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Research Article

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Oxidation kinetics of L-glutamine by µ-peroxo complex in aqueous medium

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ABSTRACT

A requisite quantity of µ-peroxo-bis[aminebis(ethylenediamine)cobalt(III)]perchlorate dihydrate was prepared by solution route method. Complex characterization was done by using FT-IR and electronic spectroscopy. Kinetic Oxidations of L-glutamine by µ-peroxo complex has been deliberated in an aqueous medium. The reaction rate measurements were carried out under pseudo first order conditions. The effect of peroxo complex and effect of hydrogen ion concentration shows first order kinetics in the oxidation reaction. Change in the concentration of ionic strength has no effect on the reaction rate during the oxidation. Kinetic measurement was carried out by potentiometric method. Activation and thermodynamics parameters were calculated and a suitable mechanism has been proposed.

Keywords: Kinetics, Oxidation, peroxo complex, L-glutamine, Activation parameters

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INTRODUCTION

Enzymes catalyze a wide range of reactions under mid conditions and often with high selectivity. Understanding their mechanism and attempting to mimic their reaction with chemical systems has provided chemists with important challenges and research goals [1]. Amino acids are biologically important organic compounds composed of amine ($-NH_2$) and carboxylic acid (-COOH) functional groups, along with a side-chain specific to each amino acid. The key elements of an amino acid are carbon, hydrogen, oxygen, and nitrogen, though other elements are found in the side-chains of certain amino acids. The development of catalysis has been devoted for a long time to the wide application of metal complexes and organometallic complexes as catalysts [2-6]. Kinetics of oxidation of amino acids by a variety of oxidants has been reported [7-13]. Due to the biological importance of amino acids, the kinetics and mechanistic study of their oxidation have received considerable attention [7 to 14].

The active catalyst contains the metal in its higher oxidation state so the transition metal ion with polydentate ligands as used as a model system [15-16]. µ-peroxo cobalt complexes with diverse polyamines have been deliberated for the effective model system. The oxidation of L-glutamine with µ- cobalt complex has been studied extensively.

EXPERIMENTAL SECTION

The chemicals employed were L-glutamine (Loba AR), H_2SO_4 and Na_2SO_4 etc were of AR grade. All solutions were prepared in doubly distilled water. The $[(en)_2(NH_3)CoO_2Co(NH_3)(en)_2](ClO_4)_4.2H_2O$ was synthesized by bubbling oxygen through a solution containing cobaltous nitrate sodium perchlorate and the appropriate ligand mixture. FT-IR and electronic spectroscopic studies are used for the characterization of the synthesized complex.

Pseudo first order conditions [L-glutamine]>> [µ-peroxo cobalt complex] has been followed for the kinetic experiments. Sulphuric acids, sodium sulphate, L-glutamine and water was pipetted out in an appropriate amount in a double walled beaker connected with an inlet and outlet water circulation from the thermostat set at the desired temperature.

Indispensible amount of µ-peroxo complex solutions was thermo stated for half an hour and the kinetic reaction was started. The total volume of the reaction was 40 ml for all the experiments. The cell [SCE$^-$/substrate-complex/pt$^+$] was used for the kinetics reaction with the reaction mixture and inserting the platinum and reference electrodes. The reaction mixture was stirred continuously using a magnetic stirrer throughout the experiment the emf of the cell was measured periodically using Equip-tronics potentiometer. Some experiments were carried out in an inert atmosphere by bubbling in nitrogen gas in the reaction mixture to study the effect of atmospheric oxygen. It was determined that the velocity constants were reproducible within ±2%. The rate of the reaction was not much variation between air and inert atmosphere; hence the entire experiment was done in air atmosphere. Sodium sulphate was used to keep the ionic strength constant in the reaction mixture.

RESULTS AND DISCUSSION

Electronic Spectrum of the µ-peroxo complex

The synthesized complex µ-peroxo-bis[aminebis(ethylenediamine)cobalt(III)]perchlorate dihydrate shows an absorption band at 305 nm. The electronic spectrum shows that there is no characteristics transition in visible region, but the spectrum shows an intense change transfer band near 205 nm. This band is due to the transfer of electron from the peroxide to metal. This band clearly prove that the presence of a single bridge peroxo ligand in the µ-peroxo complex.

FT-IR spectrum of the complex

FT-IR characterization of the µ-peroxo complex has been done by The perkin elmer RSI spectrometer using kBr pellet in the wave length region 400-4000 cm^{-1} .The peaks at 3446, 3208 and 2897 cm^{-1} show the presence of N-H stretching in the µ-peroxo complex. The nitrogen coordination present in the complex was affirmed by the peak at 2395 cm^{-1}. The strong peaks at 1588, 1381cm^{-1} confirms the presence of NH3, C-H and O-H bending vibrations respectively. The peak at 1079cm^{-1} shows the presence of C-N stretching and ClO_4 stretching vibrations in the peroxo complex [17-19]. The assignment of IR band frequencies are given in the Table-1

Table-1 FT-IR data for µ-peroxo complex

Wavelength(cm^{-1})	Assignments
3446,3208,2987	$\nu(NH_2)_s$
2385	$_\delta$(N-H)
1588	$\rho(NH_2)$
1381	$\nu(NH_2)_s$, $\nu(C\text{-}H)_b$, $\nu(O\text{-}H)_b$
1055	ν(C-N)

S-Stretching B-Bending, $_\delta$ -Deformation, ν - bond stretching, ρ – rocking

All the kinetic runs were conceded out with [L-glutamine] always ten times in excess of µ-peroxo cobalt complex. To study the effect of complex, initial concentration of the µ-peroxo complex was varied and the oxidation reaction of L-glutamine is processed. The rate constants were increased by increasing the initial concentration of the complex. The reaction is first order with respect to complex.

In order to study the effect of [L-glutamine], the oxidation of the substrate was carried out with different initial concentration of the substrate. The reaction is zero order with respect to substrate. The effect acid on the rate oxidation was studied by changing the concentration of added Sulphuric acid. The rate constants were found to be increased by increasing the hydrogen ion concentration. Hence the order with respect to hydrogen ion concentration was found to be one.

The effect of added salt on the rate of oxidation of L-glutamine was studied by varying the concentration of added sodium sulphate. The rate of the reaction was virtually constant with increasing the initial concentration of added salt of the medium. This shows that the ionic strength is negligible on the reaction rate.

Table-2 Effect of µ-peroxo cobalt Complex

[L-glutamine] =2x10^{-2}mol dm^{-3} [H$^+$] =2x10^{-2}mol dm^{-3}
[Na$_2$SO$_4$] =2.5x10^{-2}mol dm^{-3}

[peroxo complex] mol dm^{-3}	10^4 k$_{obs}$ S^{-1}
2.0	3.7
2.5	4.0
3.0	4.6
3.5	5.1

Table-3 Effect of L-glutamine

[complex] =2x10^{-3}mol dm^{-3} [H$^+$] =2x10^{-2}mol dm^{-3}
[Na$_2$SO$_4$] =2.5x10^{-2}mol dm^{-3}

10^{-2}[L-glutamine] moldm^{-3}	10^4k$_{obs}$ S^{-1}
2.0	3.7
2.5	3.9
3.0	3.6
3.5	3.8

Table-4 Effect of acid

[L-glutamine] =2x10^{-2}mol dm^{-3} [complex] =2x10^{-3}mol dm^{-3}
[Na$_2$SO$_4$] =2.5x10^{-2}mol dm^{-3}

10^2[H$_2$SO$_4$] moldm^{-3}	10^4k$_{obs}$ S^{-1}
2.0	3.7
2.5	4.2
3.0	5.0
3.5	5.6

Table-5 Effect of added Salt

[L-glutamine] =2x10^{-2}mol dm^{-3} [complex] =2x10^{-3}mol dm^{-3}
[H$^+$] =2x10^{-2}mol dm^{-3}

10^2[Na$_2$SO$_4$] moldm^{-3}	10^4k$_{obs}$ S^{-1}
2.5	3.7
3.0	3.7
3.5	3.6
4.0	3.7

Table-6 Effect of Temperature

[L-glutamine] =2x10^{-2}mol dm^{-3} [complex] =2x10^{-3}mol dm^{-3}
[H$^+$] =2x10^{-2}mol dm^{-3} [Na$_2$SO$_4$] =2.5x10^{-2}mol dm^{-3}

Temperature in K	10^4k$_{obs}$ S^{-1}
313	3.7
318	4.7
323	5.8
328	6.6

The Arrhenius plot of log K$_{obs}$ versus 1/T and the plot of log (K/T) vs 1/T gave a straight line with a very fine correlation. The energy of activation, enthalpy of activation, free energy of activation, entropy of activation and A were found to be 32.76 KJmol^{-1}, 30.16 KJmol^{-1}, 61.64 KJmol^{-1}, -100.58 KJmol^{-1}and 3.746 at 313K respectively. Positive value of free energy of activation $\Delta G^{*\ \mathrm{and}}$ the enthalpy of activation indicate that the transition state is highly solvated while the negative entropy of activation ΔS^* suggests the formation of an activated complex with a reduction in the degree of freedom of molecules. It also suggests the compactness of the transition state as compared to the ground state and also in cyclic nature [20].

Mechanism and Rate law

In general the mechanism of oxidation reactions [21] may be divided into three steps. The first step is activation of molecular oxygen. The second step is the formation of reactive intermediate. The final step is the Trans formation of intermediate into the final product. The suitable mechanism in accordance with the experimental observation has b en proposed. From the above results the most suitable mechanism for the oxidation behavior of µ-peroxo complex is given as :

$$\underset{\mu\text{- peroxo complex}}{[CoL_2L'O_2CoL'L_2]^{4+}} + H^+ \underset{K_1}{\overset{K_1}{\rightleftharpoons}} [HCoL_2L^{'}O_2CoL'L_2]^{5+}$$

$$[HCoL_2L^{'}O_2CoL'L_2]^{5+} \xrightarrow{K_2} 2[CoL_2L']^{3+} + HO_2^- \text{ (slow)}$$

$$2[CoL_2L']^{3+} + HO_2^- \xrightarrow{K_3} 2[CoL_2L']^{3+} + O_2^* + H^+ \text{ (fast)}$$

$$O_2^* + S \xrightarrow{K_4} \text{Product}$$

The first step is the slow step takes place at acidic condition and it involves the formation of the mononuclear Co(III) complex and the HO_2^- ion. In this step there is equilibrium between the mono nuclear complex and the cobalt complex. The second step is the fast step and in this step, the products formed in the first step undergo a rapid release of activated oxygen molecule along with a concurrent reduction of mononuclear Co(III) complex to mononuclear Co(II) complex. And it is supported from the mechanism for release of oxygen from a μ-peroxo cobalt (III) dimer [22]. In the third step the activated oxygen molecule attacks the substrate leading to the final products. The above mechanism leads to the following rate law,

$$\text{Rate} = K_{obs}\,[\mu\text{-peroxo complex}]\,[H^+]$$

This rate law explains all the observed experimental facts.

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