

Potentiometric Studies on Transition Metal Complexes of Substituted Hydrazones

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Ligation properties of some phenyl hydrazones are investigated, using potentiometric technique in 75% dioxane-25% water (v/v) medium at 30°C and 0.1 M ionic strength using Calvin-Bjerrum technique. The dissociation constants of various substituted phenyl hydrazones and the stability constants of complexes of these with some transition metal ions are reported. The effect of substituents on the stability constants has been discussed.

Key Words: Transition metal complexes, Potentiometric studies, Hydrazone.

INTRODUCTION

Hydrazone is a class of organic compounds which is physiologically active and has applications in various diverse fields and is investigated for its significant analytical¹⁻⁵ properties.

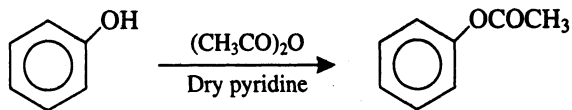
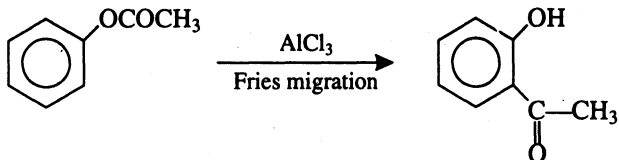
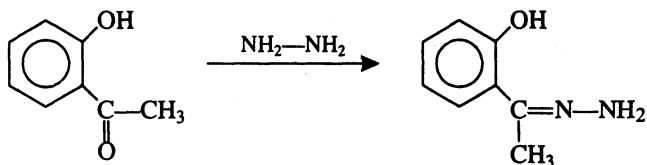
In the present investigation, the dissociation constants of various substituted phenyl hydrazones and the stability constants of complexes with some transition metal ions are studied. The effect of substituents on the stability constants has also been discussed.

EXPERIMENTAL

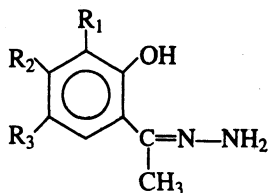
All the chemicals and reagents used were of AnalaR grade. The transition metal ions selected for this purpose were Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) and were used in the form of their nitrates. An Elico LI-120 pH-meter (accuracy ± 0.01 pH unit) with glass and calomel electrodes was used to record the pH values. All the measurements were carried out at $30 \pm 1^\circ$.

The dissociation constants of the ligands along with the stability constants of the metal ligand complexes evaluated by the procedure of Irving and Rossotti⁶. The various substituted hydrazones were synthesised from simple and substituted phenol and hydrazine hydrate by the procedures reported.

A brief account of the synthesis of these is given below.

Step I**Step II****Step III**

The following figure gives the structures of various substituted hydrazones, used in the present investigation as ligands.



The substituents R, R₂ and R₃ in the ligands were as follows:

TABLE-1

Ligand	Substituent	Compound
I	R ₁ =R ₂ =R ₃ =H	2-Hydroxy phenyl methyl hydrazone
II	R ₃ =CH ₃ , R ₁ =R ₂ =H	2-Hydroxy-5-methyl phenyl methyl hydrazone
III	R ₁ =Cl, R ₂ =R ₃ =H	2-Hydroxy-3-chloro phenyl methyl hydrazone
IV	R ₂ =Cl, R ₁ =R ₃ =H	2-Hydroxy-4-chloro phenyl methyl hydrazone
V	R ₃ =Cl, R ₁ =R ₂ =H	2-Hydroxy-5-chloro phenyl methyl hydrazone

RESULTS AND DISCUSSION

Tables 1 and 2 reveal that the dissociation constants of various phenyl methyl hydrazones under investigation are greater than *o*-hydroxy acetophenone⁷ (12.06). This decrease in the acid strength could be due to the hydrazone (N=NH₂) group

present in the structure. Nitrogen present in the hydrazone group is highly electronegative and exhibits high affinity for the proton present in the adjacent phenolic OH group. This makes its dissociation difficult.

TABLE-2
THERMODYNAMIC METAL-LIGAND STABILITY CONSTANTS FOR THE
TRANSITION METAL COMPLEXES OF SUBSTITUTED HYDRAZONES
(LIGANDS I TO III)

Metal ion	Ligand I			Ligand II			Ligand III		
H ⁺	14.59			14.90			14.46		
	log K ₁	log K ₂	log K ₃	log K ₁	log K ₂	log K ₃	log K ₁	log K ₂	log K ₃
Mn ²⁺	7.48 (8.05)	6.75 (7.16)	— —	8.08 (8.11)	7.13 (7.52)	— —	9.14 (9.17)	6.62 (6.67)	— —
Co ²⁺	8.85 (9.01)	7.83 (8.20)	6.26 —	8.62 (9.26)	9.20 (8.44)	— —	9.15 (9.36)	8.28 (8.70)	— —
Ni ²⁺	11.87 (11.88)	7.97 (8.28)	6.27 —	9.32 (9.89)	8.68 (9.04)	— —	11.13 (10.92)	9.19 (8.74)	— —
Cu ²⁺	11.98 (12.20)	11.05 (11.42)	9.79 —	10.62 (10.56)	8.74 (8.98)	— —	11.47 (12.24)	11.06 (11.31)	8.56 —
Zn ²⁺	10.24 (10.37)	9.18 (9.44)	7.57 —	9.42 (9.55)	8.39 (8.75)	— —	10.34 (10.74)	9.50 (9.91)	8.02 —

*Values in the parentheses by least square method.

TABLE-3
THERMODYNAMIC METAL-LIGAND STABILITY CONSTANTS FOR THE
TRANSITION METAL COMPLEXES OF SUBSTITUTED HYDROAZONES
(LIGANDS IV AND V)

Metal ion	Ligand IV			Ligand V		
H ⁺	14.68			14.38		
	log K ₁	log K ₂	log K ₃	log K ₁	log K ₂	log K ₃
Mn ²⁺	7.76 (8.53)	7.33 (7.61)	6.11 —	6.55 (6.61)	4.81 (5.17)	— —
Co ²⁺	7.92 (8.65)	7.52 (7.77)	6.72 —	7.75 (8.11)	6.98 (7.37)	5.79 —
Ni ²⁺	8.62 (9.23)	7.89 (8.29)	6.25 —	8.77 (8.78)	7.43 (7.75)	5.33 —
Cu ²⁺	12.29 (12.63)	11.45 (11.88)	7.74 —	10.42 (10.53)	9.31 (9.65)	— —
Zn ²⁺	9.63 (10.37)	9.23 (9.47)	7.67 —	8.49 (8.37)	8.41 (9.40)	— —

*Values in the parentheses by least square method.

The substituents, depending on their electropositive or electronegative nature influence the dissociation of the proton as investigated previously⁸⁻¹⁰. This effect is pronounced particularly when electron donating group, such as CH₃, is present in the structure. The ligands having such groups would therefore show higher pK values. This type of trend was observed in the studies of kinetics of thiourea⁸. A similar effect of methyl group is observed in the pK values of ligand II (pK = 14.91). The pK value of this ligand is higher than unsubstituted ligand I (pK = 14.59).

The presence of Cl group as a substituent is expected to increase the acid strength, since this group is well known for its electron withdrawing ability resulting from combination of its high electronegativity and presence of empty d-orbitals on it. This has been observed in the present investigations also. The unsubstituted hydrazone has pK values 14.59. The same has been reported to be 14.46 and 14.38 for ligands III and IV. This lowering of values is due to presence of Cl group in it. Similar trend was observed in case of Vartak and Menon¹¹.

The pK value of 4-chloro phenyl methyl hydrazone in the present investigations is 14.68 which is higher than unsubstituted hydrazone.

The order of stability constants of transition metal ions and various substituted hydrazone systems in the present investigation was found to be Cu > Zn > Ni > Co > Mn. This is in agreement with that of Johanstan *et al.*¹² The values observed also indicate the increase in ionic potential on passing from Mn to Zn. The order in the present investigation was Zn > Ni. This was similar to the one obtained by Pederson¹³ and Athawale *et al.*¹⁴

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