Volume - 10 | Issue - 10 | October - 2020 | PRINT ISSN No. 2249 - 555X | DOI : 10.36106/ijar

Chemistry

SPECTROPHOTOMETRIC KINETIC STUDY OF CO(II) COMPLEX WITH DEMI-MACROCYCLIC DONOR LIGAND N_2O_2

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ABSTRACT The paper envisage the complex formation of Co(II) ion with demi-macrocyclic donor ligand N_2O_2 employing kinetic approach spectrophotometrically. The role of Arrhenius thermodynamic parameters have been discussed for the proposed mechanism and rate law was derived.

KEYWORDS : Demi-macrocycles, Arrhenius parameters, Ligand, spectrophotometer, stoichiometry.

INTRODUCTION

The complexation of metal ion in aqueous solution by demi-macrocyclic ligand has been of wide importance in inorganic and analytical chemistry in recent years[1,2]. The literature provides plenty of informations regarding kinetic study of the complexation of Co(II) with demi-macrocycles particularly 14-memberd donor ligand N_2O_2[3,4]. The little text on intermediates are available on the pathways to complex formation. The existence of stable intermediate has been postulated on the basis of kinetic behaviour[5-7]. Owing to its high thermodynamic stability, the authors have decided to make complete understanding of kinetic and thermodynamics of complex of this type.

2. EXPERIMENTAL STUDY

All the chemicals used in the study were of analytical grade. The solutions were prepared in de-ionized double distilled water. The rest of the reagents including solvents were used in purest form.

The kinetic study was performed under pseudo first-order condition $[Co(II)] >> [N_2O_2]$ at constant pH. All spectroscopic measurements were carried out by well sophisticated UV-vis. Spectrophotometer at 25.0 ± 0.1^0C. The complex formation was monitored in the solvent water at different intervals of time for quantitative kinetic measurements at the fixed wave length 240 nm.

The dissolved oxygen in the solution was nullified by the passage of Nitrogen gas. The rate constant (k_{ons}) was evaluated using equation.

$$k = \frac{1}{t} \ln \frac{D_o - D_t}{De - D_t}$$

The study further reveals the formation of intermediate and complexicity of the reaction. The solvent polarity of the medium does not influence the rate and shows insignificant effect. The study rules out completely the formation of binuclear complex.

The rigidity of demi-macrocyclic complex makes reasonable to assume the existence of a relatively stable activated complex. The study of complex formation was made at four different temperatures viz. 20^0C, 25^0C, 30^0C and 35^0C. The observed data is recorded in Table-1.

The temperature coefficient of the $[Co\ L(ClO_4)_2]$ lies between 1.12 to 1.21, and 1.26 for rise in 5^0C and 10^0C temperatures (Table-2) respectively. Various thermodynamics parameters for $[Co\ L(ClO_4)_2]$ were evaluated.

The statistical analysis for the thermodynamic parameters was included in kinetic results. The thermodynamic parameters such as Energy of activation (Ea), and Enthalpy of activation ($\Delta H^{\#}$) was determined from the kinetic data by the Arrhenius plot of log k vs. 1/T (Fig.-2) and log $k_t h/k_B T$ vs. 1/T (Fig.-3) respectively. The values (Ea=19.28, and $\Delta H^{\#}$=15.74 kJ mol^{-1}) were computed from the slopes of the graphs which are in excellent agreement with experimental results, supports the present version of reported mechanism.

The Mechanism of the Complex formation

The proposed mechanism usually follows 1:2 stoichiometric ratio of $[Co(II)]$/donor ligand $[N_2O_2]$ as reported in our previous communication.[4,5]

$$Co^{2+} + 2\,L \underset{k_d}{\overset{k_d}{\rightleftharpoons}} [C_o\,L_2]^{2+} \qquad \text{.........} (1)$$

On the basis of above scheme, the rate constant expression is derived as

$$kobs = kf[C_o]^2 + \ + kd \qquad \text{.........} (2)$$

Similar mechanism has also been supported by a couple of eminent authors[8] for $[Cr\,L\,(ClO_4)_2]$.

4. CONCLUSION

The formation of $[C_O\ L(ClO_4)_2]$ complex with donor ligand N_2O_2 has been kinetically studied. Activation parameters were determined.

Table : 1. Demi-macrocyclic complex of Co(II) with N_2O_2

S. No.	$[Co(II)] \times 10^2$ (mol dm^3)	Temperature ^{0}C			
		20	25	30	35
		$10^3\ k_1\ (s^{-1})$			
1	5.00	3.87	4.38	4.91	5.53

Table : 2. Temperature coefficient (CoL (ClO4)2] Demi-macrocyclic complex

Sr. No.	$[Co(II)] \times 10^2$ (mol dm^3)	k_{25}/k_{20}	k_{30}/k_{25}	k_{35}/k_{30}	k_{30}/k_{20}	k_{35}/k_{25}
1.	5.00	1.13	1.21	1.12	1.26	1.26

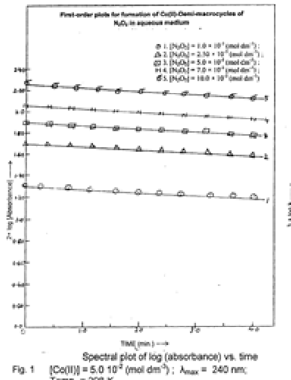

Fig. 1 Spectral plot of log (absorbance) vs. time [Co(II)] = 5.0 10^{-2} (mol dm^{-3}); λ_{max} = 240 nm; Temp. = 298 K

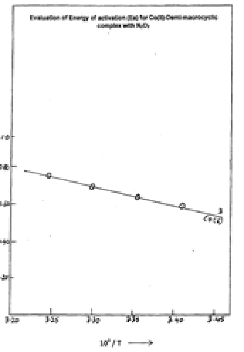

Fig. 2 Arrhenius plot of log k vs. 1/T [Co(II)] = 5.0 10^{-2} (mol dm^{-3}); λ_{max} = 240 nm

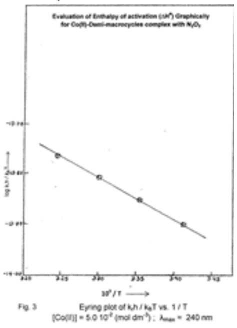

Fig. 3 Eyring plot of $k_t h/k_B T$ vs. 1/T [Co(II)] = 5.0 10^{-2} (mol dm^{-3}); λ_{max} = 240 nm

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