

A KINETIC APPROACH ON THE OXIDATION OF L-PROLINE BY AMINE μ -PEROXO COMPLEX IN AQUEOUS MEDIUM

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Abstract : This article gives a short information about the preparation of amine μ -peroxo cobalt complex and its oxidizing property over the organic substrate L-Proline. Kinetic and mechanistic investigation of the reaction in the aqueous medium were followed appropriately by using equip-tronics potentiometer. The reaction was found to be zero order with respect to the organic substrate concentration. The oxidant μ -peroxo cobalt complex and the acid concentration shows first order on changing its concentration. There was no effect on added salt. Calculation of Arrhenius and thermodynamic parameters helped in understanding the feasibility of the reaction; which lead to propose a suitable mechanism.

Keywords : μ -peroxo complex, oxidation, kinetics, L-Proline, mechanism.

I. INTRODUCTION

It has been observed that peroxidases are potentially suitable catalyst which involved in biological oxidation of organic compounds. Knowledge about its kinetic studies and attempting to mimic its reaction at in vitro condition is a toilsome for the chemist. Therefore it was found that μ -peroxobis[aminebis(ethylenediamine)Cobalt(III)]perchlorate-dihydrate complex can be used as an oxidant. The formation of such dimetal complex gave more polar coordinate bonds that resulted in increased charge separation between the metal ion and the oxygen. The best solvent water having high dielectric constant stabilizes the charge separation [1]. Due to the biological importance of amino acids, the kinetics and mechanistic study of their oxidation by a variety of oxidants has been reported [2-9]. Proline responsible for tissue repair, collagen formation, arteriosclerosis prevention etc., was the organic substrate taken for the oxidation. The kinetic study of the amino acid by the amine μ -peroxo cobalt complex and its mechanism have been discussed.

II. EXPERIMENTAL METHODS

The dioxygen complex $[(en)_2(NH_3)CoO_2Co(NH_3)(en)_2](ClO_4)_5 \cdot 2H_2O$ was synthesized according to the reported procedure[10]. Reagents and solvents were of commercially analytical grade. The substrate [L-Proline] \gg [μ -peroxo complex] so that pseudo first order condition is maintained throughout the reaction. The required solution was prepared by using doubly distilled water and the constant concentration of the complex was fixed as $2.0 \times 10^{-3} \text{ mol dm}^{-3}$. A total volume of 40ml of the reaction mixture was taken in a double walled beaker which was connected to the thermostat such that the required temperature was maintained. The emf of the cell was measured systematically using Equip-Tronics potentiometer. The rate constants were calculated by least square method by using lotus1-2-3 macro software and basic program. Graphs were plotted using MS-Excel software.

III. RESULTS AND DISCUSSIONS

3.1 Electronic spectrum of the complex

The complex was characterized by Electronic spectroscopy. The electronic spectrum of the μ -peroxo complex showed that there was an absorption band at 305 nm which proved the presence of a single bridge peroxo ligand in the μ -peroxo complex.

3.2 FT-IR spectrum of the complex

FT-IR characterization of the μ -peroxo complex had been done by using perkin elmer RSI spectrometer. The presence of NH_3 , C-H, O-H bending, C-N stretching and N-H stretching vibrations in the μ -peroxo complex to its corresponding wavelength is listed below in the Table-1.

Wavelength (cm^{-1})	Functional Groups
3506.23	Free (O-H) _s
3447.38, 3212.53,	$\nu(N-H)_s$, (C-H) _s
2902.65	(C-H) _s
1599.03	(N-H) _b ,

1463.50	(CH ₂) _s
1057.94	ν (C-N)

Table-1: FT-IR data of μ-peroxo complex

s – Stretching b – Bending ν – bond stretching

Table – 2 Effect of μ-peroxo cobalt complex

[L-Proline] = $2.0 \times 10^{-2} \text{ mol dm}^{-3}$ [H⁺] = $2.0 \times 10^{-3} \text{ mol dm}^{-3}$
 [Na₂SO₄] = $2.5 \times 10^{-2} \text{ mol dm}^{-3}$ Temp = 313K Solvent = water

10^2 [L-Proline] mol dm ⁻³	$10^4 k_{\text{obs}} \text{ S}^{-1}$
1.0	3.8
2.0	3.9
3.0	3.9
4.0	3.9

Table – 3 Effect of L-Proline

[μ-peroxo complex] = $2.0 \times 10^{-3} \text{ mol dm}^{-3}$ [H⁺] = $2.0 \times 10^{-3} \text{ mol dm}^{-3}$
 [Na₂SO₄] = $2.5 \times 10^{-2} \text{ mol dm}^{-3}$ Temp = 313K Solvent = water

10^3M [peroxo complex] mol dm ⁻³	$10^4 k_{\text{obs}} \text{ S}^{-1}$
1.0	2.5
2.0	3.9
3.0	6.1
4.0	7.5

Table – 4 Effect of acid

[L-Proline] = $2.0 \times 10^{-2} \text{ mol dm}^{-3}$ [μ-peroxo complex] = $2.0 \times 10^{-3} \text{ mol dm}^{-3}$
 [Na₂SO₄] = $2.5 \times 10^{-2} \text{ mol dm}^{-3}$ Temp = 313K Solvent = water

10^3 [H ₂ SO ₄] mol dm ⁻³	$10^4 k_{\text{obs}} \text{ S}^{-1}$
4.0	2.4
8.0	3.9
12.0	6.1
16.0	10.0

Figure 1 Effect of acid

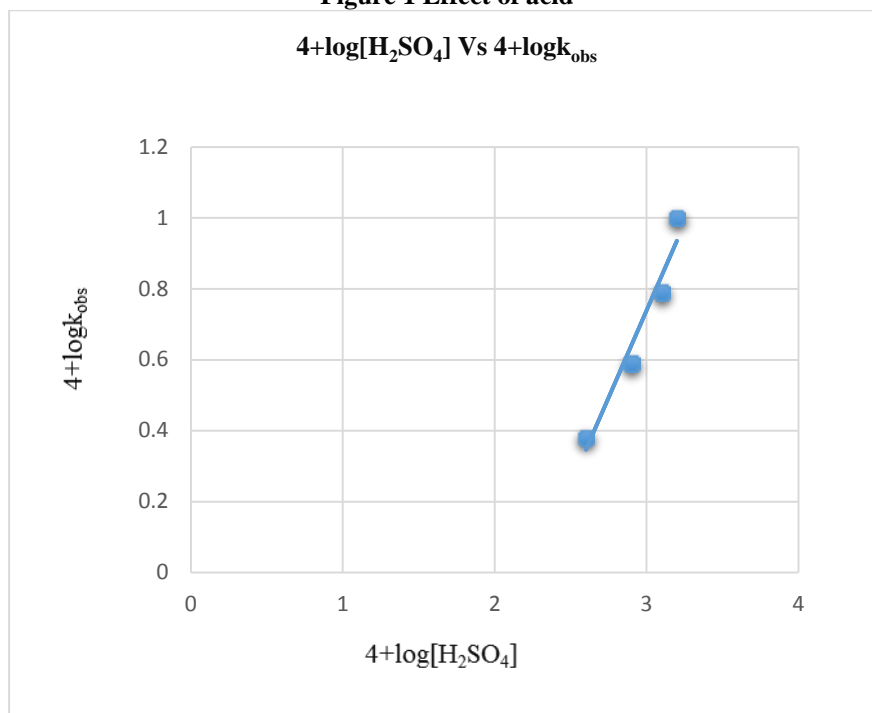


Table – 5 Effect of added salt

[L-Proline] = $2.0 \times 10^{-2} \text{ mol dm}^{-3}$ [μ-peroxo complex] = $2.0 \times 10^{-3} \text{ mol dm}^{-3}$
 [H⁺] = $2.0 \times 10^{-3} \text{ mol dm}^{-3}$ Temp = 313K Solvent = water

$10^2[\text{Na}_2\text{SO}_4] \text{ mol dm}^{-3}$	$10^4 k_{\text{obs}} \text{ S}^{-1}$
1.25	3.9
2.5	3.9
3.75	3.9
5.0	3.9

Table – 6 Effect of Temperature

[L-Proline] = $2.0 \times 10^{-2} \text{ mol dm}^{-3}$ [complex] = $2.0 \times 10^{-3} \text{ mol dm}^{-3}$
 [H⁺] = $2.0 \times 10^{-3} \text{ mol dm}^{-3}$ [Na₂SO₄] = $2.5 \times 10^{-2} \text{ mol dm}^{-3}$ Solvent = water

Temperature in K	$10^4 k_{\text{obs}} \text{ S}^{-1}$
313	3.9
318	6.1
323	10.2
328	13.7

Figure 2 Effect of Temperature

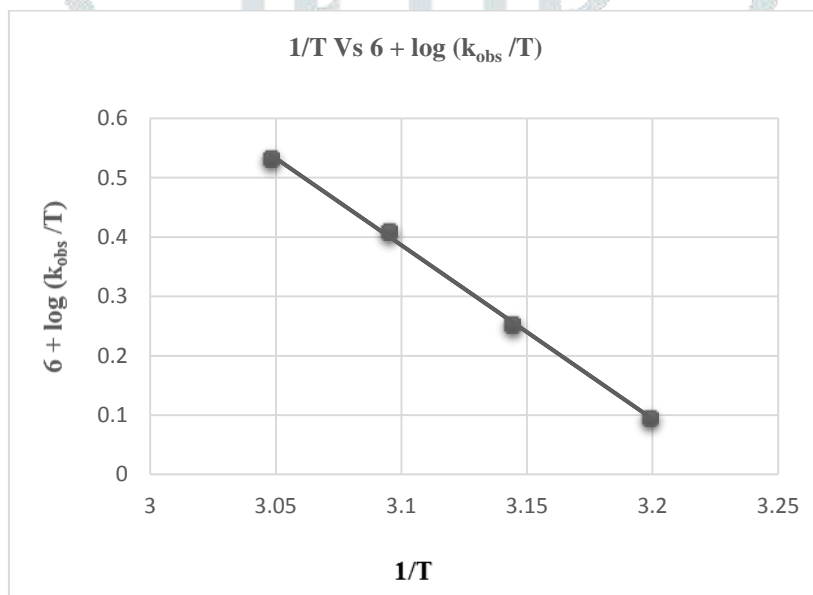
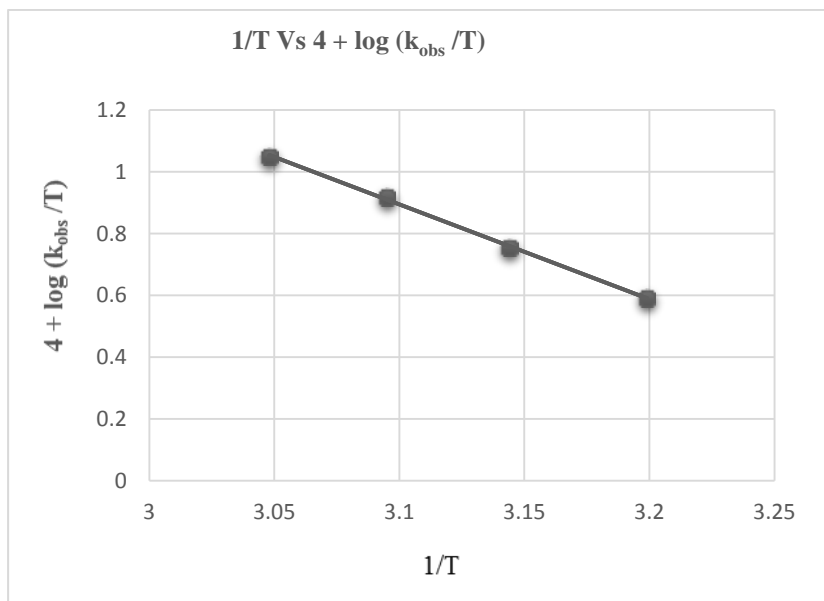


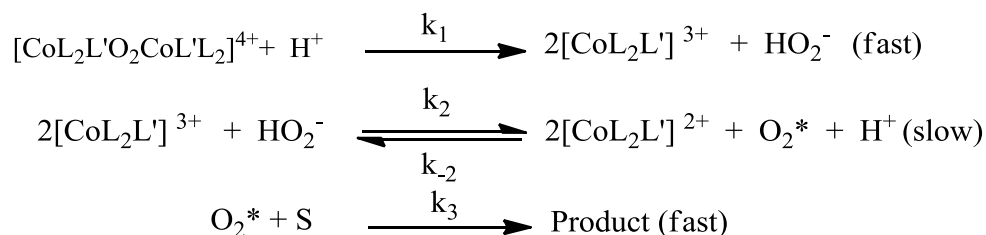
Table – 7

Arrhenius and Thermodynamic Parameter

E_a	58.672 k J mol ⁻¹
ΔH[*]	56.085 k J mol ⁻¹
ΔS[*]	-21.59 J K ⁻¹ mol ⁻¹
ΔG[*]	62.71 k J mol ⁻¹
log A	2.2038

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 Arrhenius and thermodynamic parameters were calculated as given in the table-7.

IV. KINETIC MECHANISM



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

In the proposed mechanism at acidic condition the first step involved the formation of $2[\text{CoL}_2\text{L}']^{3+}$ complex ion from the peroxo complex $[\text{CoL}_2\text{L}'\text{O}_2\text{CoL}'\text{L}_2]^{4+}$. In the second equilibrium step there is a slow release of activated oxygen with the concurrent reduction of mononuclear Co(III) complex to mononuclear Co(II) complex. This step was supported by the mechanism which released oxygen from a μ -peroxo complex Co(III) dimer [11]. The activated oxygen reacted with the substrate and gave the product in the final step. Thus the rate law explains all the observed experimental facts.

V. CONCLUSION

The μ -peroxobis[aminebis(ethylenediamine)Cobalt(III)]perchloratedihydrate complex has been synthesized and characterized by FT-IR. The observed rate constant values and the calculated parameters showed that the organic substrate has undergone kinetic oxidation. The reaction was found to be zero order with respect to the organic substrate concentration. The oxidant μ -peroxo cobalt complex and the acid concentration shows first order on changing its concentration. There was no effect on added salt. Therefore complex proves itself as a good dioxygen carrier suitable for biological oxidation in mimic of the peroxidase enzyme.

VI. REFERENCES

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