ kJ mol^{-1}, $\Delta S^{\#} = -231 \pm 11$ J K^{-1} mol^{-1}, $\Delta G^{\#} = 85.4 \pm 4$ kJ mol^{-1}.

Test for Free Radicals

The intervention of free radicals was examined for reaction is as follows, the reaction mixture, to which a known quantity of acrylonitrile scavenger has been added initially, was kept in an inert atmosphere for 2 h. Upon diluting the reaction mixture with methanol, precipitate resulted, suggesting there is participation of free radicals in the reaction.

DISCUSSION

In the later period of 20th century 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 researchers due to their relative stability [13]. 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 Ag(III) [6, 7, 14] are considerably stable; the DPA is used in highly alkaline medium and EBS is used in highly acidic medium.

The literature survey [9] revels that the water soluble diperiodatoargentate(III) (DPA) has a formula $[Ag(IO_6)_2]^{7-}$ with *dsp*^{2} configuration of square planar structure, similar to doperiodatocopper(III) complex with two bidentate ligands, periodate to form a planar molecule. When the same molecule is used in alkaline medium, it is unlike to be existed as $[Ag(IO_6)_2]^{7-}$, as periodate is known to be in various protonated forms [15] depending on pH of the solution as given in following multiple equilibria:

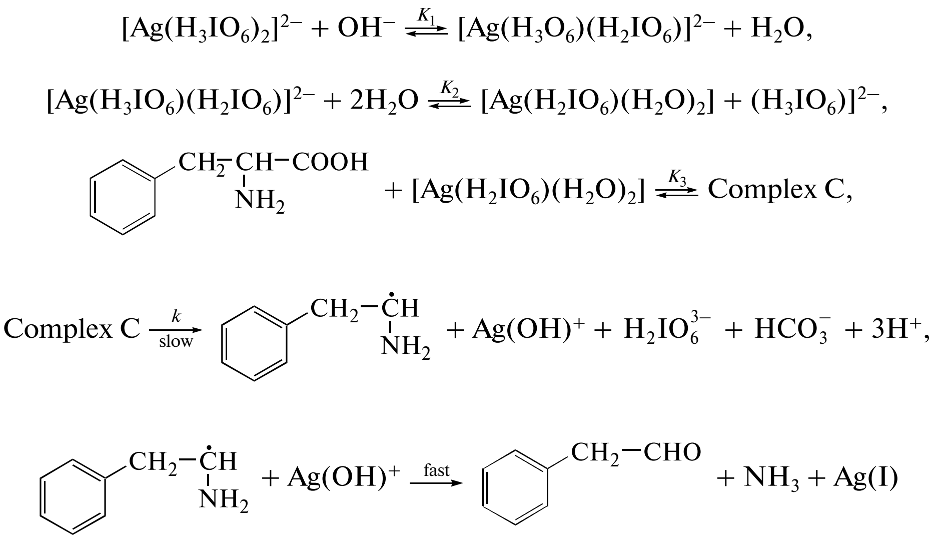
$$H_5IO_6 \rightleftharpoons H_4IO_6^- + H^+, \quad (2)$$

$$H_4IO_6^- \rightleftharpoons H_3IO_6^{2-} + H^+, \quad (3)$$

$$H_3IO_6^{2-} \rightleftharpoons H_2IO_6^{3-} + H^+. \quad (4)$$

Periodic acid exists as (H_5IO_6) in acid medium and as $H_4IO_6^-$ at pH 7. Thus, under the present alkaline conditions, the main species are expected to be $H_3IO_6^{2-}$ and $H_2IO_6^{3-}$. At higher concentrations, periodate also tends to dimerise [4]. On contrary, the authors [6] 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 and HL is a protonated periodate of uncertain number of protons. This can be ruled out by considering the alternative form [15] of IO_4^- at $pH > 7$ which is in the form $H_3IO_6^{2-}$ or $H_2IO_6^{3-}$. Hence, DPA could be as $[Ag(H_3IO_6)_2]^-$ or $[Ag(H_2IO_6)_2]^{3-}$ in alkaline medium. Therefore, under the present condition, diperiodatoargentate(III), may be depicted as $[Ag(H_3IO_6)_2]^-$. The similar speciation of periodate in alkali was proposed [16] for diperiodatonickelate (IV).

The reaction between DPA and L-phenylalanine in alkaline medium presents a 1 : 1 stoichiometry of oxidant to reductant. Since, the reaction was enhanced by $[OH^-]$, added periodate retarded the rate and first order dependency in [DPA] and fractional order in [L-Phe] and $[OH^-]$, the following mechanism has been proposed which also explains all other experimental observations (Scheme 1).



Scheme 1.

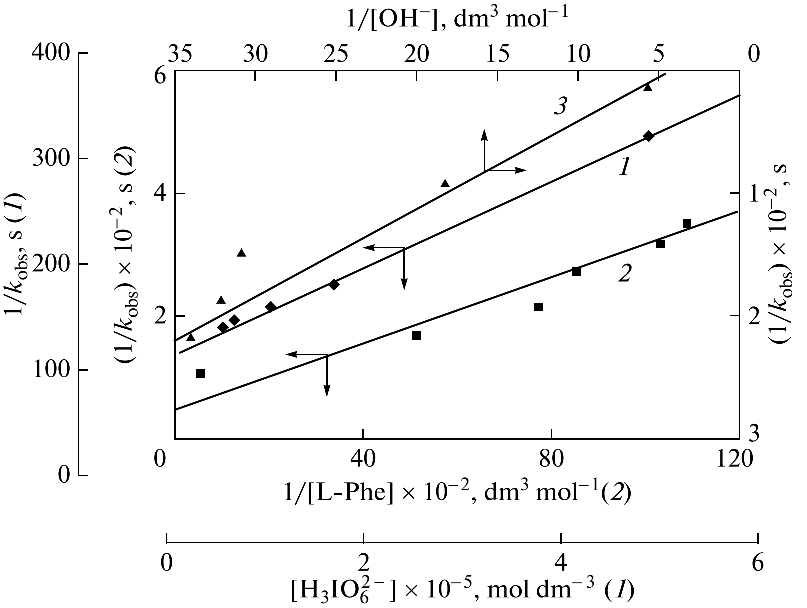
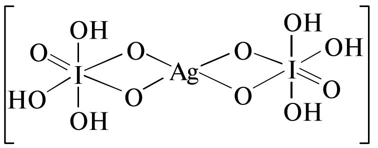


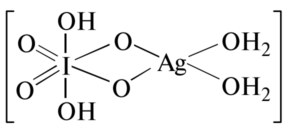
Fig. 3. Verification of rate law (3) for the oxidation of L-phenylalanine diperiodatoargentate(III) at 27°C.

In the prior equilibrium step 1, the [OH$^-$] deprotonates the DPA to give a deprotonated diperiodatoargentate(III); in the second step displacement of a ligand, periodate takes place to give free periodate which is evidenced by decrease in the rate with increase in [periodate] (Table 1). It may be expected that lower Ag(III) periodate species such as monoperiodatoargantate(III) (MPA) is more important in the reaction than the DPA. The inverse fractional order in $[H_3IO_6]^{2-}$ might also be due to this reason. In the prerate determining stage, this monoperiodateargentate (MPA), combines with a molecule of L-Phe to give an intermediate complex C, which decomposes in a slow step to give free radical derived from L-phenylalanine, acetate ion and Ag(II) species by one equivalent changes of Ag(III) in a single step as intervention of free radical has been observed. This free radical of L-phenylalanine reacts with Ag(II) species in a fast step to yield the products. The plot of $1/k_{obs}$ vs. 1/[L-Phe] proved the complex formation between oxidant and reductant, which explains less than unit order in [L-Phe].

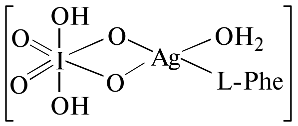
Since Scheme 1 is in accordance with generally well-accepted principle of non-complementary oxidations taking place in sequence of one-electron steps, the reaction between the substrate and oxidant would afford a radical intermediate. A free radical scavenging experiment revealed such a possibility as given in experimental section. This type of radical intermediate has been observed in earlier work [17]. On the basis of square planar structure of DPA, the structure of MPA and complex may be proposed as below:



(DPA)



(MPA)



(Complex)

Spectroscopic evidence for the complex formation between oxidant and substrate was obtained from UV-VIS spectra of L-phenylalanine (5.0 × 10^{-4}), [DPA] = 5×10^{-5}, [OH$^-$] = 0.05 mol/dm^{-3}) and mixture of both. A hypsochromic shift of about 5 nm from 237 to 232 nm in the spectra of DPA was observed. However, the Linewear–Burk plot proved the complex formation between oxidant and reductant, which explains less than unit order in [L-Phe]. Such a complex between a substrate and a oxidant has been observed in other studies [18]. The rate law for the Scheme 1 could be derived as (see Appendix),

Table 3. Thermodynamic quantities using K_1, K_2, and K_3

Quantities	From K_1	From K_2	From K_3
ΔH, kJ mol^{-1}	65.4 ± 3	39.2 ± 1.8	−80.9 ± 3.8
ΔS, J K^{-1} mol^{-1}	208 ± 9	60.0 ± 2.5	−191 ± 0.8
ΔG_{300}, kJ mol^{-1}	3.3 ± 0.15	20.9 ± 0.9	−22.5 ± 1.02

$$\text{Rate} = \frac{d[\text{DPA}]}{dt} = \frac{kK_1K_2K_3[\text{DPA}][\text{L-Phe}][\text{OH}^-]}{[\text{H}_3\text{IO}_6^{2-}] + K_1[\text{OH}^-][\text{H}_3\text{IO}_6^{2-}] + K_1K_2[\text{OH}^-] + K_1K_2K_3[\text{OH}^-][\text{L-Phe}]},$$

$$k_{\text{obs}} = \frac{kK_1K_2K_3[\text{L-Phe}][\text{OH}^-]}{[\text{H}_3\text{IO}_6^{2-}] + K_1[\text{OH}^-][\text{H}_3\text{IO}_6^{2-}] + K_1K_2[\text{OH}^-] + K_1K_2K_3[\text{OH}^-][\text{L-Phe}]}.$$

The rate law can be rearranged in to the following form which is suitable for verification

$$\frac{1}{k_{\text{obs}}} = \frac{[\text{H}_3\text{IO}_6^{2-}]}{kK_1K_2K_3[\text{L-Phe}][\text{OH}^-]} + \frac{[\text{H}_3\text{IO}_6^{2-}]}{kK_2K_3[\text{L-Phe}]} + \frac{1}{kK_3[\text{L-Phe}]} + \frac{1}{k}.$$

According to this equation, the plots of $1/k_{\text{obs}}$ vs. $[\text{H}_3\text{IO}_6^{2-}]$ ($r \geq 0.9995$, $S \leq 0.00132$), $1/k_{\text{obs}}$ vs. $1/[\text{OH}^-]$ ($r \geq 0.9996$, $S \leq 0.00086$), and $1/k_{\text{obs}}$ vs. 1/[L-Phe] ($r \geq 0.9992$, $S \leq 0.00089$) were linear (Fig. 3). From the intercepts and slopes of such plots, the reaction constants, K_1, K_2, K_3, and k were calculated as 0.25 ± 0.01 $\text{dm}^3\ \text{mol}^{-1}$, (2.08 ± 0.08) × 10^{-4} mol dm^{-3} (1.34 ± 0.06) × 10^4 $\text{dm}^3\ \text{mol}^{-1}$, 8.0 × 10^{-3} s^{-1} respectively. The values of K_1 and K_2 obtained were in agreement with earlier work [19]. These constants were used to calculate rate constant and compared with the experimental k_{obs} values and found to be reasonable agreement with each other, which fortifies the Scheme 1 (Table 1). The equilibrium constant K_1 is far greater than K_2 which may be attributed to the greater tendency of DPA to undergo deprotonation compared to the formation of hydrolysed species in alkaline medium.

The thermodynamic quantities for the different equilibrium steps, in Scheme 1 can be evaluated as follows. The L-phenylalanine and hydroxide ion concentration (Table 1) were varied at different temperatures. The plots of $1/k_{\text{obs}}$ vs. 1/[L-Phe] ($r \geq 0.9993$, $S \leq 0.00131$) and $1/k_{\text{obs}}$ vs. 1/[OH] ($r \geq 0.9994$, $S \leq 0.00087$) should be linear as shown in (Fig. 3). From the slopes and intercepts, the values of K_1 are calculated at different temperatures. A van't Hoff's plot was made for the variation of K_1 with temperature [i.e., $\log K_1$ vs. $1/T$ ($r \geq 0.9993$, $S \geq 0.1107$)] 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 3. A comparison of the latter values with those obtained for the slow step of the reaction shows that these values mainly refer to the rate-limiting step, supporting the fact that the reaction before the rate-determining step is fairly slow and involves a higher activation energy [20]. In the same manner, K_2 and K_3 values were calculated at different temperatures and the corresponding values of thermodynamic quantities are given in Table 2.

The negative value of $\Delta S^{\#}$ suggests that the intermediate complex is more ordered than the reactants [19]. The observed modest activation energy and sizeable entropy of activation supports a complex transition state in the reaction.

APPENDIX

According to Scheme 1

$$\text{Rate} = k[\text{C}] = kK_1K_2K_3[\text{Ag}(\text{H}_3\text{IO}_6)_2][\text{OH}^-][\text{L-Phe}]/[\text{H}_3\text{IO}_6^{2-}],$$

$$[\text{DPA}]_{\text{T}} = [\text{DPA}]_{\text{f}} + [\text{Ag}(\text{H}_3\text{IO}_6)\cdot(\text{H}_2\text{IO}_6)]^{2-} + [\text{Ag}(\text{H}_3\text{IO}_6)\cdot(\text{H}_2\text{O})_2] + [\text{C}],$$

$$[\text{DPA}]_{\text{f}} = \frac{[\text{DPA}]_{\text{T}}[\text{H}_3\text{IO}_6^{2-}]}{[\text{H}_3\text{IO}_6^{2-}] + K_1[\text{OH}^-][\text{H}_3\text{IO}_6^{2-}] + K_1K_2[\text{OH}^-] + K_1K_2K_3[\text{OH}^-][\text{L-Phe}]},$$

$$\begin{aligned}[\text{OH}]_{\text{T}} &= [\text{OH}]_{\text{f}} + [\text{Ag}(\text{H}_3\text{IO}_6)\cdot(\text{H}_2\text{IO}_6)]^{2-} + [\text{Ag}(\text{H}_3\text{IO}_6)\cdot(\text{H}_2\text{O})_2] \\ &= [\text{OH}]_{\text{f}} + K_1[\text{DPA}][\text{OH}^-] + K_2[\text{DPA}]/[\text{H}_3\text{IO}_6^{2-}].\end{aligned}$$

In view of the low concentration of [DPA] and $[\text{H}_3\text{IO}_6^{2-}]$ used

$$[\text{OH}^-]_{\text{T}} = [\text{OH}^-]_{\text{f}}. \quad (5)$$

Similarly,

$$[\text{L-Phe}]_T = [\text{L-Phe}]_f + [C] = [\text{L-Phe}]_f + K_1K_2K_3[\text{DPA}][\text{OH}^-][\text{L-Phe}]/[\text{H}_3\text{IO}_6]^{2-}$$

$$= [\text{L-Phe}]_f[1 + K_1K_2K_3[\text{DPA}][\text{OH}^-]/[\text{H}_3\text{IO}_6^{2-}]].$$

In view of the low concentration of [DPA], [OH⁻], and $[\text{H}_3\text{IO}_6^{2-}]$ used

$$[\text{L-Phe}]_T = [\text{L-Phe}]_f. \tag{6}$$

Substituting (2), (3), and (4) in (1) and omitting the subscripts T and f, we get

$$\text{rate} = \frac{kK_1K_2K_3[\text{DPA}][\text{L-Phe}][\text{OH}^-]}{[\text{H}_3\text{IO}_6^{2-}] + K_1[\text{OH}^-][\text{H}_3\text{IO}_6^{2-}] + K_1K_2[\text{OH}^-] + K_1K_2K_3[\text{OH}^-][\text{L-Phe}]}.$$

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