Thermodynamic quantities for the different steps involved in the mechanism of osmium(VIII) catalysed oxidation of L-lysine by a new oxidant, diperiodatoargentate(III) (stopped flow technique)

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Abstract

The kinetics of Os(VIII) catalysed oxidation of L-lysine by diperiodatoargentate(III) (DPA) in alkaline medium at $T = 298$ K and a constant ionic strength of $0.50 \text{ mol} \cdot \text{dm}^{-3}$ was studied spectrophotometrically. The oxidation products are aldehyde (5-aminopentanal) and Ag(I). The stoichiometry is *i.e.* [L-lysine]:[DPA] = 1:1. The reaction is of first order in [Os(VIII)] and [DPA] and is less than unit order in both [L-lys] and [alkali]. Addition of periodate has no effect on the reaction. Effect of added products, ionic strength, and dielectric constant of the reaction medium have been investigated. The oxidation reaction in alkaline medium has been shown to proceed *via* a Os(VIII)-L-lysine complex, which further reacts with one molecule of deprotonated DPA in a rate determining step followed by other fast steps to give the products. The main products were identified by spot test, IR, and GC-MS. The reaction constants involved in the different steps of the mechanism are calculated at different temperatures. The catalytic constant (K_c) was also calculated at different temperatures. From the plots of $\lg K_c$ *versus* $1/T$, values of activation parameters with respect to the catalyst have been evaluated. The activation parameters with respect to slow step of the mechanism are computed and discussed and thermodynamic quantities are also determined. The active species of catalyst and oxidant have been identified.
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1. Introduction

Amino acids act not only as the building blocks in protein synthesis but they also play a significant role in metabolism. Amino acids can undergo many types of reaction depending upon whether a particular amino acid contains non-polar groups or polar substituents. The oxidation of amino acids is of interest as the oxidation products differ for different oxidants [1,2]. Thus, the study of amino acids becomes important because of their biological significance and selectivity towards the oxidant. L-lysine (2,6-diaminohexanoic acid and alpha, epsilon-diaminocaproic acid) [L-lys] is a protein amino acid. L-lysine is a basic amino acid

and carries a positive charge at physiological pH. L-lysine, along with other amino acids, participates in protein biosynthesis.

Diperiodatoargentate(III) (DPA) is a powerful oxidizing agent in alkaline medium with the reduction potential [3a] 1.74 V. It is widely used as a volumetric reagent for the determination of various organic and inorganic species [4]. Jayaprakash Rao *et al.* [5] 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 observe 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.* [6] worked to provide evidence for the reactive

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form of DPA for the large scale alkaline pH. In the present investigation, we have obtained the evidence for the reactive species for DPA in alkaline medium.

In recent years, the use of transition metal ions such as osmium, ruthenium, and iridium, either alone or as binary mixtures, as catalysts in various redox processes has attracted considerable interest [7]. The role of osmium-(VIII) as a catalyst in some redox reactions has been reviewed [8]. Although the mechanism of catalysis depends on the nature of the substrate, oxidant, and under experimental conditions, it has been shown [9] that metal ions act as catalysts by one of these different paths such as the formation of complexes with reactants or oxidation of the substrate itself or through the formation of free radicals. Osmium(VIII) catalysis in redox reactions involves several complexes, different oxidation states of osmium, *etc.* The uncatalysed reaction of oxidation of L-lysine by DPA has been studied [10]. We have observed that osmium(VIII) catalyzes the oxidation of L-lysine by DPA in alkaline medium in micro amounts.

In earlier reports [11] of DPA oxidation, periodate had a retarding effect in almost all the reactions and monoperiodatoargentate(III) (MPA) was considered to be the active species. However, in the present study, we have observed entirely different kinetic observations, *i.e.*, deprotonated diperiodatoargentate(III) (DPA) is found to be active form of the oxidant. In order to understand the active species of oxidant and catalyst, and to propose the appropriate mechanism, the title reaction is investigated in detail.

2. Experimental

2.1. Materials and reagents

All chemicals used were of reagent grade and double distilled water was used throughout the work. A solution of L-lysine (s.d-Fine) was prepared by dissolving an appropriate amount of re-crystallized sample in double distilled water. The purity of L-lysine sample was checked by comparing its I.R. spectrum with literature data and with its m.p. $T_f = (534 \text{ to } 536) \text{ K}$ [lit. $T_f = 536 \text{ K}$]. The required concentration of L-lysine was obtained from its stock solution. The osmium(VIII) solution was prepared by dissolving OsO_4 (Johnson Matthey) in $0.50 \text{ mol} \cdot dm^{-3}$ NaOH. The concentration was ascertained [12] by determining the unreacted $[Fe(CN)_6]^{4-}$ with standard Ce(IV) solution in an acidic medium. 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 for 24 h. Its concentration was ascertained by iodometrically [13] at neutral pH maintained using phosphate buffer. The pH of the medium in the solution was measured by ELICO (LI613) pH meter.

2.2. Preparation of DPA

The DPA was prepared by oxidizing Ag(I) in the presence of KIO_4 as described elsewhere [14]: the mixture of 28 g of KOH and 23 g of KIO_3 in 100 cm^3 of water along with 8.5 g $AgNO_3$ was heated just to boiling and 20 g of $K_2S_2O_8$ were 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 $T = 353 \text{ K}$ 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 re-crystallized from water.

The complex was characterized from its UV spectrum, which exhibited three peaks at (216, 255, and 362) nm. These spectral features were identical to those reported earlier for DPA [14]. The magnetic moment study revealed that the complex is diamagnetic. The compound prepared was analysed [15] for silver and periodate by acidifying a solution of the material with HCl, recovering and weighing the AgCl for Ag and titrating the iodine liberated when excess of KI was added to the filtrate for IO_4^-. The stock solution of DPA was used for the required [DPA] solution in the reaction mixture. During the kinetics a constant concentration *viz.* $1.0 \cdot 10^{-4} \text{ mol} \cdot dm^{-3}$ of KIO_4 was used throughout the study unless otherwise stated. Thus, the possibility of oxidation of L-lysine by periodate was tested and found that there was no significant interference due to KIO_4 under experimental condition. The effect of dissolved oxygen on the rate of reaction was checked by preparing the reaction mixture and following the reaction in an atmosphere of nitrogen. No significant difference between the results under nitrogen atmosphere and in the presence of air was observed.

2.3. Kinetic measurements

Since the initial reaction was too fast to be monitored by usual methods, kinetic measurements were performed on a Hitachi 150-20 Spectrophotometer connected to a rapid kinetic accessory (HI-TECH SFA-12).

The kinetics were followed under pseudo-first order condition where [L-lys] > [DPA] at $T = (298 \pm 0.1) \text{ K}$, unless specified. The reaction was initiated by mixing the DPA to L-lysine solution which also contained the required concentration of KNO_3, KOH, catalyst Os(VIII), 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 $(13,900 \pm 100) \text{ dm}^3 \cdot mol^{-1} \cdot cm^{-1}$. 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_T', were determined from the lg(absorbance) against time plots. The plots were linear up to 85% completion of reaction under the range of [OH⁻] used. The total periodate concentration