

A Biomimic Oxidation Behaviour of Cobalt μ -Peroxo Complex on L-Asparagine -A Kinetical Approach

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Abstract : The cobalt μ -peroxo complex viz bis-(ethylenediamine)bis-(diethylenetriamine) μ -peroxodicobalt(III)perchlorate had been prepared by appropriate method and characterization of the prepared complex was done by FTIR and electronic spectroscopy. Potentiometric method had been employed to determine the rate of the reaction. First order kinetics was observed with respect to the effect of complex and the effect of acid concentration. The order with respect to the substrate concentration was found to be zero. The effect of added salt concentration was found to be negligible. Arrhenius and thermodynamic parameters had been calculated from the effect of temperature on the reaction rate. A probable mechanism had been proposed based on the experimental results which considered this kinetic approach as a biomimic of a model system.

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

I. INTRODUCTION

Enzymes are biocatalysts that quicken biochemical reactions in living organisms (1). Peroxidase is an iron enzyme, which is accountable for the oxidation of many organic substrates in our living system (2,3). In the present investigation the oxidation behaviour of cobalt (III) μ -peroxo complex on various organic substrates had been studied as a constructive mimic of a model system (4,5). The oxidation kinetics and mechanistic investigation of amino acids by various oxidants had been proclaimed (6-13). The substrate L-Asparagine is known for its key role in the biosynthesis of glycoproteins and benefits of nervine health and liver protection. It is further required for the synthesis of many important cellular proteins in normal human cells. Hence oxidation of L-Asparagine by cobalt (III) μ -peroxo complex had been studied extensively as biomimetics of a model system.

II. EXPERIMENTAL METHODS

All the chemicals used were AR Grade. Stock molar concentrations of H_2SO_4 , Na_2SO_4 , substrate, complex were prepared using doubly distilled water. Potentiometric measurements were done to study the rate of the reaction. The cobalt μ -peroxo complex $[(Co)_2(en)_2(dien)_2O_2](ClO_4)_4 \cdot 2H_2O$ was prepared in the laboratory by bubbling oxygen through a solution containing cobaltous nitrate, sodium perchlorate and the suitable ligand mixtures (14,15). The characterization of the complex was done by FTIR and electronic spectroscopic techniques.

The kinetical runs were administered under pseudo first order condition. $[L\text{-Asparagine}] \gg [Cobalt \mu\text{-peroxo complex}]$. Essential amounts of L-Asparagine, sulphuric acid, sodium sulphate solution and water were pipetted out in a double walled beaker supported with an inlet and outlet for water circulation from the thermostat fixed at desired temperature. The kinetic reaction was initiated by the addition of appropriate amount of μ -peroxo complex solution, which had also been thermostated for nearly half an hour. The overall volume of the reaction mixture was fixed 40ml for all the experiments. Equipronics potentiometer was used to measure the emf of the cell periodically. Calculation of rate constants were done by plotting linear ($r > 0.99$) plots of $\log(E_t - E_\infty)$ versus time by least square method by using lotus 1-2-3 macro software and basic program. The velocity constants were reproducible within $\pm 2\%$ and all the experiments were examined in duplicate. The pseudo- first order rate constant (k_{obs}) was expressed in per second.

III. RESULTS AND DISCUSSIONS

The absorption maximum of single bridged μ -peroxo complex was observed at 305 nm. This clearly determined the presence of a single bridged peroxo-ligand in the cobalt μ -peroxo complex. The FT-IR spectrum of cobalt μ -peroxo complex was recorded on a Perkin Elmer Spectrum RSI spectrometer using KBr pellet technique in the wavelength range (400- 4000) cm^{-1} . The absorption peaks at 3437, 3220, 2959 and 2859 cm^{-1} indicated the presence of N-H stretching in cobalt μ -peroxo complex. The band at 2383 cm^{-1} was observed due to the presence of co-ordinated nitrogen in this complex. Strong peaks at 1589 and 1385 cm^{-1} confirmed the presence of NH_3 , C-H and -OH bending vibration respectively. The peak at 1085 cm^{-1} showed the presence of C-N stretching and ClO_4 stretching vibration in the cobalt μ -peroxo complex. The assignments of IR band frequencies are given in the table I.

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

Wavelength (cm^{-1})	Frequencies of absorption
3437, 3220, 2959 and 2895	ν (NH_2) _s
2383	δ (N-H)
1589	ρ (NH_2) _b
1385	ν (NH_3), ν (C-H) _b , & ν (-OH) _b
1085	ν (C-N)

s- stretching, b – Bending, ν – bond stretching, δ - deformation, ρ - rocking.

Table – 2

Effect of μ -peroxo cobalt complex

[L-Asparagine] = $2.0 \times 10^{-2} \text{ mol dm}^{-3}$ [H₂SO₄] = $6.0 \times 10^{-3} \text{ mol dm}^{-3}$
 [Na₂SO₄] = $3.0 \times 10^{-2} \text{ mol dm}^{-3}$ Temp = 313K Solvent = water

[peroxo complex] $\times 10^3 \text{ mol dm}^{-3}$	$10^4 \text{ k}_{\text{obs}} \text{ S}^{-1}$
1.0	4.9
2.0	6.5
3.0	8.4
4.0	9.1

Table – 3

Effect of [L-Asparagine]

[μ -peroxo complex] = $2.0 \times 10^{-3} \text{ mol dm}^{-3}$ [H₂SO₄] = $6.0 \times 10^{-3} \text{ mol dm}^{-3}$
 [Na₂SO₄] = $3.0 \times 10^{-2} \text{ mol dm}^{-3}$ Temp = 313K Solvent = water

[L-Asparagine] $\times 10^2 \text{ mol dm}^{-3}$	$10^4 \text{ k}_{\text{obs}} \text{ S}^{-1}$
1.0	6.3
2.0	6.5
3.0	6.6
4.0	6.5

Table – 4

Effect of [H₂SO₄]

[μ -peroxo complex] = $2.0 \times 10^{-3} \text{ mol dm}^{-3}$ [L-Asparagine] = $2.0 \times 10^{-2} \text{ mol dm}^{-3}$
 [Na₂SO₄] = $3.0 \times 10^{-2} \text{ mol dm}^{-3}$ Temp = 313K Solvent = water

[H ₂ SO ₄] $\times 10^3 \text{ mol}$	$10^4 \text{ k}_{\text{obs}} \text{ S}^{-1}$	4+log [H ₂ SO ₄]	4+ log k _{obs}	slope
3.0	3.8	2.4771	0.5798	0.85
6.0	6.5	2.7781	0.8129	
9.0	9.0	2.9542	0.9542	
12.0	12.7	3.0792	1.1038	

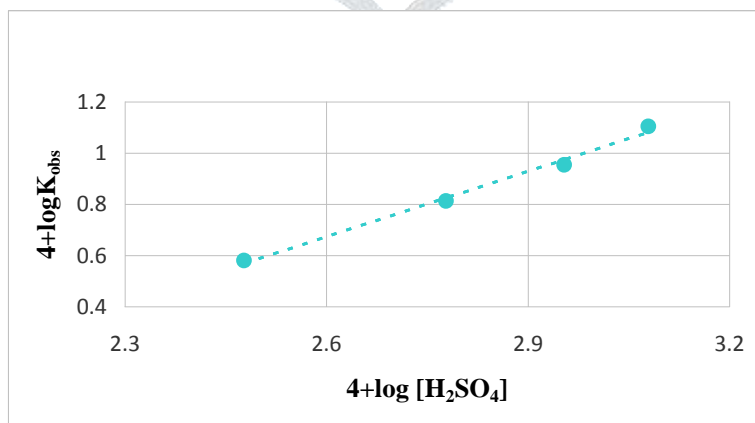


Figure 1 : Plot of log k_{obs} Vs log [H₂SO₄]

Table – 5

Effect of added salt

[L- Asparagine] = $2.0 \times 10^{-2} \text{ mol dm}^{-3}$ [μ-peroxo complex] = $2.0 \times 10^{-3} \text{ mol dm}^{-3}$
 [H₂SO₄] = $6.0 \times 10^{-3} \text{ mol dm}^{-3}$ Temp = 313K Solvent = water

[Na ₂ SO ₄] x 10 ² mol dm ⁻³	10 ⁴ k _{obs} S ⁻¹
1.5	6.4
3.0	6.5
4.5	6.7
6.0	6.5

Table – 6

Effect of Temperature

[L- Asparagine] = $2.0 \times 10^{-2} \text{ mol dm}^{-3}$ [μ-peroxo complex] = $2.0 \times 10^{-3} \text{ mol dm}^{-3}$
 [H₂SO₄] = $6.0 \times 10^{-3} \text{ mol dm}^{-3}$ [Na₂SO₄] = $3.0 \times 10^{-2} \text{ mol dm}^{-3}$ Solvent = water

Temperature in K	10 ⁴ k _{obs} S ⁻¹	1/T x 10 ³	5+ log k _{obs}	7+log(k _{obs} /T)
313	6.5	3.194	1.8129	1.3174
318	9.4	3.114	1.9731	1.4707
323	12.0	3.095	2.0792	1.5699
328	16.3	3.048	2.2122	1.6963

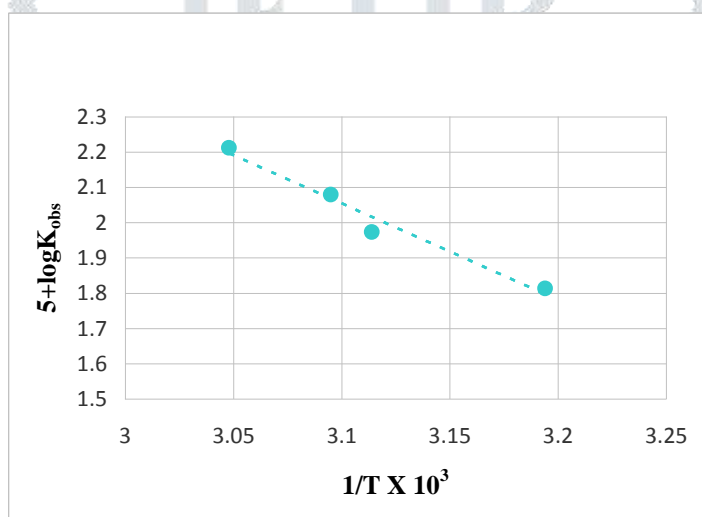


Figure 2 : Plot of log k_{obs} Vs 1/T

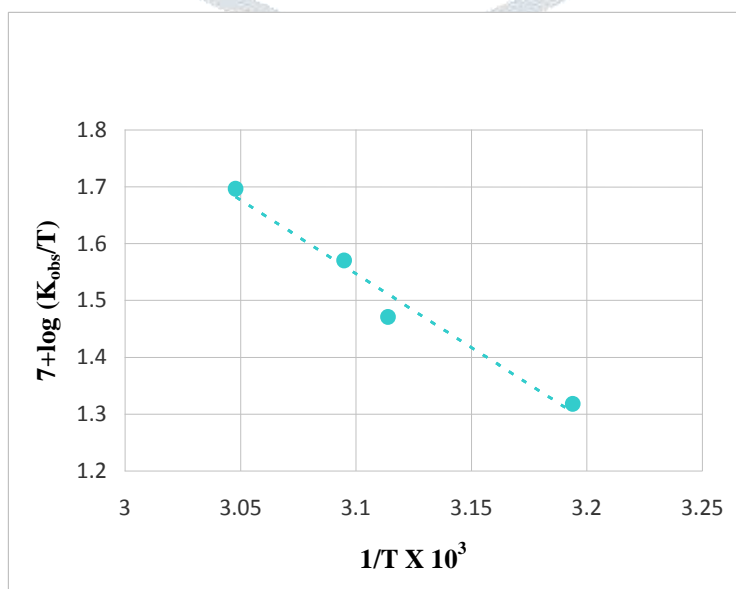


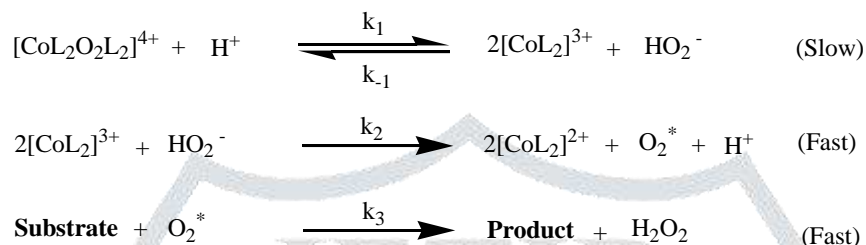
Figure 3 : Plot of log k_{obs} /T Vs 1/T

Table -7
Arrhenius and Thermodynamic Parameters

Ea	52.35 k J mol ⁻¹
log A	10.53
ΔH*	49.67 k J mol ⁻¹
ΔS*	-18.86 J K ⁻¹ mol ⁻¹
ΔG*	55.57 k J mol ⁻¹

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



The above mentioned mechanism indicated the evolution of complex ion, 2[CoL₂]³⁺ from the μ-peroxo complex [CoL₂O₂L₂]⁴⁺ in the first step, a reversible and slow step under the presence of acid. In the second step there occurred a release of molecular activated oxygen along with a simultaneous reduction of Co(III) complex to Co(II) complex. This activated oxygen was found to react with the substrate resulting in product formation in the latter step.

Therefore the rate law interprets the entire discerned experimental aspects.

V. CONCLUSION

The μ-peroxo complex had been prepared in the laboratory and designated by FTIR and electronic spectroscopy. The measured framework and the rate constant values which were observed, illustrated that L-Asparagine had encountered kinetic oxidation. On varying the added acid concentration and μ-peroxo complex concentration it showed first order dependence with respect to each. The reaction was noticed to be zero order with respect to substrate concentration. Added salt had negligible effect. The Arrhenius and thermodynamic parameters were calculated. A probable mechanism based on the experimental results was suggested and the mechanism was considered as a mimic of a model system.

VI. REFERENCES

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