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Chemistry

EFFECT OF DIELECTRIC CONSTANT ON THE SPECTRAL KINETIC STUDY OF COMPLEXES OF CR(II), FE(II), AND CO(III) WITH DEMI-MACROCYCLIC DONOR LIGAND N_2O_2

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ABSTRACT The comparative kinetic study of dielectric constant of the medium for complexes of Cr(II) Fe(II), and Co(II) with demi-macrocyclic donor ligand N_2O_2 have been reported spectrophotometrically. The rate law almost remains constant for all $[ML(ClO_4)_2]$ complexes at their maximum wave lengths. Various other related properties of the complexes were discussed.

KEYWORDS : dielectric constant, methanol, Demi-macrocyclic complexes, donor ligand, Iso-kinetic plot.

1. INTRODUCTION

Recently 14-membered demi-macrocyclic complexes have attracted much attention in several national and international Laborations. The effect of dielectric constant[1-5] of the medium was studied kinetically using water and methanol for all complexes. It was observed that the rate of formation of complexes is influenced by the solvent polarity of the medium. The rate of some reactions is enhanced in polar solvents while that of others in non-polar using the equation $D = V_1D_2 + V_2D_2$. Solvents always play important role in the synthesis of particular complex in methanol-water which is a much weaker ligand than the desired quadri-dentate demi-macrocyclic ligand N_2O_2. The Amis plot between log k and 1/D was drawn. The exchange of water has been found to be first-order rate obeying Gray and Long Ford classification. The iso-kinetic[6-11] linear relationship between the enthalpy ($\Delta H^{\#}$) and entropy (Δ-$S^{\#}$) of activation has been found in accordance with the equation $\Delta H\# = \Delta H_o^{\#} + \beta\Delta S^{\#}$.

2. EXPERIMENTAL STUDY

The synthesis of ligand N_2O_2, elemental analysis and demi-macro cyclic complexes of Cr(II), Fe(II) and Co(II) have already been reported in detail in our previous communication[9,11]. UV-spectra of all the complexes have been recorded at room temperature as well as at liquid nitrogen temperature in methanol-water within the concentration range kinetically. The absorbance measurements were made for the formation of complexes M(II) and ligand donor N_2O_2 at their maximum wave-lengths choosen between 235nm to 240nm.

3. RESULTS AND DISCUSSION

The effect of dielectric constant of the medium by varying the composition of solvent MeOH-H_2O of demi-macrocyclic complexes of donor ligand N_2O_2 with M(II) (M = Cr(II), Fe(II) and Co(II)) at preset conditions of fixed temperature 25^{0}C and λ_{max} 235 to 240 nm was studied by the UV- spectrophotometer. The results are recorded in Table 1. The study reveals that di-electric constant of the medium (D) had no effect on the rate of formation of demi-macrocyclic complexes M(II). The Amis plots of log k vs. 1/D (Volume fractions) result straight lines with no significant change (Fig.1). Though the kinetic rates of the complexes were not affected by dielectric constant of the medium but slight decrease in values of thermodynamic parameters were observed Table-2. All the demi-macrocyclic complexes follow the same mechanism and rate which is illustrated by iso-kinetic plot made between $\Delta H^{\#}$ and -$\Delta S^{\#}$ (Fig.2).

4. CONCLUSION

The effect of dielectric constant of the medium has been discussed. The iso-kinetic and Amis plots were drawn in support of similar operative mechanism among the demi-macrocyclic complexes of M(II) with donor ligand N_2O_2.

Table:1. Dependence of rate on dielectric constant of the medium

SN	MeOH-H_2O%, (v/v)	10^3/ D	$\leftarrow k_{obs} \times 10^3\ (s^{-1}) \rightarrow$		
			$[Cr\ L(ClO_4)_2]$ (1)	$[Fe\ L(ClO_4)_2]$ (2)	$[Co\ L(ClO_4)_2]$ (3)
1	1	12.76	2.87	3.58	4.39
2	5	13.06	2.85	3.61	4.38
3	10	13.46	2.88	3.63	4.41
4	15	13.89	2.89	3.62	4.45

$10^2 \times [M(II)]\ (mol\ dm^3) = 5.0\ (1\text{-}3)$; $10^3 \times [N_2O_2]\ (mol\ dm^3) = 5.0\ (1\text{-}3)$; $\lambda_{max} = 235\ (2), 2.40\ (1, 3)$; Temp. K = 298 (1-3)

Table : 2.Thermodynamic parameters for M(II) Demi-macrocycles of N2O2 complexes

SN	Demi-macrocycles complexes	Ea kJ (mol^{-1})	$\Delta H^{\#}$ kJ (mol^{-1})	$\Delta G^{\#}$ kJ (mol^{-1})	$-\Delta S^{\#}$ JK^{-1} (mol^{-1})
1.	$[Cr\ L(ClO_4)_2]$	23.85	16.41	69.30	176.0
2.	$[Fe\ L(ClO_4)_2]$	19.47	15.83	80.04	210.87
3.	$[Co\ L(ClO_4)_2]$	19.28	15.74	79.59	212.48

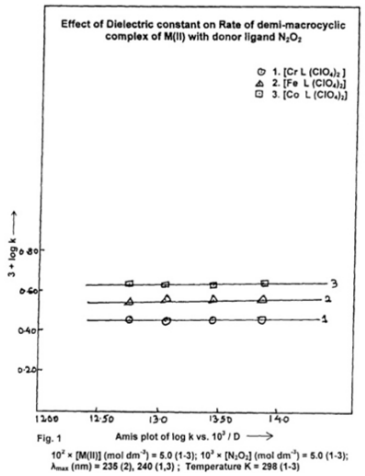

Fig.-1. Effect of Dielectric constant on Rate of demi-macrocyclic complex of M(II) ions with donor ligand N2O2

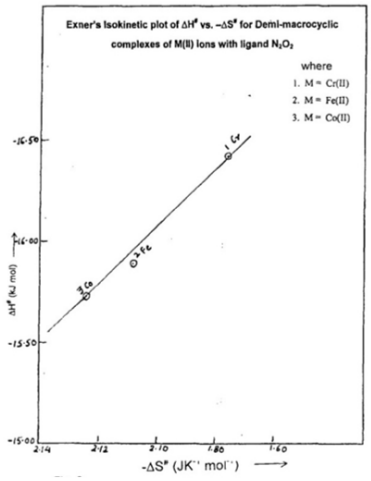

Fig-2. Exner's Isokinetic plot of ΔH#vs.- ΔS#for demi-macrocyclic complex of M(II) ions with donor ligand N2O2

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