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S Ignatius Arockiam
 Department of Chemistry,
 St. Joseph's College,
 Tiruchirappalli, Tamil Nadu,
 India

A Peter Pascal Regis
 Department of Chemistry,
 St. Joseph's College,
 Tiruchirappalli, Tamil Nadu,
 India

Oxidation kinetics of thiamine by μ -peroxo complex in aqueous medium

S Ignatius Arockiam and A Peter Pascal Regis

Abstract

μ -peroxo-bis [aminebis (ethylenediamine) cobalt (III)] perchlorate dihydrate was prepared by solution route method. The prepared complex was characterized by FT-IR and electronic spectroscopy. Oxidation kinetics of thiamine hydrochloride by μ -peroxo complex has been investigated in an aqueous medium. The reaction rate measurements were carried out under pseudo first order conditions. The effect of complex and effect of hydrogen ion concentration shows first order kinetics in the oxidation reaction. Change in the concentration of sodium sulphate has no effect on the reaction rate during the oxidation. potentiometric method has been used for the Kinetic measurement. Thermodynamic and Activation parameters were calculated and a plausible mechanism has been proposed.

Keywords: Kinetics, Oxidation, peroxo complex, Thiamine hydrochloride, Activation parameters

Introduction

Chemical kinetics provides the useful information about the mechanism and the rate of chemical reaction. It helps to carry out the reaction successfully by a way of selecting optimum condition for a considerable amount of the product. The kinetic study also helps us to study the factors which influence the rate of the chemical reaction such as temperature, concentration of the substrate and oxidant, composition of the reaction mixture. Oxidation of the organic compounds have been carried by various oxidants ^[1-3]. thiamine hydrochloride is known as vitamin family B₁ and it was the first member of vitamin B family ^[4]. The oxidation of thiamine has been carried out with various oxidants has been studied ^[5-17]. The transition metal ion with polydentate ligands as used as a model system ^[18-19] because of the active catalyst contains the metal in its higher oxidation state. μ -peroxo cobalt complexes with diverse polyamines have been used for the effective model system. The oxidation of Thiamine hydrochloride with μ -peroxo cobalt complex has been extensively studied.

Experimental

The chemicals employed were Thiamine hydrochloride (Loba AR), H₂SO₄ and Na₂SO₄ etc were of AR grade. All solutions were prepared in doubly distilled water. The [(en)₂(NH₃)CoO₂Co(NH₃)(en)₂](ClO₄)₄.2H₂O was synthesized by bubbling oxygen through a solution containing cobaltous nitrate sodium perchlorate and the suitable ligand mixture. FT-IR and electronic spectroscopic studies are used for the characterization of the synthesized complex. kinetic experiments has been carried out under Pseudo first order conditions [Thiamine hydrochloride] >> [μ -peroxo cobalt complex]. Sulphuric acid, sodium sulphate, Thiamine hydrochloride 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.

Requisite 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.

Correspondence
S Ignatius Arockiam
 Department of Chemistry,
 St. Joseph's College,
 Tiruchirappalli, Tamil Nadu,
 India

It was determined that the velocity constants were reproducible within $\pm 2\%$. The entire experiment was done in air atmosphere because the rate of the reaction was not much varied between air and an inert atmosphere. In order to keep the ionic strength constant sodium sulphate was used in the reaction mixture.

Results and discussions

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 charge transfer band near 205 nm due to the transfer of electron from the peroxide to metal. This band confirms 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 $400-4000\text{ cm}^{-1}$. 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 presence of NH_3 , C-H and O-H bending vibrations has been confirmed by the strong peaks at 1588 , 1381 cm^{-1} . The peak at 1079 cm^{-1} shows the presence of C-N stretching and ClO_4 stretching vibrations in the peroxo complex [20-22]. 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 | $\nu(\text{NH}_2)_s$ |
| 2385 | $\delta(\text{N-H})$ |
| 1588 | $\rho(\text{NH}_2)$ |
| 1381 | $\nu(\text{NH}_2)_s$, $\nu(\text{C-H})_b$, $\nu(\text{O-H})_b$ |
| 1055 | $\nu(\text{C-N})$ |

S-Stretching B-Bending, δ -Deformation, ν - bond stretching, ρ - rocking

All the kinetic runs were conceded out with [Thiamine hydrochloride] always ten times in excess of μ -peroxo cobalt complex. The initial concentration of the μ -peroxo complex was varied and the oxidation reaction of Thiamine hydrochloride was carried out and then the effect of complex has been observed. The rate constants were increased by increasing the initial concentration of the complex. The reaction is first order with respect to complex. To study the effect of [Thiamine hydrochloride], the oxidation of the substrate was carried out with different initial concentration of the substrate. The reaction is zero order with respect to substrate. By changing the initially added concentration of sulphuric acid The effect acid on the rate of oxidation was studied. The rate constants were found to be increased by increasing the initial concentration of hydrogen ion concentration. Henceforth the order with respect to hydrogen ion concentration was found to be one. The effect of added salt on the rate of oxidation of Thiamine hydrochloride was studied by varying the concentration of sodium sulphate. The rate of the reaction was almost 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

| [peroxo complex] mol dm^{-3} | $10^4 k_{\text{obs}} \text{ S}^{-1}$ |
|---------------------------------------|--------------------------------------|
| 2.0 | 2.6 |
| 2.5 | 3.1 |
| 3.0 | 3.7 |
| 3.5 | 4.3 |

[Thiamine. HCl] = $2 \times 10^{-2} \text{ mol dm}^{-3}$ $[\text{H}^+] = 2 \times 10^{-2} \text{ mol dm}^{-3}$ $[\text{Na}_2\text{SO}_4] = 2.5 \times 10^{-2} \text{ mol dm}^{-3}$

Table 3: Effect of Thiamine. HCl

| $10^2 [\text{Thiamine. HCl}] \text{ mol dm}^{-3}$ | $10^4 k_{\text{obs}} \text{ S}^{-1}$ |
|---|--------------------------------------|
| 2.0 | 2.6 |
| 2.5 | 2.7 |
| 3.0 | 2.7 |
| 3.5 | 2.8 |

[Complex] = $2 \times 10^{-3} \text{ mol dm}^{-3}$ $[\text{H}^+] = 2 \times 10^{-2} \text{ mol dm}^{-3}$ $[\text{Na}_2\text{SO}_4] = 2.5 \times 10^{-2} \text{ mol dm}^{-3}$

Table 4: Effect of acid

| $10^2 [\text{H}_2\text{SO}_4] \text{ mol dm}^{-3}$ | $10^4 k_{\text{obs}} \text{ S}^{-1}$ |
|--|--------------------------------------|
| 2.0 | 2.6 |
| 2.5 | 2.8 |
| 3.0 | 3.6 |
| 3.5 | 4.5 |

[Thiamine. HCl] = $2 \times 10^{-2} \text{ mol dm}^{-3}$ [complex] = $2 \times 10^{-3} \text{ mol dm}^{-3}$ $[\text{Na}_2\text{SO}_4] = 2.5 \times 10^{-2} \text{ mol dm}^{-3}$

Table 5: Effect of added Salt

| $10^2 [\text{Na}_2\text{SO}_4] \text{ mol dm}^{-3}$ | $10^4 k_{\text{obs}} \text{ S}^{-1}$ |
|---|--------------------------------------|
| 2.5 | 2.6 |
| 3.0 | 2.7 |
| 3.5 | 2.7 |
| 4.0 | 2.7 |

[Thiamine. HCl] = $2 \times 10^{-2} \text{ mol dm}^{-3}$ [complex] = $2 \times 10^{-3} \text{ mol dm}^{-3}$ $[\text{H}^+] = 2 \times 10^{-2} \text{ mol dm}^{-3}$

Table 6: Effect of Temperature

| Temperature in K | $10^4 k_{\text{obs}} \text{ S}^{-1}$ |
|------------------|--------------------------------------|
| 313 | 2.6 |
| 318 | 3.5 |
| 323 | 4.5 |
| 328 | 5.6 |

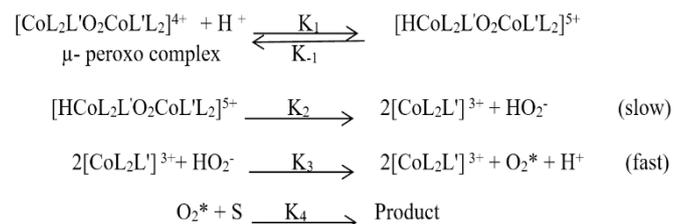
[Thiamine. HCl] = $2 \times 10^{-2} \text{ mol dm}^{-3}$ [complex] = $2 \times 10^{-3} \text{ mol dm}^{-3}$ $[\text{H}^+] = 2 \times 10^{-2} \text{ mol dm}^{-3}$ $[\text{Na}_2\text{SO}_4] = 2.5 \times 10^{-2} \text{ mol dm}^{-3}$

The Arrhenius plot of $\log K_{\text{obs}}$ 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 43.56 KJmol^{-1} , 40.95 KJmol^{-1} , 72.84 KJmol^{-1} , $-101.88 \text{ KJmol}^{-1}$ and 2.6439 at 313K respectively. The transition state is highly solvated and it was obtained by positive value of free energy of activation ΔG^\ddagger and the enthalpy of activation ΔH^\ddagger . while the negative entropy of activation ΔS^\ddagger suggests the formation of an activated complex with a reduction in the degree of freedom of molecules. It also recommends the compactness of the transition state as compared to the ground state and also in cyclic nature [23].

Mechanism and Rate law

In general the mechanism of oxidation reactions [24] may be divided into three steps. Activation of molecular oxygen is the first step. The second step is the formation of reactive intermediate. Transformation of intermediate into product is the final step. The appropriate mechanism in accordance

with the experimental observation has been proposed. The most suitable mechanism for the oxidation behavior of μ -peroxo complex is given as



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. There is an equilibrium between the mono nuclear complex and the cobalt complex has been observed in this step. 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. The mechanism for the release of oxygen from a μ -peroxo cobalt (III) dimer supports this step [25]. 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,
Rate = K_{obs} [μ -peroxo complex] $[\text{H}^+]$

This rate law explains all the observed experimental facts.

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