THINK INDIA (Quarterly Journal)

ISSN: 0971-1260
Vol-22-Issue-4-October-December-2019

A Kinetic Enquiry On The Biological Bxidation Of Fructose By µ-Peroxo Complex

R Betsy Clarebel[1], M Amaladasan[2]
[1]Research scholar, PG and Research, St. Joseph's College, Tiruchirappalli, India.
2Associate Professor, Department of Chemistry,
Affiliated to Bharathidasan University, Tiruchirappalli, India.

ABSTRACT

The cobalt µ-peroxo complex viz bis-(ethylenediamine)bis-(diethylenetriamine)µ-peroxodicobalt(III)perchlorate has been prepared by proper method and characterization of the prepared complex was done by FTIR and electronic spectroscopy. Potentiometric method has 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. Acrylamide test verified the absence of free radical formation. Arrhenius and thermodynamic parameters had been calculated from the effect of temperature on the reaction rate. A probable mechanism is 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, Fructose, mechanism.

1. INTRODUCTION

A wide variety of organic compounds were oxidised by peroxidases which are water soluble monomeric heme proteins [(1)]. The human peroxidases are haemoproteins that utilize H_2O_2 to oxidise a variety of endogenous and exogenous substrates [(2)]. Enzymes play an essential role in each living cell of our body. Peroxidase is an enzyme which is a protein molecule that function as catalyst [(3)]. The current investigation attemps to study the kinetics of oxidation of fructose by cobalt µ-peroxo complex potentiometrically. Fructose or fruit sugar is a simple ketonic monosacharride present in many plants. When consumed in excess may contribute insulin resistance, obesity, elevated LDL cholesterol and triglycerides which leads to metabolic syndrome, type 2 diabetes and cardiovascular disease [(4,5)]. An increase in high consumption fructose corn syrup, as well as total fructose, over the past 10 to 20 years has been lead to a rise in metabolic disorders and obesity [(6)]. Diversity of cobalt compounds with molecular oxygen of this kind had been investigated and characterised in solution [(7-12)]. Inorder to examine the biological oxidation of fructose by µ-peroxo complex, a kinetical investigation had been carried out.

EXPERIMENTAL METHODS

Molar concentrations of stock solutions of substrate, acid, salt and complex were made by using doubly distilled water. The standard Macron fine chemicals grade of analytical reagents were used. The reaction rate was determined by the emf measurements taken from the potentiometer. Oxygen was passed through a solution mixture of sodium perchlorate, cobaltous nitrate and the appropriate ligand mixtures and thus prepared the cobalt µ-peroxo complex [(13, 14)]. Electronic spectroscopy and FTIR studies were done in order to characterize the complex.

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Characteristic kinetic runs were carried out under pseudo first order conditions [Fructose] >>[µ-peroxo complex]. Requisite amounts of fructose, H_2SO_4, Na_2SO_4 solution and water were pipetted out in a glass beaker having double layers provided with an inlet and outlet for circulation of water from the thermostat fixed with appropriate temperature. Desired amount of µ-peroxo complex and solutions were thermo stated for about half an hour. The kinetic reaction was then started by adding required amount of the thermo stated chemicals. For all the experimental runs, the total volume of 40ml of the mixture was fixed constant. The reaction mixture was continuously stirred with the help of magnetic stirrer from the beginning till the end of the experiment. The emf of the cell was studied periodically by using equiptronics potentiometer.

By plotting linear (r > 0.99) plots of log (Et - E∞) versus time by least square method by using lotus 1-2-3 macro software and basic program the rate constants were calculated. It was ascertained that the velocity constants were reproducible within ±2% and all the experiments were examined in duplicate. Sodium sulphate was used to keep the ionic strength constant in the reaction mixture.

2. RESULTS AND DISCUSSIONS

Presence of maximum absorption at 305nm of single bridged µ-peroxo complex was noted from the electronic spectrum and this distinctly confirmed the existence of a single bridged µ-peroxo ligand in the µ-peroxo complex. By making use of KBr pellet technique in the wavelength range (400-4000) cm^{-1}, the FT-IR spectrum of cobalt µ-peroxo complex was recorded on a Perkin Elmer Spectrum. Presence of N-H stretching in this complex was determined on observing peaks at 3437, 3220, 2959, and 2859 cm^{-1}. Co-ordinated nitrogen was found to be present in this complex whose absorption band was observed at 2383 cm^{-1}.The bending vibration of NH_3, C-H, and –OH was confirmed on observation of strong peaks at 1589 and 1385 cm^{-1} respectively. The peak at 1085 cm^{-1} indicated the presence of C-N stretching and ClO_4 stretching vibration in the cobalt µ-peroxo complex. The distribution of IR band frequencies are given in the table-1.

FT-IR DATA FOR M-PEROXO COMPLEX

WAVELENGTH (CM^{-1})	FREQUENCIES OF ABSORPTION
3437, 3220, 2959 and 2895	$\nu\ (NH_2)_S$
2383	δ (N-H)
1589	$\rho\ (NH_2)_b$
1385	$\nu\ (NH_3)$, ν (C-H)$_b$, & $\nu\ (-OH)_b$
1085	ν (C-N)

TABLE NO. 1

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

EFFECT OF µ-PEROXO COBALT COMPLEX

[Fructose] = 2.0 x 10^{-2} mol dm^{-3} $[H^+]$ = 6.0 x 10^{-3} mol dm^{-3}
$[Na_2SO_4]$ = 3.0 x 10^{-2} mol dm^{-3} Temp = 313K Solvent = water

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[PEROXO COMPLEX] X 10^3 mol DM^{-3}	10^4 K_{obs} S^{-1}
1.0	5.2
2.0	7.1
3.0	8.0
4.0	9.2

TABLE NO. 2

EFFECT OF SUBSTRATE

[μ-peroxo complex] = 2.0 x 10^{-3} mol dm^{-3} $[H^+]$ = 6.0 x 10^{-3} mol dm^{-3}
$[Na_2SO_4]$ = 3.0 x 10^{-2} mol dm^{-3} Temp = 313K Solvent = water

[SUBSTRATE] X 10^2 mol	10^4 K_{obs} S^{-1}
1.0	7.1
2.0	7.1
3.0	7.2
4.0	7.1

TABLE NO. 3

EFFECT OF ACID

[μ-peroxo complex] = 2.0 x 10^{-3} mol dm^{-3} [Fructose] = 2.0 x 10^{-2} mol dm^{-3}
$[Na_2SO_4]$ = 3.0 x 10^{-2} mol dm^{-3} Temp = 313K Solvent = water

$[H_2SO_4]$X 10^3 mol	10^4 K_{obs} S^{-1}	4+LOG $[H_2SO_4]$	4+ LOG K_{obs}	SLOPE
3.0	3.9	2.4771	0.5910	0.94
6.0	7.1	2.7781	0.8513	
9.0	10.4	2.9542	1.0170	
12.0	14.7	3.0792	1.1673	

TABLE NO. 4
PLOT OF LOG K_{OBS} VS LOG $[H_2SO_4]$

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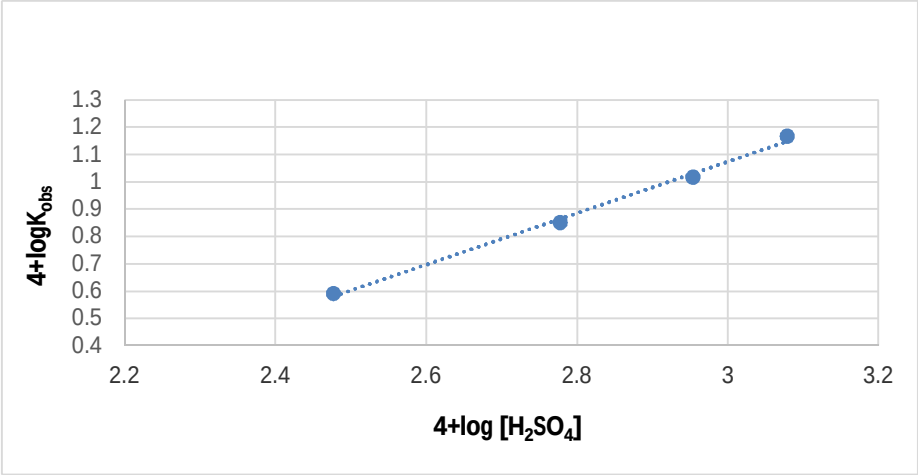

FIGURE 1

EFFECT OF ADDED SALT

[Fructose] = 2.0 x 10^{-2} mol dm^{-3} [μ-peroxo complex] = 2.0 x 10^{-3} mol dm^{-3}
$[H^+]$ =6.0 x 10^{-3} mol dm^{-3} Temp = 313K Solvent = water

[salt] x 10^2 mol	10^4 k_{obs} S^{-1}
1.5	7.1
2.0	7.1
4.5	7.1
6.0	7.3

TABLE NO. 5

EFFECT OF TEMPERATURE

[Fructose] = 2.0 x 10^{-2} mol dm^{-3} [μ-peroxo complex] = 2.0 x 10^{-3} mol dm^{-3}
$[H^+]$ =6.0 x 10^{-3} mol dm^{-3} $[Na_2SO_4]$ = 3.0 x 10^{-2} mol dm^{-3} Solvent = water

TEMPERATURE IN K	10^4 k_{obs} S^{-1}	$1/T \times 10^3$	5+ log k_{obs}	7+log(k_{obs}/T)
313	7.1	3.194	1.8513	1.3557
318	10.5	3.114	2.0212	1.5188
323	13.9	3.095	2.1430	1.6338
328	16.5	3.048	2.2175	1.7016

TABLE NO. 6

PLOT OF LOG k_{obs} Vs 1/T

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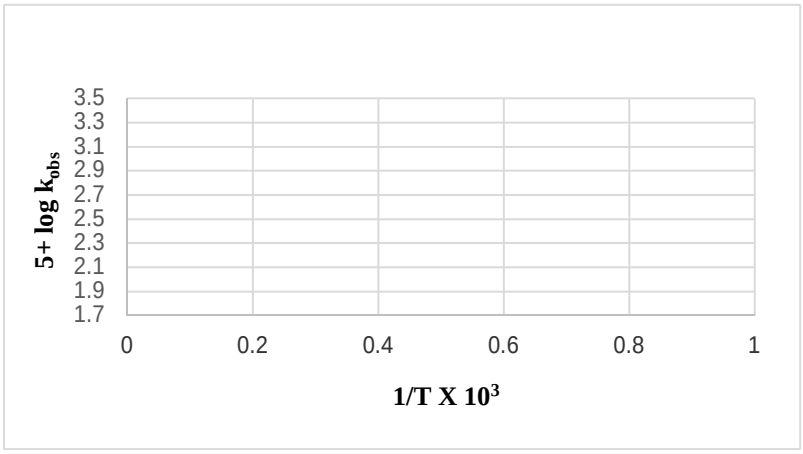

FIGURE 2

PLOT OF LOG k_{obs} /T Vs 1/T

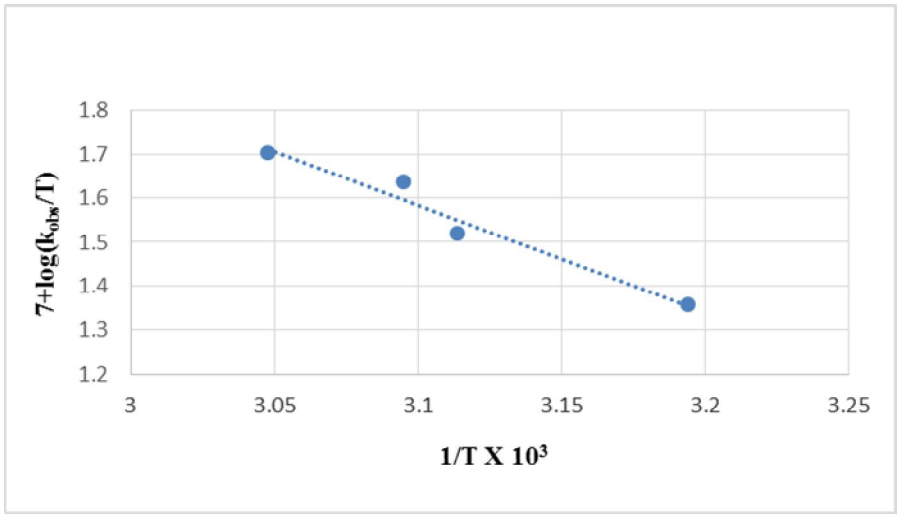

FIGURE 3

ARRHENIUS AND THERMODYNAMIC PARAMETERS

Ea	49.42 k J mol^{-1}
log A	10.09
ΔH*	46.74 k J mol^{-1}
ΔS*	-27.19 J K^{-1} mol^{-1}
ΔG*	38.23 k J mol^{-1}

TABLE NO. 7

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A straight line with a very fine correlation was observed from the Arrhenius plot of log k_{obs} versus 1/T and the plot of log (k_{obs}/T) Vs (1/T). The Arrhenius and thermodynamic parameters were calculated as given in the table-7.

KINETIC MECHANISM

$$[CoL_2O_2L_2]^{4+} + H^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2[CoL_2]^{3+} + HO_2^- \quad \text{(Slow)}$$

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

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

From the mechanism shown above , the formation of complex ion $2[CoL_2]^{3+}$ from the µ-peroxo complex $[CoL_2O_2L_2]^{4+}$ can be well seen in the first step which was a slow and reversible step in the presence of acid. The second step indicated the reduction of Co(III)complex to Co(II)complex with a simultaneous release of molecular activated oxygen. The product formation was found to occur in the last step by the reaction of substrate with activated molecular oxygen.

Thus the rate law clearly explains the whole recognized aspects of the experiment.

3. CONCLUSION

Preparation of µ-peroxo complex had been done in the laboratory and classified by electronic spectroscopy and FTIR techniques. The kinetical oxidation experienced by Fructose was proved by the observed rate constant values and the entire work is studied. On changing the µ-peroxo complex concentration and added acid concentration , it showed first order with respect to each. The reaction was found to be zero order with respect to substrate concentration. Negligible effect was observed with respect to added salt. Calculation of Arrhenius and thermodynamic parameters were done. Based on the experimental results a suitable mechanism was recommended and thus the entire study poses as a kinetical investigation which is considered as a mimic of a model system.

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