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Research Article

KINETIC AND THERMODYNAMIC BASED STUDIES OF DEMI-MACROCYCLIC COMPLEX DONOR LIGAND N_2O_2 WITH FE(II) ION

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14-membered demi-macrocyclic ligand incorporating N_2O_2 donor has been kinetically studied in region on a varion carry 50 UV spectrophotometer under pseudo first-order conditions in the pH range 6.55. Both the nature of ligand substituents as well as the size of demi-macrocyclic ring influence relative stability of complex. The determined rate constant was found excellent giving yield more than 80%.

INTRODUCTION

The study of the dissociation in aqueous acid of a series of complex of these N_2O_2 donor macrocyclic[1-4] from our laboratory. The observed first-order dissociation rate constants are independent of acid concentration for the complex of 14 to 17 memberd unsubstitutents macrocycles. A clear cut relationship between macrocycle ring size and kinetic lability has been established. The dissociation rate reaches minimum at 16 memberd ring complex the role of thermodynamic in dealing the stability of demi-marocycle of[5-16] in water has been investigated the Fe(II) Demi-macrocycle donor ligand field strength showed the diminution with increase in macrocyclic ring size.[17-20]

MATERIALS AND METHODS

Experimental study

The kinetic study was made under pseudo first-order conditions using an excess of Fe(II) over the $[N_2O_2]$. The concentrations of Fe(II) ions used in this experiment was in the range of 1.0 10^{-2} to 5.0×10^{-2} mol dm^{-3} changes in absorbance over time was measured using Carry 210 UV-Vis. spectrophotometer equipped with temperature controlled cell holder. The titration of solutions of Fe (II) ions in aqueous medium with macro-cyclic donor ligand N_2O_2 was examined spectrophotometrically.

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The complex formation was studied in the solvent water at 0.1M $[NaClO_4]$ by recording a series of consecutive spectra at adequate time intervals. The temperature was maintained at 25.0 ± 01^0 C by means of an external water bath. The plots of log ln ($A\infty - At$) Or ln ($At - A\infty$) against time were linear for at least 3 half-lives, yielding pseudo first-order rate constant (k_{obs}) that were reproducible within $\pm$5%. An absorbance measurement was made at wave length 235 nm.

The effect of dissolved oxygen, on the rate of reaction in a atmosphere of nitrogen, was studied. No significant difference between the results obtained in the presence and absence of nitrogen was observed. At regular intervals of time, the value of optical density/ absorbance is noted down. The experimental data is fed into the integrated rate equation:

$$k = \frac{2.303}{t} \quad \log \quad \frac{D_o = D_e}{D_t = D_t} \qquad \ldots\ldots\ldots (1)$$

The initial rates were evaluated from the tangential slope of the plots made between optical density and time at different concentration of ligand effect graphically.

RESULTS AND DISCUSSION

Effect of temperature

The influence of temperatures on the rate of reaction for the formation of demi-macrocyclic complex of Fe(II) ion with N_2O_2 donor ligand in aqueous medium was studied at temperatures 20, 25, 30 and 35^0C. It is observed that the rate of formation of complexes increase with rise of temperature. The various thermodynamic parameters are recorded in Tables 1 to 3.

Table 1 *Demi-macrocylic complex of Fe(II) with N_2O_2*

Sr. No.	Temperature / [Fe(II) x 10^2 (mol adm^{-3})]	10^3 k_1 (s^{-1}) 20	25	30	35
1.	5.00	3.16	3.61	4.11	4.73

Table 2 Temperature Coefficient [Fe L $(ClO_4)_2$] demi-macrocyclic complex

Sr. No.	[Fe(II)] $\times 10^2$ (mol dm^{-3})	$\frac{K_{25}}{K_{20}}$	$\frac{K_{30}}{K_{25}}$	$\frac{K_{35}}{K_{30}}$	$\frac{K_{30}}{K_{20}}$	$\frac{K_{30}}{K_2}$
1.	5.00	1.14	1.13	1.138	1.30	1.31

Table 3 Thermodynamic parameters for Fe(II) demi-macrocycles of N_2O_2 complex

Sr. No.	Demi-macrocycles complex	Ea kJ (mol^{-1})	$\Delta H^{\#}$ kJ (mol^1)	$\Delta G^{\#}$ kJ (mol^1)	$-\Delta S^{\#}$ kJ (mol^1)
1.	[Fe L$(ClO_4)_2$]	19.47	15.83	80.04	210.87

Thermodynamic considerations

The rate constant k of the slow steps of mechanism scheme were obtained iron the slopes and intercepts of the plots drawn at four different temperatures. The energy of activation (Ea) and enthalpy of activation ($\Delta H^{\#}$) was evaluated from the plots of log k vs. 1/T (Fig.1, 2) and log k_rh/k_BT vs. 1/T as shown from which the activation parameters were calculated in Table 3 The activation parameters were studied by using linear regression analysis one for most sets of kinetics.

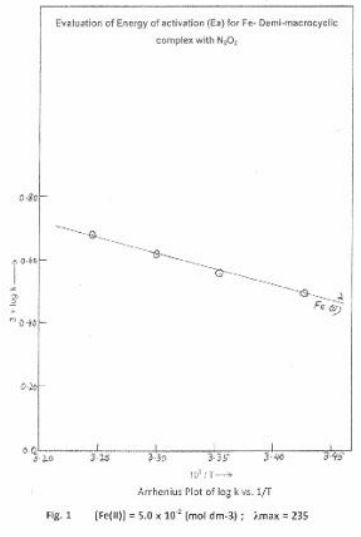

Fig. 1 [Fe(II)] = 5.0 x 10^{-2} (mol dm-3) ; λmax = 235

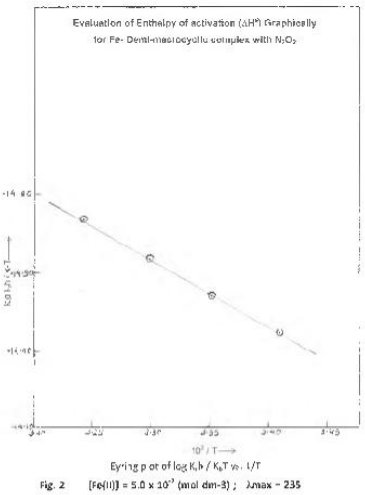

Fig. 2 [Fe(II)] = 5.0 x 10^{-3} (mol dm-3) ; λmax = 235

The entropy of activation ($\Delta S^{\#}$) for formation of demi-macrocyclic complexes and free energy ($\Delta G^{\#}$) were evaluated different temperatures which supports our mechanism, in the rate determing step. Rate is fairly slow as it involved high activation energy for the complex. The values of $\Delta S^{\#}$ (-210.87 JK^{-1} mol^{-1}) and $\Delta H^{\#}$ (15.83 KJ mol^{-1}) are both favourable for electron transfer processes. The constancy in $\Delta G^{\#}$ (80.04 KJ mol^{-1}) indicates that similar mechanism prevails the Fe(II) demi-macrocyclic complex with N_2O_2 donor ligand.

The high negative values of ($\Delta S^{\#}$) (-210.87 JK mol^{-1}) suggests that the complex was not stiff but flexible exists momentary formation takes place with the donor ligand N_2O_2 bond fission was confirmed spectroscopically. The effect of demi-macrocyclic ring size on complex stability may be better understood $\Delta H^{\#}$ and $\Delta S^{\#}$ data. The stabilities of the Fe(II) complex of the 14-membered demi-macrocycle was determined at different temperatures.

$$Fe^{2+} + 2\,L \underset{}{\overset{k}{\rightleftharpoons}} Fe\ L^{2+}$$

CONCLUSION

Kinetic studies of demi-macrocycles of N_2O_2 with complex of Fe(II) is generally inert, flexible and thermodynamically stable. The activation parameters were evaluated which favours the processes occurring in demi-macrocyclic complex.

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