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Kinetic and Mechanism of Complex Formation of Demi-Macrocycles of N2O2 with Cr (II) and Co (II) Ions

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Abstract: *All the kinetic measurements were carried out under pseudo first-order conditions 4,4,9.9-tetramethyle-5,5-diazonium deca-2,11 dione diperchlorate [amke+H_2](ClO_4)$_2$] reacting with metal ions Cr(II), Fe(II) ions in aqueous solution at 25^{0}C. The pH ranges 6.97, 6.90 respectively. The pH analysed in forms of different reactivities for the various kind of species. The rate constant was determined for excellent yield 80% reaction. The complex complexation of are found to be first-order with concentrations of respect to three metal ions at least five fold excess of total concentrations ligand the protonated ligand species participate in formation of demi-macrocyclic complex formation. The mechanism was discussed proposed.*

Keywords: Pendant, chelating, cavity, promoting, Entrance.

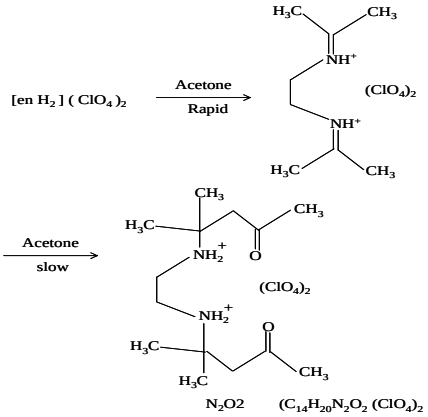
1. INTRODUCTION

The complexation of metal ions in aqueous solution by multidentate amino carboxylate chelating agents has been important in inorganic, analytical and biochemistry[1] for tetraazamerocyclic ligands the dynamics of complexation and dissociation are influenced by simple substituents on donor nitrogens as well as by attachment of pendant donor atoms and groups capable of binding of metal ions exo to the macrocyclic cavity[2-10] . The presence of a donor atoms and groups able of to binding of metal ions exo to the macrocyclic cavity. The presence of a donor atoms out side the macrocyclic basic structure offers a point for initial attachments for metal ions.[11-14] This compensates for electrostatic repulsion with protons in the cavity and promoting macrocycle entrance in it.

2. MATERIALS AND METHODS

Experimental (Synthesis of ligand N_2O_2)

4,4,9,9-tetramethyl-5, 8-diazonium dodec-2, 11-dione diperchlorate [amke+H_2] (ClO_4)$_2$. Ethane-1, 2-damine (20 ml) was added to acetone (300 ml) in a 500 ml flask and the solution cooled in an ice bath. Perchloric acid (72%) was added dropwise with constant stirring. Below temperature 20^{0}C. The flask was completely filled with acetone and left without agitation. After few hours, fine crystals of the product, which is very insoluble in acetone, commenced to separate and continued to form for week. The bulk of the product being present after 10 days was filtered off, washed with acetone until the brown colour vanished and the product remained was colourless and was air dried. The yield was equal to 85%.



(4, 4, 9, 9-tetramethylene-5, 8-diazonium dodec-2, 11-dione diperchlorate)

Spectral kinetic measurements

The kinetic measurements was performed by UV-visible spectrophotometer under pseudo first-order condition. The progress of reaction was monitored spectro photometrically at required have length by recording decrease in absorbance of complex with time Beer-Lambert law was verified on the basis of plot drawn absorbance vs. time [11-14] the observed rate constant was calculated by the equation k = 1/T ln (Do-De) / (dt-De) the effect of concentration of ligand N_2O_2, dielectric constant pH and thermodynamic parameters was also studied at four different temperatures.

3. RESULTS AND DISCUSSION

Mechanism of complex formation

One kinetic process was observed to reverse reaction

$$M^{+2} + 2\,L \underset{k_d}{\overset{k_f}{\rightleftharpoons}} [ML^{+2}] \qquad \ldots. (1)$$

The rate expression may be written as :

$$d/dt\,[NL^{2+}] = k_f\,[N^{2+}]\,[L] - kd\,[N \qquad \ldots. (2)$$
$$= kobs\,[L]$$

Final rate law was derived as:

$$K = k_f\,[N^{2+}] + kd \qquad \ldots. (3)$$

This is an excellent conformity with the experimental facts of M(II) demi-macrocycles with N_2O_2 complexes effect of concentration of M(II) ions on the rate of formation of demi-macrocyclic complexes with N_2O_2 in aqueous medium.

The dependence of rate on M(II) complex formation was examined by varying its five-fold concentrations of M(II) at 298 K. The concentrations of other reactants was maintained constant results summarized in Table (Fig. 2).

Effect of dielectric constant of the medium

The dielectric constant of medium was studied by varying composition of solvents at solvent concentration of N_2O_2 M(II) and fixed quantity of water. The dielectric constant of the medium at various composition of methanol- water UV were calculated.

$$D = V_1\,D_1 + V_2\,D_2$$

Where, D_1 and D_2 are the dielectric constant of water (D=78.8) and CH_3OH (D= 33.33) at 25^0C V_1 and V_2 are volume fractions respectively. It was found that dielectric constant of the medium had no significant effect on the rate of reaction.

Effect of pH on the rate of formation of demi-macrocycles of N_2O_2 with Cr(II) and Co(II) ions. It has been noticed that pH effect the rate considerable to high rate. The results of with rate velocity obtained at high pH for the formation of demi-macrocycles of N_2O_2 complexes with Cr(II) and Fe(II) ions. The pH of medium varied at constant acetate buffer (pH = 6.55, 6.90) which affects the formation of complexes. The plots of log (absorbance) vs. time, at various pH values for demi-macrocyclic complexes of Cr(II) and Co(II) are linear for several half lives of lower pH, whereas at high pH values, the linearity did not persist for longer time intervals due to formation of complexes.

4. CONCLUSION

Formation of demi-macrocycles of N_2O_2 with Cr(II) and Fe(II) ions were studied under one step pseudo first-order conditions, specific rate constants for the ligand species were calculated for Cr(II) and Fe(II) ions. At various pH values for demi-macorcyclic complexes of Cr(II) and Co(II) are linear for several half lives at lower pH at high pH values the linearity does not persist.

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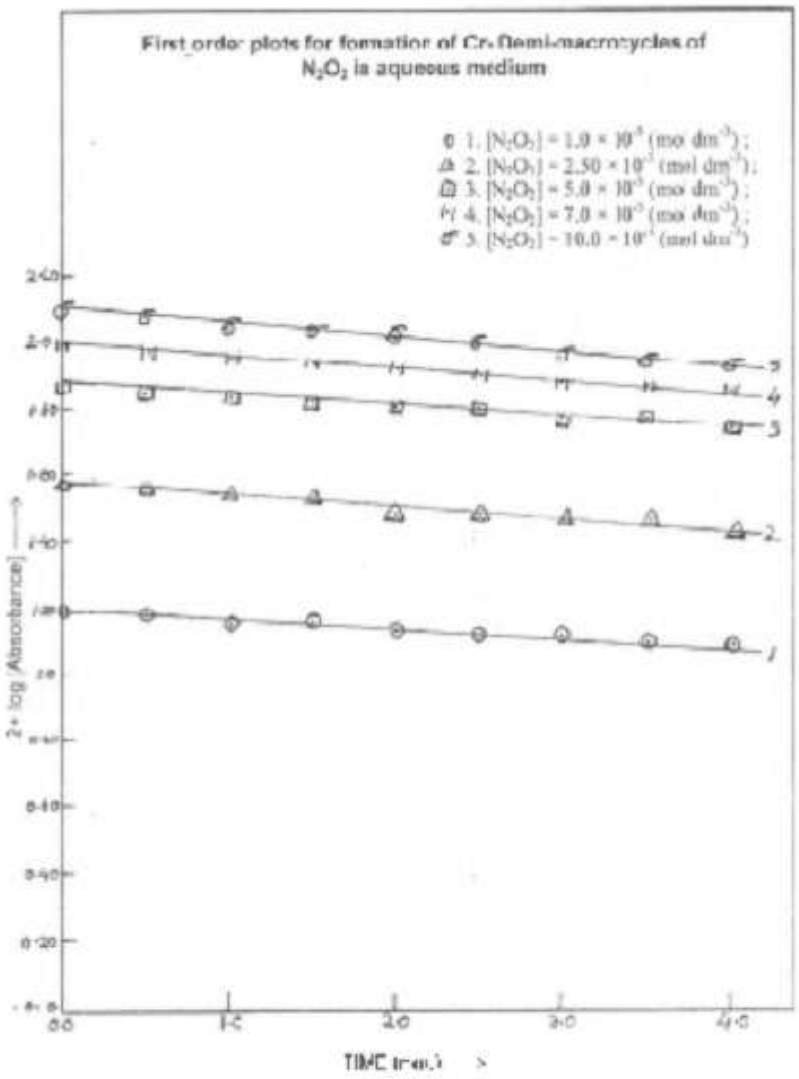

Spectral plot of log (absorbance) vs. time

Fig. 1 $[Cr(II)] = 5.0 \times 10^{-3}$ (mol dm-3) ; $\lambda max = 240$ nm
Temp. = 298 K

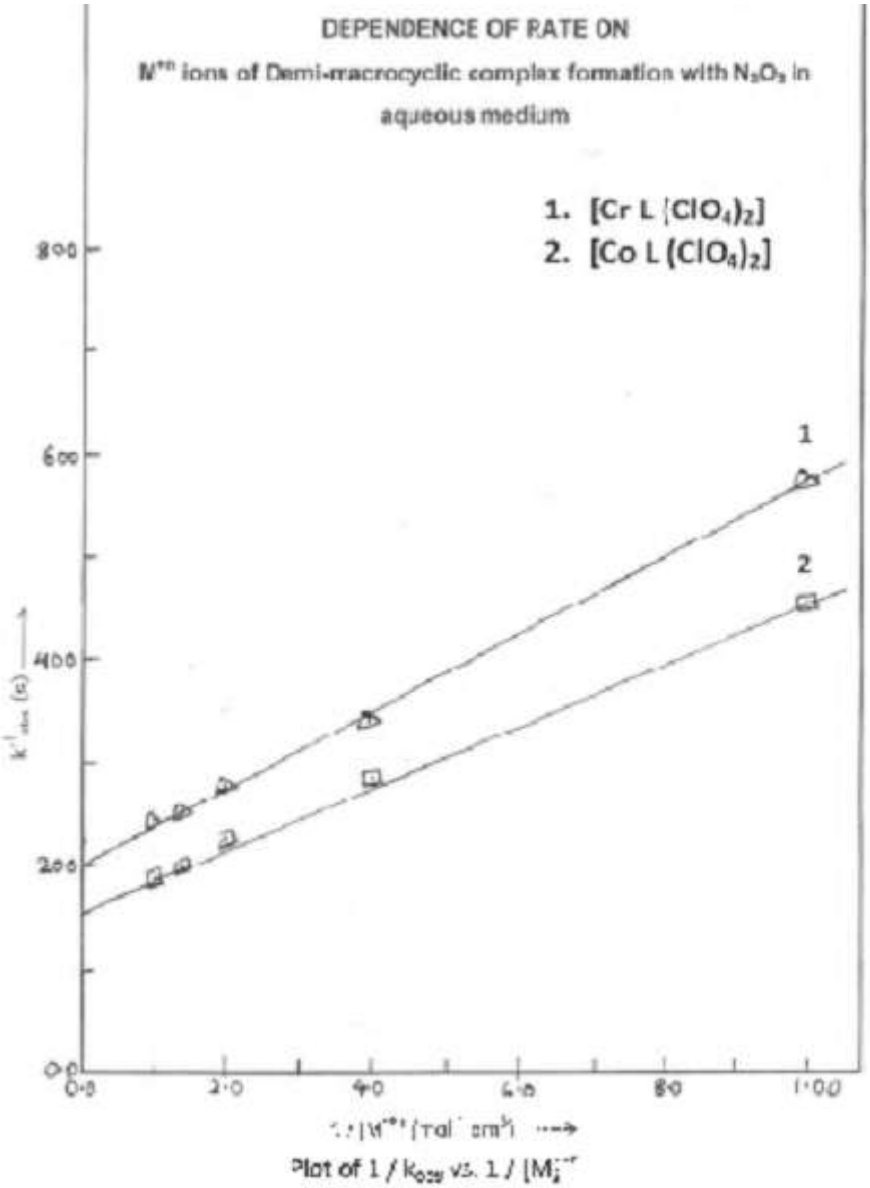

Fig. 2 λmax – 235 (1) nm, 240 (2) nm ; Temp. K = 298 (1,2)