Asian Journal of Chemistry; Vol. 23, No. 1 (2011), 265-267

ASIAN JOURNAL OF CHEMISTRY

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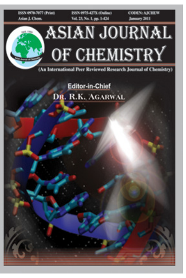

Biomimic Oxidation of Pyridoxine by Peroxo Complex: A Kinetic and Mechanistic Study

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(*Received*: 17 February 2010; *Accepted*: 27 August 2010) AJC-9034

Bis-(ethylene diamine),*bis*-(diethylene triamine)peroxo dicobalt(III) perchlorate complex is synthesized by solution route. The prepared *m*-peroxo complex is characterized by FT-IR and electronic spectroscopy. The biomimic kinetics oxidations of pyridoxine by peroxo complex have been studied in aqueous medium. The reaction is first order each in the concentration of peroxo complex and H^+ concentration. Increase in ionic strength has no effect on the reaction rate. The reaction does not induce the polymerization of acryl amide. The main products of the reaction has been isolated and identified by the spot test. The Arrhenius and the thermodynamic parameters have been calculated from the effect of temperature on the reaction rate. A suitable mechanism has been proposed and the experimental result is derived.

Key Words: Kinetics, Oxidation, Peroxo complex, Pyridoxine, Activation parameters.

INTRODUCTION

Enzymes play an indispensable role in living systems. The enzymes that catalyze and peroxidases are widely distributed in all plants and animals. Metal low oxidation potentials and high Lewis acidity in their higher oxidation state as superior catalyst. The active catalyst contains the metal in its higher oxidation state. So the transition metal ion with polydentate ligands used as model system[1,2]. The peroxo complexes of Co(III) with different polyamines have been studied for effective model system. In part of the investigations on the oxidation of pyridoxine with *m*-peroxo complex has been studied extensively.

EXPERIMENTAL

The reagents employed were pyridoxine (Loba AR) and H_2SO_4, Na_2SO_4 *etc*., which were of AR grade. All solutions were prepared in doubly distilled water. The $[(Co)_2(en)_2(dien)_2O_2](ClO_4)_4{\cdot}2H_2O$ was prepared[3] by bubbling oxygen through a solution containing cobaltous nitrate, sodium perchlorate and the appropriate ligand mixtures. The complex is characterized by FT-IR and electronic spectroscopic methods.

The kinetic runs were carried out under pseudo first order condition [pyridoxine] >> [μ-peroxo complex]. Requisite amounts of pyridoxine, sulphuric acid, sodium sulphate and water were pipetted out in a double walled beaker provided with an inlet and outlet for water circulation from the thermostat set at desired temperature. The kinetic reaction was started by the addition of appropriate quantity of μ-peroxo complex solution, which had also been thermo stated for nearly 0.5 h. The total volume of the reaction mixture was 40 mL for all the experiment.

The kinetic reaction was followed by setting up a cell [SCE^-/substrate-complex/Pt^+] made up of the reaction mixture into which the platinum electrode and reference electrode (SCE) were dipped. 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.

In order to study the effect of atmospheric oxygen, some experiments were carried out in an inert atmosphere by bubbling in nitrogen gas in the reaction mixture and it was ascertained that the velocity constants were reproducible within ± 2 %. The rate of reaction was not in much variation between the air and inert atmosphere; hence the entire experiment was done in air atmosphere. Sodium sulphate solution (2.5×10^{-2} mol dm^{-3}) was used to keep ionic strength constant in the reaction mixture.

The rate constants were calculated from linear (r > 0.99) plots of log (E_t - E_∞) *versus* time by least square method by using lotus1-2-3 macro software and basic program. All the experiments were studied in duplicate and the velocity constants were reproducible within ± 2 %. The pseudo-first order rate constant (k_{obs}) was expressed in terms of second. The product pyridoxal, carbon dioxide, was identified by spot test[4].

RESULTS AND DISCUSSION

The single bridged complex μ-peroxo complex has an absorption maximum at 305 nm. The spectrum shows that there is no characteristic transition in visible region, but an intense charge transfer band near 200 nm due to the transfer of electron from the peroxide to metal. This clearly shows the presence of a single bridge peroxo-ligand in the μ-peroxo complex.

The FT-IR spectrum of μ-peroxo complex was recorded on a Perkin Elmer Spectrum RSI spectrometer using KBr pellet technique in the wavelength range 4000-400 cm^{-1}. The peak arising at 3437, 3220, 2959 and 2895 cm^{-1} shows the presence of N-H stretching in μ-peroxo complex. The band at 2383 cm^{-1} confirms the presence of coordinated nitrogen in μ-peroxo complex. The strong peaks of 1589 and 1385 cm^{-1} confirm the presence of NH_3, C-H and -OH bending vibration, respectively. The peak at 1085 cm^{-1} shows the presence of C-N stretching and ClO_4 stretching vibrations in the μ-peroxo complex. The assignments of IR band frequencies[5-7] are given in the Table-1.

TABLE-1
FT-IR DATA FOR μ-PEROXO COMPLEX

Wavelength (cm^{-1})	Assignments
3437, 3220, 2959 and 2895	$\nu(NH_2)$
2383	δ(N-H)
1589	
1385	$\rho(NH_2)$
1085	$\nu(NH_3)$, ν(C-H) and ν(-OH), ν(C-N)

All the kinetic runs were carried out with [pyridoxine] always at least ten times, in excess of [μ-peroxo complex]. In the case of pyridoxine, the log $[E_t - E_\infty]$ against time is linear, the reactions indicating first order dependence on [μ-peroxo complex]. Applying linear regression analysis to these, k_{obs} was found to be 1.4×10^{-4} s^{-1} (r = 0.9893).

The oxidation of pyridoxine was carried out with different initial concentrations of μ-peroxo complex. The rate constants were increased by increasing the initial concentration of the oxidants. The reaction is first order with respect to oxidation at every one of these concentrations (Table-2).

TABLE-2
EFFECT OF [PEROXO COMPLEX] ON THE RATE OF OXIDATION OF PYRIDOXINE
[Pyridoxine] = 2.0×10^{-2} mol dm^{-3}, $[Na_2SO_4] = 2.5 \times 10^{-2}$ mol dm^{-3}, $[H_2SO_4] = 4.0 \times 10^{-2}$ mol dm^{-3}, temperature = 313 K, solvent = water

10^3 [Peroxo complex] (mol dm^{-3})	10^4 k_{obs} (s^{-1})
1	4.1
2	4.8
3	6.2
4	7.6

In order to study the effect of pyridoxine on the rate, the rate of oxidation was determined by measuring first order rate constant, over a wide range of initial pyridoxine concentration at 313 K at a constant ionic strength of 2.2×10^{-2} mol dm^{-3}. The rate of the reaction is independent of initial concentration of the substrate. Hence the order with respect to amino acid is zero (Table-3). The effect of variation of added mineral acid concentration on the rate of oxidation was studied by varying the concentration of added sulphuric acid (Table-4). The rate constant was found to be increasing as the concentration of hydrogen ion concentration increases initially. The plot of log k_{obs} *versus* log $[H_2SO_4]$ was linear with a slope 1.0335. Hence, the order with respect to hydrogen ion concentration found to be one.

TABLE-3
VARIATION OF k_{obs} WITH [PYRIDOXINE]
[Peroxo complex] = 2.0×10^{-3} mol dm^{-3}, $[Na_2SO_4] = 2.5 \times 10^{-2}$ mol dm^{-3}, $[H_2SO_4] = 4.0 \times 10^{-2}$ mol dm^{-3}, temperature = 313 K, solvent = water

10^2 [Peroxo complex] (mol dm^{-3})	10^4 k_{obs} (s^{-1})
1	5
2	5
3	5
4	5

TABLE-4
EFFECT OF $[H_2SO_4]$ ON THE OXIDATION OF [PYRIDOXINE]
[Pyridoxine] = 2.0×10^{-2} mol dm^{-3}, temperature = 313 K, [peroxo complex] = 2.0×10^{-3} mol dm^{-3}, $[Na_2SO_4] = 2.5 \times 10^{-2}$ mol dm^{-3}, solvent = water

10^2 $[H_2SO_4]$ (mol dm^{-3})	10^4 k_{obs} (s^{-1})	4 + log $[H_2SO_4]$	4 + log k_{obs}	Slope
2	2.4	2.3010	0.3802	1.0335
3	4.8	2.6020	0.6812	
4	6.1	2.7781	0.7853	
5	7.3	2.9030	0.8633	

The effect of variation of added salt strength on the rate of oxidation of a vitamin was studied by varying the concentration of the initially added sodium sulphates. The rate of the reaction was almost constant with increasing concentration of added salt of the medium (Table-5). This revealed that ionic strength has negligible on the rate. The addition of acrylamide to the reaction mixture did not alter the rate. There was no polymerization showing the absence of free radical in the reaction.

TABLE-5
EFFECT OF IONIC STRENGTH ON THE RATE OF OXIDATION OF PYRIDOXINE
[Pyridoxine] = 2.0×10^{-2} mol dm^{-3}, temperature = 313 K, [peroxo complex] = 2.0×10^{-3} mol dm^{-3}, $[H_2SO_4] = 4.0 \times 10^{-2}$ mol dm^{-3}, solvent = water

10^2 $[Na_2SO_4]$ (mol dm^{-3})	10^4 k_{obs} (s^{-1})
1.0	3.5
1.5	3.5
2.0	3.5
2.5	3.5

The Arrhenius plot of log k_{obs} *versus* 1/T and the plot of log (k/T) *versus* 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 log A were found to be 40.29 KJ mol^{-1}, 37.62 KJ mol^{-1}, 55.38 KJ mol^{-1}, -59.60 J K^{-1} mol^{-1} and 7.401 at 313 K, respectively.

A plot of $\Delta H^{\#}$ against $\Delta S^{\#}$ (isokinetic plot) gave a straight line with a very fine correlation coefficient[8]. The Exner plot also gave a straight line with a very fine correlation coefficient indicating that pyridoxine is undergoing oxidation by a common mechanism[9]. The enthalpy of activation $\Delta H^{\#}$ value is high value suggesting a stepwise mechanism as proposed. The entropies of activation $\Delta S^{\#}$ is negative indicating extensive salvation of the transition state over the reactants.

Mechanism and rate law: In general, the mechanism[10] of oxidation reactions may be divided into three steps. The first step is activation of molecular oxygen. The second step is the formation of reactive intermediate. The third step involves the transformation of such an intermediate into the final product.

The probable mechanism in accordance with the experimental observation has been proposed. From the above results the most probable mechanism for the oxidation behaviour of μ-peroxo complex is given as

$$\underset{\mu\text{-peroxo complex}}{[CoL_2O_2CoL_2]^{4+}} + H^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2[CoL_2]^{3+} + HO_2^- \quad \text{(Slow)}$$

$$2[CoL_2]^{3+} + HO_2^- \xrightarrow{k_2} 2[CoL_2]^{2+} + O_2^* + H^+ \quad \text{(Fast)}$$

$$\underset{\text{(Substrate)}}{S} + O_2^* \xrightarrow{k_3} \text{Product} + H_2O_2 \quad \text{(Fast)}$$

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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