

The Effect of pH on formation of Demi-macrocycles of N₂O₂ with complexes Cr (II) Fe (II) and Co (II) ions”

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Abstract: The kinetic measurements was carried out under pseudo first-order conditions are followed in different pH range kinetic integration and graphical method at different pH range 6.55, 7.0 and 9.2 at constant acetate buffer respectively. Its effect was observed in terms of different activities. These complexes were found stable at pH range the ligands forms coordinate bond with obeyed Beer's law.

Key Words : pseudo, acetate, activity, ligand, investigation.

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I. Introduction

Complexes with chelating ligands generally have increased stability relative to those of monodentate ligands, and even greater stability when the donor atoms are incorporated in to cyclic ligand surrounds the metal ion, commonly referred to as a macrocyclic effect.¹⁻³ The chemistry transition metal ion with macrocyclic ligands is an interesting field in chemistry the kinetic study of fast complex formation of first low transition metal ions Cr(II), Fe(II) and Co(II) with donor ligand N₂O₂ in aqueous solution have been studied spectra photometrically the complex observed pseudo first-order rate in presence of excess of ligand⁴⁻¹⁴ in UV region. The pH was maintained 7-8 at 25⁰C with wave length $\lambda = 235, 240$ nm respectively. The complex formation exhibited first-order kinetics.

II. Materials And Methods

Experimental (Synthesis of ligand N₂O₂)

4,4,9,9-tetramethyl-5, 8-diazonium dodeca-2, 11-dione diperchlorate [amke+H₂] (ClO₄)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°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%.

Synthesis of Cr(II) complex

4, 4, 9, 9-tetramethyl-5, 8 diazonium dodeca-2,11-dione Cr(II) complex

Cr(II) perchlorate (20 ml) was dissolved in water followed by (amke + H₂) (ClO₄)₂ (24 gm, 0.052 mol). The mixture was refluxed until the colours of the solution changed from red brown to violet. After sometime, the product was filtered, recrystallised from methanol and evaporated to dryness in vacuum.

Synthesis of Iron(II) complex

4,4, 9, 9-tetramethyl-5, 8-diazadodeca-2, 11-dione Iron(II) complex

Iron (II) perchlorate (10 ml) was dissolved in water followed by (amke + H₂) (ClO₄)₂ (24 gm, 0.052 mol). The mixture was refluxed until the colour of the solution changed from green to reddish brown. After sometime the product was filtered, recrystallised from methanol and evaporated to dryness in vacuum.

Synthesis of Cobalt (II) complex

4, 4, 6, 6-tetramethyl-5, 1,8-diazadodeca-2,11-dione Cobalt(II) complex

Cobalt(II) perchlorate (20 ml) was dissolved in water followed by [amke+H₂] (ClO₄)₂ (24 gm, 0.052 mol). The mixture was refluxed until the colour of the solution changed from green to red. After sometime, the product was filtered, recrystallised from methanol and evaporated to dryness in vacuum.

Kinetic Measurements

The kinetic study were performed under pseudo first-order conditions using an excess of M(II) over the [N₂O₂]. The concentrations of M(II) ions used in this experiment were in the range of 1.0 10⁻² to 5.0 × 10⁻² mol dm⁻³

changes in absorbance over time were measured using Carry 210 UV-Vis. spectrophotometer equipped with temperature controlled cell holder. The titration of solutions of M(II) ions [M=Cr(II), Fe(II) and Co(II)] in aqueous medium with macro-cyclic ligand N₂O₂ was performed spectrophotometrically.

The complex formation was studied in the solvent water at 0.1M [NaClO₄] by recording a series of consecutive spectra at adequate time intervals. The temperature was maintained at 25.0 ± 01⁰ C by means of an external water bath. The plots of log ln (A_∞ - A_t) Or ln (A_t - A_∞) against time were linear for at least 3 half-lives, yielding pseudo first-order rate constant (k_{obs}) that were reproducible within ±5%. Absorbance measurements were made at wave lengths chosen between 235 and 240 nm.

III. Results And Discussion

Effect of pH on formation of M(II)-demi-macrocyclic complexes with N₂O₂

The M(II)- demi-macrocyclic complex formation with N₂O₂ donor ligands was kinetically studied by UV-vis. spectrophotometer at pH 6.55, 7.0 and 9.2 respectively. Cr(II) complex was studied, the values so derived for the first-order rate constant are included in the (Table 1) respectively. They show small changes with the pH. When the kinetic experiments are carried out in the presence of ligand excess, there are no significant formation of binuclear complexes. The linear dependence with the ligand concentration illustrated in (Fig. 1). However, the data show clearly now a marked dependence of k₁ with the pH which must be interpreted in terms of different reactivity of the species present in the reaction mechanism, any pH dependence must be related to a different reactivity of the protonates form of ligand.

Table 1: Effect of pH on formation of M(II)-demi-macrocyclic complexes with N₂O₂

[M(II)] × 10² (mol dm⁻³) = 5.0 (1, 2, 3);

λ_{max} = 235 (2), 240 (1, 3) ;

pH = 6.55 (1), 7.0 (2), 9.2 (3) ;

Temp. K = 298 (1, 2,3)

Sr. No.	[N ₂ O ₂] × 10 ³ (mol dm ⁻³)	[Cr L(ClO ₄) ₂]	[Fe L(ClO ₄) ₂]	[Co L(ClO ₄) ₂]
		(1)	(2)	(3)
		← 10 ³ k (s ⁻¹) →		
1	1.00	0.56	0.75	1.03
2	2.50	1.27	1.70	2.11
3	5.00	2.85	3.61	4.38
4	7.00	3.23	4.64	5.57
5	10.00	4.62	6.43	8.15

where M = 1. Cr(II), 2. Fe(II) and 3.Co(II), acetate buffer used, L= Ligand (N₂O₂)

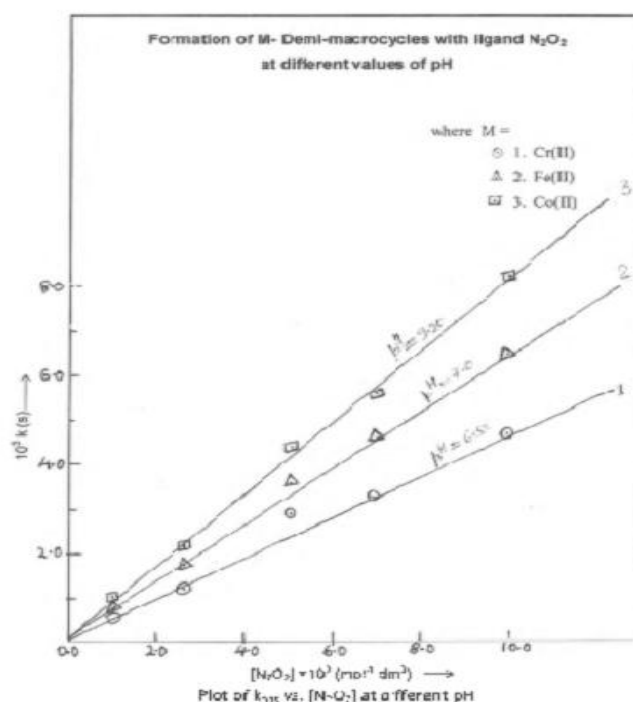


Fig. 1 10² [M(II)] (mol dm⁻³) = 5.0 (1,2,3) ;
λ_{nm} = 235 (2), 240 (1, 3) ; Temp. K = 298 (1, 2, 3)

Table 2 : Observed first-order rate constant k_{obs} (s⁻¹) for the M(II)-demi-macrocyclic complexes with N₂O₂ under various pH conditions

[M(II)] × 10² (mol dm⁻³) = 5.0 (1,2,3);

10³ [N₂O₂] (mol dm⁻³) = 5.0 (1, 2, 3)

λ_{max} = 235 (2), 2.40 (1, 3) ;

Temp. = 298 K

Sr. No.	pH	[Cr L(ClO ₄) ₂]	[Fe L(ClO ₄) ₂]	[Co L(ClO ₄) ₂]
		(1)	(2)	(3)
$k_{obs} \times 10^3$ (s ⁻¹)				
1	6.55	2.85	3.61	4.38
2	7.00	3.21	4.22	5.41
3	9.20	4.19	5.75	6.78
4	9.80	4.82	6.62	8.52

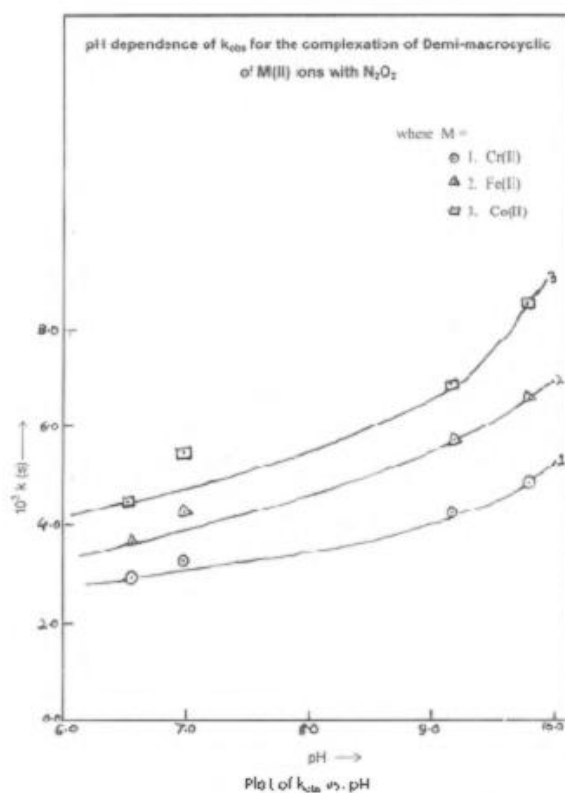


Fig. 2 10³ [N₂O₂] (mol dm⁻³) = 5.0 (1,2,3) ; [M(II)] × 10² (mol dm⁻³) = 5.0 (1,2,3) ;
 λ_{max} = 235 (2), 240 (1, 3) ; Temp. K = 298 (1, 2, 3)

It is found that the increase in concentration, slightly increase the rate in the pH range from 6.55 to 9.80. The increase of k_1 should be much smaller than that of observed experimentally. Kinetic data in (Table 2) indicates that the coordination M(II) ions to macrocycles L at pH close to 6.55 occurs into separate kinetics steps with comparable rate constants. When pH range 6.55 to 9.80 are used, the linearity of plot $D_f - D_t$ /time or k_{obs} vs. [M(II)] × 10² (mol dm⁻³) or [N₂O₂] × 10³ (mol dm⁻³) for the complexation was found that, rate of reaction increases with increase in pH whereas plot of k_{obs} vs. pH gives non-linear, slightly curve type graph (Fig. 2).

In case of Cr(II) when pH range for 1:1 anation pH range 6.55 to 9.80 is maintained. The rate of reaction increases with increasing in absorbance [Cr(II) L] complex data approximate this situation, as much as times of observation are more accurately measurable than the chemical or physical quantities relates to reactant concentrations. The straight line selected by common linear regression analysis is that which minimises the sum of the squares of the derivations of the 't' variable from the line.

IV. Conclusion

Effect of pH on formation of DMC of N₂O₂ donor ligands with first series transition metals divalent ion Cr(II) Fe(II) and Co(II) ions discussed spectro photometrically the coordinate bond was farmed at constant buffer solution which increase the rate of formation with increase in pH.

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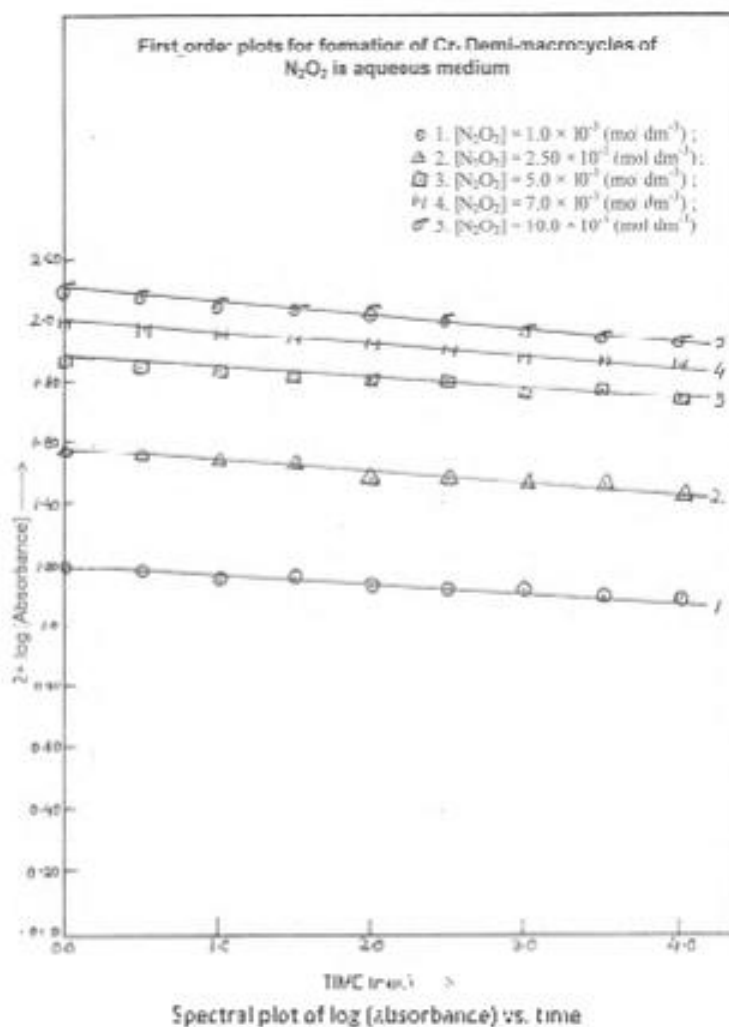


Fig. 1 $[Cr(II)] = 5.0 \times 10^{-2}$ (mol dm⁻³); $\lambda_{max} = 240$ nm
Temp. = 298 K

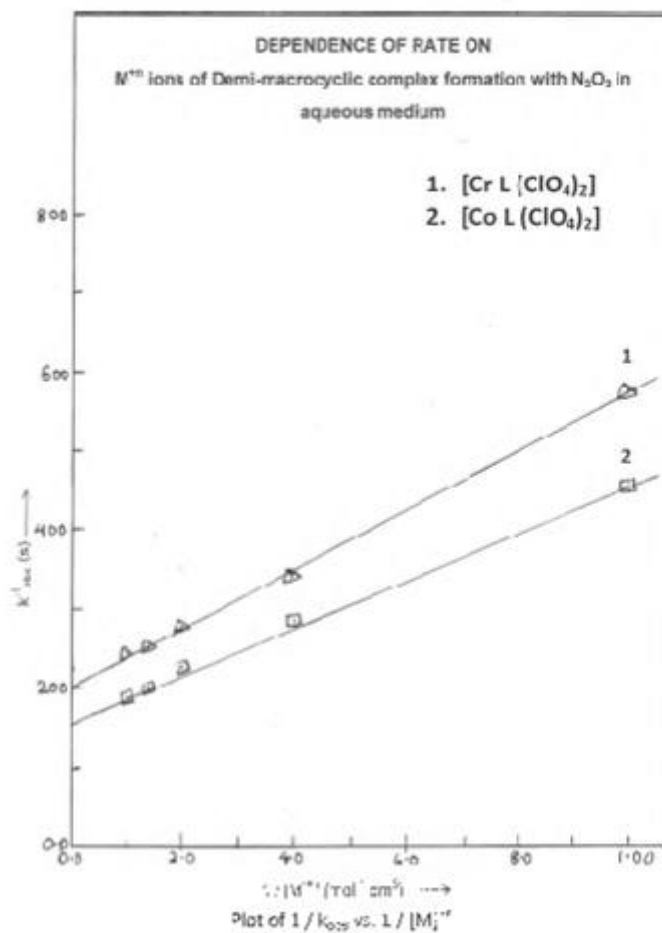


Fig. 2 $\lambda_{max} - 235$ (1) nm, 240 (2) nm; Temp. K = 298 (1,2)

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