

KINETIC AND MECHANISTIC STUDY OF BIO-MIMIC OXIDATION OF L-VALINE BY μ -PEROXO COMPLEX IN ACID MEDIUM

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Abstract: (μ -peroxo)(μ -hydroxo)bis[bis(bipyridyl)-cobalt(III)] complex was synthesized by solution route. The prepared μ -peroxo complex was characterized by FT-IR and Electronic spectroscopy. The kinetics of biomimic oxidation of L-Valine by μ -peroxo complex in aqueous medium was studied potentiometrically. The reaction shows a first order dependence of rate with respect to each in the μ -peroxo complex concentration and hydrogen ion concentration. Variation of ionic strength has no significant effect on the rate. The reaction did not induce the polymerization by the addition of acrylonitrile. The activation and thermodynamic parameters have been calculated from the effect of temperature on the reaction rate. The main product was identified as the α -keto acid by spot test. A mechanism consistent with the observed kinetic results was proposed and discussed.

Keywords: Kinetics, μ -peroxo complex, L-Valine, oxidation, mechanism.

1. INTRODUCTION

Oxygen requiring enzymes are of major importance in a large number of metabolically, medicinally and industrially relevant systems [1]. The attention has been focused on the mechanism of enzymatic reaction. A large number of model systems have been established. There are still many unsolved problems for most enzymes utilizing oxygen. The studies on the non-enzymatic oxygenation reactions as biomimic have contributed to understanding of oxidation reactions.

L-Valine is one of the essential basic amino acid classified as non-polar and forms active sites of enzymes and helps in maintaining proper conformation by keeping them in proper ionic states and useful in biological research, metabolism, nutrition and drug industry. It has been oxidized by some oxidizing agents. The importance of oxidation of α -amino acids from chemical point of view is on its mechanism of metabolism [2]. Consequently, it is imperative to explore more redox reactions of this compound with a wide range of oxidants. Hence oxidation of L-Valine may help in understanding some aspect of enzyme kinetics.

The kinetics of oxidation of L-Valine have been studied by many reagents such as potassium permanganate [3], ruthenium(III) catalyzed oxidation of L-Valine by potassium permanganate in alkaline medium [4], silver (I) catalyzed oxidation of valine by cerium (IV) [5], Cr (III) catalyzed oxidation of L-Valine by permanganate in alkaline medium [6], Mn (II)-catalyzed oxidation of α -amino acids by peroxomonosulfate in alkaline medium [7], Ruthenium(III) chloride catalyzed oxidation of valine by N-Bromophthalimide [8], Pd(II) catalyzed oxidation of valine by N-Bromophthalimide [9], and many other well-known oxidizing agents.

However the kinetics of oxidation of L-Valine by (μ -peroxo) (μ -hydroxo) bis[bis(bipyridyl)-cobalt(III)] complex has not been reported. Hence we have considered it to study the kinetics and mechanism of oxidation of L-Valine by this μ -peroxo complex.

2. EXPERIMENTAL METHODS

2.1 Complex preparation

Reagents and solvents were of commercially available reagent quality without further purification. All solutions were prepared with distilled water. The (μ -O₂)(μ -OH)(Co(bpy)₂)₂³⁺ (bpy=bipyridyl) complex was prepared [10] by bubbling oxygen in the dark through a solution containing 2,2'-dipyridyl and cobalt nitrate with pH adjusted to 9 and subsequently NaClO₄.H₂O dissolved in ethanol was added. The resulting solution was maintained at 10°C. Brown crystals were filtered, washed with cold ethanol and were characterized using UV-Visible and Fourier Transformed Infrared (FTIR) spectrophotometers.

2.2 Kinetic procedure

The kinetic runs were carried out under pseudo first order condition with [Amino acid] >> [μ -peroxo complex]. Requisite amounts of amino acid, sulphuric acid, sodium sulphate and water were pipetted out into 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 half an hour. The total volume of the reaction mixture was 40 ml for all the experiment.

The kinetic reaction was followed by setting up a cell [SEC⁻/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 Equiptronics potentiometer.

In order to study the effect of atmospheric oxygen, some experiments were carried out in an inert atmosphere by bubbling nitrogen gas in the reaction mixture and it was ascertained that the velocity constants were reproducible within $\pm 3\%$. 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 ($2.5 \times 10^{-2} \text{ mol dm}^{-3}$) was used to keep ionic strength constant in the reaction mixture.

The rate constants were calculated from linear ($r > 0.99$) plots of $\log(E_t - E_{\infty})$ versus time by least square method by using Microsoft Office Excel program. Duplicate kinetic runs showed that the rate constants were reproducible to within $\pm 3\%$. The pseudo first order rate constant (K_{obs}) was expressed in terms of seconds.

3. RESULTS AND DISCUSSION

3.1 Characterization of μ -peroxo complex

The electronic absorption spectrum of the μ -peroxo complex was recorded in aqueous medium. The bridged 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 200nm 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 $400\text{--}4000 \text{ cm}^{-1}$. The broad band centered at 3443 cm^{-1} shows the presence of O-H stretching in μ -peroxo complex. The band at 2346 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 C-H and -OH bending vibrations respectively. The peak at 1091 cm^{-1} and 624 cm^{-1} shows the presence of C-N stretching and ClO_4 stretching vibrations in the μ -peroxo complex. The peak at 855 cm^{-1} shows the presence of O-O stretching vibration in the μ -peroxo complex.

3.2 Effect of concentration of L-Valine on the rate of reaction

In order to study the effect of substrate (L-Valine) on the rate, the rate of oxidation was determined over a wide range of initial valine concentration and by keeping constant [peroxo complex], $[\text{Na}_2\text{SO}_4]$ and $[\text{H}_2\text{SO}_4]$ at 313K. The rate of the reaction is independent of initial concentration of the substrate. Hence the order with respect to valine is zero (Table 1).

Table 1: Effect of varying [L-Valine] on the rate of oxidation by μ -peroxo complex

[Peroxo Complex] = $2.0 \times 10^{-3} \text{ mol dm}^{-3}$ Solvent = Water
 $[\text{Na}_2\text{SO}_4]$ = $2.5 \times 10^{-2} \text{ mol dm}^{-3}$ Temperature = 313K
 $[\text{H}_2\text{SO}_4]$ = $4.0 \times 10^{-2} \text{ mol dm}^{-3}$

10^2 [L-Valine] (mol dm^{-3})	1.0	2.0	3.0	4.0
$10^4 k_{\text{obs}} \text{ S}^{-1}$	7.2	7.2	7.2	7.2

3.3 Effect of concentration of peroxo complex on the rate of oxidation of L-Valine

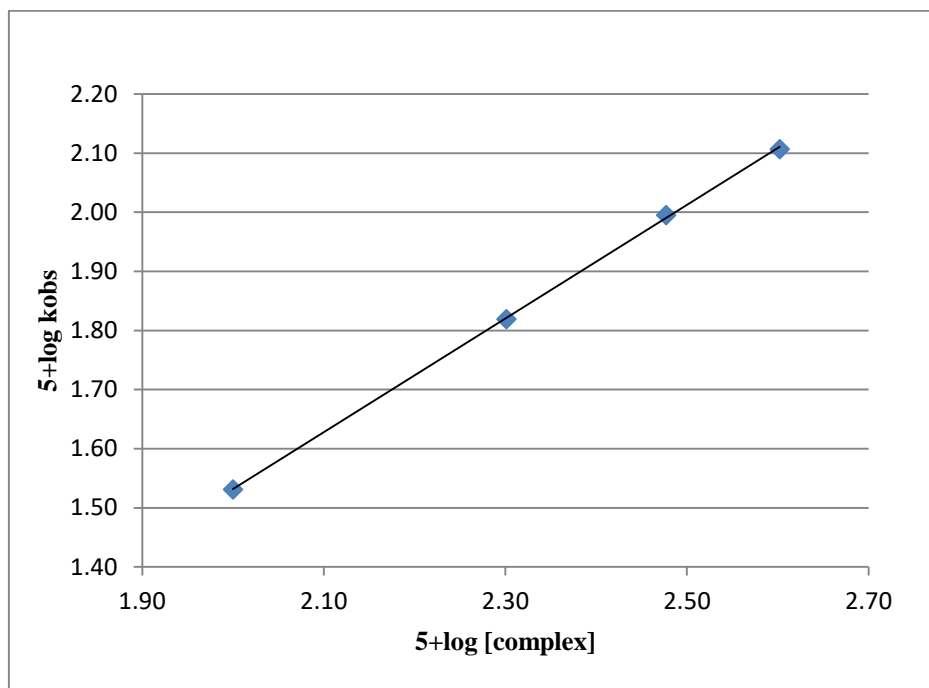
The oxidation of L-Valine was carried with different initial concentrations of the oxidant i.e. μ -peroxo complex and by keeping constant [Valine], $[\text{Na}_2\text{SO}_4]$ and $[\text{H}_2\text{SO}_4]$ at 313K. The rate constants were increased by increasing the initial concentration of the oxidant. The reaction is first order with respect to oxidant at every one of these concentrations (Table 2).

The plot of $5 + \log[\text{complex}]$ versus $5 + \log k_{\text{obs}}$ for different initial concentration of μ -peroxo complex is linear with positive unit slope presents the first order dependence of rate on μ -peroxo complex (Fig 1).

Table 2: Effect of varying [μ -peroxo complex] on the rate of oxidation of L-Valine

[L-Valine] = $2.0 \times 10^{-2} \text{ mol dm}^{-3}$ Solvent = Water
 $[\text{Na}_2\text{SO}_4]$ = $2.5 \times 10^{-2} \text{ mol dm}^{-3}$ Temperature = 313K
 $[\text{H}_2\text{SO}_4]$ = $4.0 \times 10^{-2} \text{ mol dm}^{-3}$

$10^3 [\text{Complex}]$ (mol dm ⁻³)	1.0	2.0	3.0	4.0
$10^4 k_{\text{obs}} \text{ S}^{-1}$	3.4	6.6	9.9	12.8

Fig1 Plot of 5+ log [complex] versus 5+log k_{obs}

3.4 Effect of ionic strength on the rate of reaction

The effect of variation of added salt strength on the rate of oxidation of L-Valine was studied by varying the concentration of the initially added sodium sulphate and by keeping the concentrations of L-Valine, H₂SO₄ and peroxy complex constant. The rate of the reaction was almost constant with increasing concentration of added salt (Table 3).

Table 3: Effect of varying [Na₂SO₄] on reaction rate at 313K

[Peroxy Complex] = $2.0 \times 10^{-3} \text{ mol dm}^{-3}$ Solvent = Water
 [Valine] = $2.0 \times 10^{-2} \text{ mol dm}^{-3}$ Temperature = 313K
 [H₂SO₄] = $4.0 \times 10^{-2} \text{ mol dm}^{-3}$

$10^2 [\text{Na}_2\text{SO}_4]$ (mol dm ⁻³)	1.0	1.5	2.0	2.5
$10^4 k_{\text{obs}} \text{ S}^{-1}$	7.1	7.1	7.1	7.1

3.5 Effect of concentration of Acid on the rate of reaction at 313K

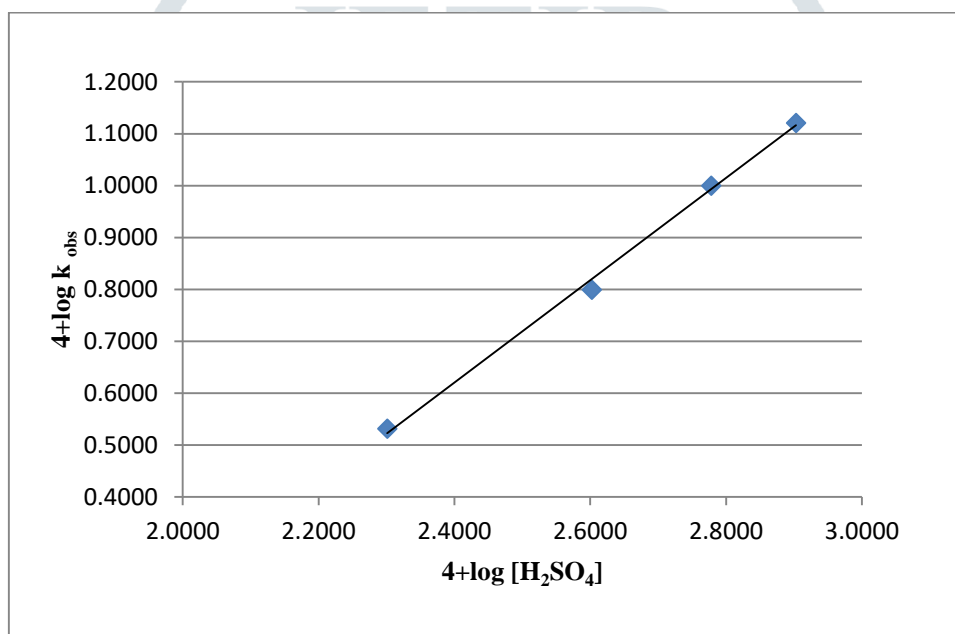
The effect of variation of added mineral acid concentration on the rate of oxidation was studied by varying the concentration of added sulphuric acid. The rate constant was found to be increasing as the concentration of hydrogen ion increases. The plot of log k_{obs} versus log [H₂SO₄] was linear with a unit slope indicating first order on [H⁺] (Table 4 & Fig. 2).

Table 4: Effect of varying [H₂SO₄] on the rate of oxidation

[Peroxo Complex] = $2.0 \times 10^{-3} \text{ mol dm}^{-3}$
 [Na₂SO₄] = $2.5 \times 10^{-2} \text{ mol dm}^{-3}$
 [L-Valine] = $2.0 \times 10^{-2} \text{ mol dm}^{-3}$

Solvent = Water
 Temperature = 313K

$10^2 [\text{H}_2\text{SO}_4]$ (mol dm ⁻³)	$10^4 k_{\text{obs}} \text{ S}^{-1}$	$4+\log[\text{H}_2\text{SO}_4]$	$4+\log k_{\text{obs}}$	Slope
2.0	3.4	2.3010	0.5315	0.9853
4.0	6.3	2.6021	0.7993	
6.0	10.0	2.7782	1.0000	
8.0	13.2	2.9031	1.1206	

Fig. 2 Plot of $4+\log [\text{H}_2\text{SO}_4]$ versus $4+\log k_{\text{obs}}$

3.6 Effect of Temperature on the oxidation of L-Valine

The reactions were studied at 313, 318, 323 and 328 K. The activation parameters (E_a & A) and the thermodynamic parameters ΔH^\ddagger , ΔG^\ddagger & ΔS^\ddagger have been evaluated (Table 5). The Arrhenius plot of $\log k_{\text{obs}}$ versus $1/T$ and the Eyring plot of $\log(k/T)$ versus $1/T$ were found to be linear (Fig 3 & Fig 4). The negative values of entropy of activation (ΔS^\ddagger) reflect that the transition state is more rigid than initial state. The nearly constant ΔG^\ddagger value indicates that similar mechanism is operative for the oxidation of L-Valine.

Table 5: The activation parameters for the oxidation of L-Valine by μ -peroxo complex

[Peroxo Complex] = $2.0 \times 10^{-3} \text{ mol dm}^{-3}$
 [L-Valine] = $2.0 \times 10^{-2} \text{ mol dm}^{-3}$

[Na₂SO₄] = $2.5 \times 10^{-2} \text{ mol dm}^{-3}$
 Solvent = Water

$$[\text{H}_2\text{SO}_4] = 4.0 \times 10^{-2} \text{ mol dm}^{-3}$$

$10^4 k_{\text{obs}} \text{ S}^{-1}$				Ea KJ mol ⁻¹	ΔH^\ddagger KJ mol ⁻¹	ΔG^\ddagger KJ mol ⁻¹	ΔS^\ddagger JK mol ⁻¹	log A
313K	318K	323K	328K					
5.7	9.3	16.1	27.6	90.19	87.47	55.11	-100.95	15.79

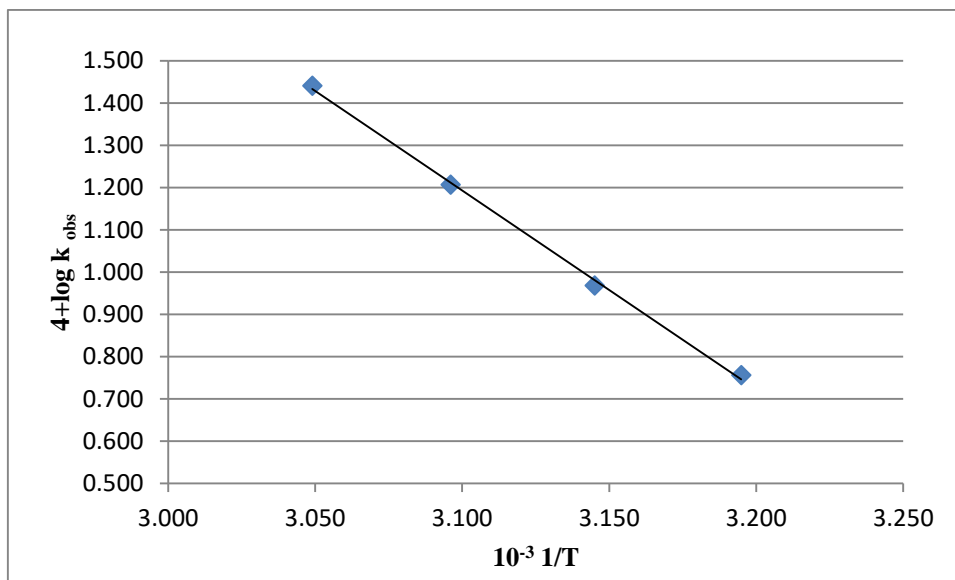


Fig. 3 Arrhenius plot of log k_{obs} versus 1/T

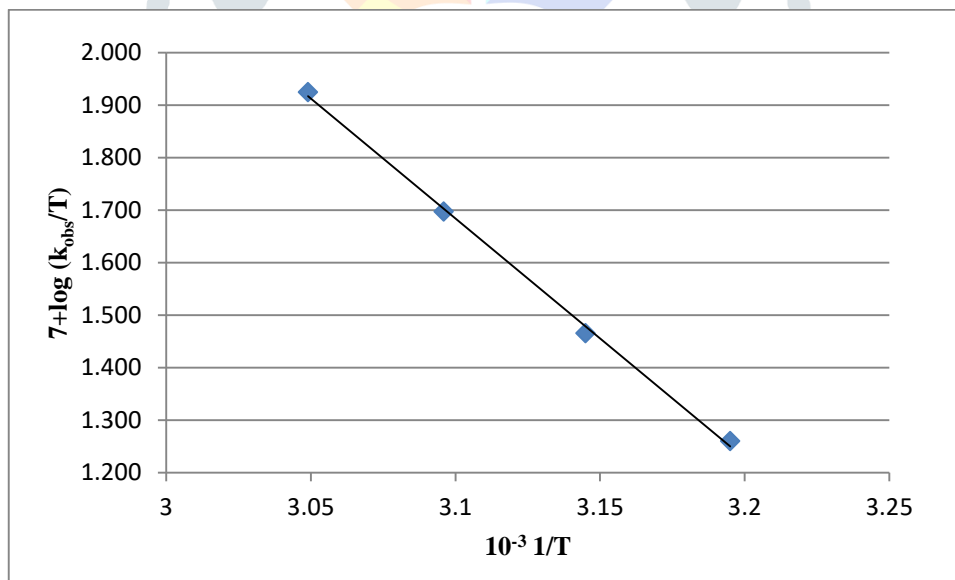
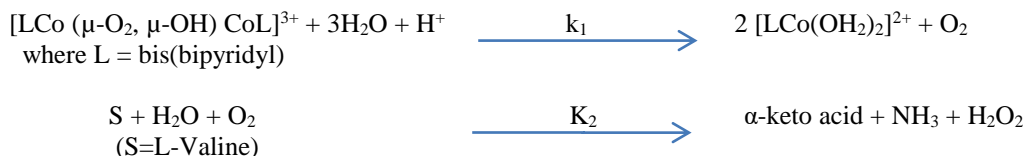


Fig. 4 Eyring plot of log (k_{obs}/T) versus 1/T

3.7 Mechanism and rate law

The mechanism of oxidation reaction may be divided into two steps. The first step is the release of caged oxygen molecule from a μ -peroxy cobalt(III) complex along with the reduction of Co(III) complex to Co(II) complex [11, 12]. In the second step, the released oxygen molecule attacks the substrate leading to the final products. From the above results the most probable mechanism for the oxidation behavior of μ -peroxy complex is given as



The above mechanism leads to the following rate law and this rate law explains all the observed experimental facts,

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

4. CONCLUSION

The μ -peroxo cobalt(III) complex has been prepared. The oxidation of biologically important substrate L-Valine by μ -peroxo complex in presence of sulphuric acid was studied in the temperature range 313-328K. The rates were measured potentiometrically. It shows a first order dependence on $[\mu\text{-peroxo complex}]$ and zero order dependence on $[\text{substrate}]$. The effect of added salt on the rate of oxidation was negligible. The rate of oxidation increases with increase in the initial concentration of sulphuric acid. The oxidation process did not induce the polymerization of the added acrylonitrile and confirmed the absence of free radical formation. The Arrhenius parameters (E_a & A) and the thermodynamic parameters (ΔH^\ddagger , ΔG^\ddagger and ΔS^\ddagger) have been evaluated. A suitable kinetic mechanism and the rate law in accordance with the experimental observation have been proposed.

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