© 2017 IJSRSET | Volume 3 | Issue 2 | Print ISSN: 2395-1990 | Online ISSN : 2394-4099
Themed Section : Engineering and Technology

pH-Metric Study of Metal-Liagand Stability Constants of Co(II), Cu(II), Ni(II) and Zn(II) Complexes with some Substituted Chalcones

P. J. Parmar

Department of Chemistry, Nanasaheb Y. N. Chavan Arts, Science and Commerce College, Chalisgaon, Jalgaon, India

ABSTRACT

The interactions of Co(II), Cu(II) and Zn(II) with 1-(2"-Hydroxy-3"-nitro-5"-methylphenyl)-3-(3'-nitrophenyl)-2-propen-1-one (Ligand-I) and 1-(2"-Hydroxy-3"-nitro-5"-methylphenyl)-3-(3'4'-methylene dioxyphenyl)-2-propen-1-one (Ligand-II) have been studied by Bjerrum method as adopted by Calvin and Wilson. The stability constant of 1:1 and 1:2 complexes of C0(II), Cu(II) and Zn(II) have been studied at constant temperature (27±0.1°C) and 0.1 M ionic strength (NaOH) in 70% DMF-water mixture. It is observed that formation of 1:1 and 1:2 complexes in occurring simultaneously.

Keywords: pH-Metric Study, Co(II), Cu(II), Ni(II) and Zn(II), Metal-ligand stability constant, substituted chalcones.

I. INTRODUCTION

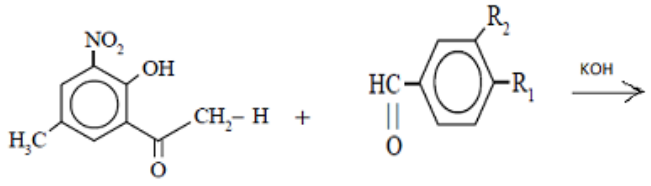
Chalcones constitute an important group of natural products and some of them possess wide range of biological activities such as antibacterial[1,2], anticancer[3,4], antitubercular[5], antiviral[6,7], antiinflammatory[8], etc. The presence of a reactive , β-unsaturated keto function in chalcones is found to be responsible for their antimicrobial activity, which may be altered depending on the type and position of substituent on the aromatic rings. In the present communication, the reaction of 2-hydroxy-3-nitro-5-methyl acetanaphthone (1) with different aromatic aldehydes (2) to form chalcones (Ligand I and Ligand II) is reported. The structures of the various synthesized compounds were assigned on the basis of elemental analysis, IR and ^{1}H NMR spectral data. These Compounds were also screened for their antimicrobial activity.

Since the last four decades considerable research work has been done on the study of complexes in solution[9,10]. Bjerrum's dissertation[11] has taken the initative to develop the field. Some of the important characteristics added to the drugs play an important role in biological activities, e.g., low dissociation constant, special rodox potential, electron distribution and solubilities which has been imparted by the metal complex formation. The effect on solubilities of the drug in the lipids and their transfer through the cell membrane have been marked by these characteristics. The group transfer reactions, bond formation, bond cleavage are the natural processes which have been processed by metal-complex formation. Metal complexations not only bring the reacting molecules together to give activated complex[12] but also polarize electrons from the ligands towards the metal. The relation between stability and basicity of the ligands is indicated by the formation constant and free energy charge value. Bulkier group increases the basicity of the ligands as well as stability. The stability of the complexes is determined by the nature of central metal atom and the ligands. The stability of the complex compounds is influenced by the most important characteristics like the degree of oxidation, the radius and electronic structure. Stability of the

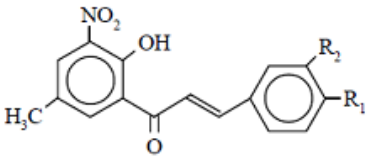
complexes depends on the same characteristics of the ligand as considered for the cation as complexes reacted with monoatomic ligands. In addition, the strength of binding for ligand molecules and polytomic ions depends on the ligand molecule and the nature of the atoms which is directly linked to the central atom or icon.

By comparing the ionic radius and second ionization potentialsof the metal ions, the stability order of metal complexes of transition metal ions was studied by Irving and Williams[13] because it is valid for most nitrogen and oxygen donor ligands. In stability of complexes, the size and number of chelating ring plays an important role. The structure of chelating agents determines the size of chelating ring and the number of rings formed on chelation. The work of amino acid chelates and identification of five and six-membered rings as the most stable is reported by Ley[14]. In the past a number of workers[15-23] have reported their results on metal-ligand chemistry.

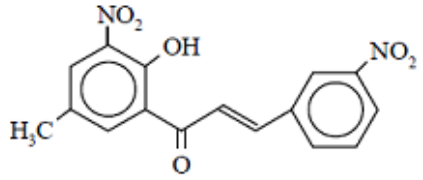
In the present work, substituted chalcones have been synthesized in view of analytical applications and biological activities. Additional to fungicidal activity, chalcones, especially nitro chalcones are found to possess antihelminthic activities. It is reported that the substituted diketones which are different in nature act as antimicrobial agents, anti-infalmmatory agnets, insecticidals, bactericidals, pharmaceuticals and fungicidals.



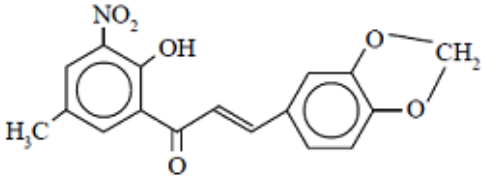
(1) (2)



(Ligand I and Ligand II)



Ligand-I



Ligand-II

II. EXPERIMENTAL

All chemicals such as NaOH, HNO_3, KNO_3 and metal salts of AR grade were used in the present work.

1-(2"-Hydroxy-3"-nitro-5"-methylphenyl)-3-(3'-nitrophenyl)-2-propen-1-one (Ligand-I) and 1-(2"-Hydroxy-3"-nitro-5"-methylphenyl)-3-(3'4'-methylene dioxyphenyl)-2-propen-1-one (Ligand-II) were synthesized by literature method. Both ligands were crystalixed and their purity was checked by TLC before use. The solutions of purified ligends were prepared in 70% dioxane-water mixture and standardized by pH-metric techniques.

Systronics microprocessor based instrument with accuracy ±0.01 unit with glass electrode and saturated calomel electrode was used for the measurements. It was calibrated by buffer solution of pH 4.00, 7.00 and 9.20 at 27° C before processing the titrations.
The experimental procedure involved potentiometric titration of:

1. Free acid(0.01 M),
2. Free acid(0.01 M) and ligand ($20X10^{-4}$ M).
3. Free acid(0.01 M), ligand ($20X10^{-4}$ M) and metal ion ($4X10^{-4}$ M) against standard NaOH solution.

The ionic strgnth of all the solutions was maintained constant (0.1 M) by adding appropriate quantity of 1 M KNO_3 solution.

The titrations were carried out in 100 mL pyrex glass beaker kept in a ice-cold water bath maintained at constant temperature (27±0.1°C). Nitrogen gas was purged for chemically inert atmosphere. The readings were recorded for each addition of 0.5 mL. The graph of volume of alkali against pH were plotted. The pH-meter readings were taken only after the gas bubbing completely stopped.

III. RESULTS AND DISCUSSION

Determination of proton-ligand stability constants

The dissociation constants of substituted diketones (1, 2) were determined at 0.1 M ionic strength pH-metrically. The reagents or ligands used in the present investigation are monobasic acids having only one dissociate H^+ ion from OH group and can therefore be represented as HL.

$HL=H^++L^-$

The titration curves of the acid and the ligand deviate at about pH 1.7 and then increase upto pH 7.9. The deviations betweena acid curve from ligand for all the systems showed the dissociation of H^+ ions from –OH groups of the ligands.

Proton-ligand formation numbers (ŋ A) were calculated by the Irving and Rossotti expression.

$$ŋA=Y\frac{(E°+N)\Delta V}{(V_o+V^1)T°L}$$

Where V_o=Initial volume of solution(50 mL)

N=Normality of sodium hydroxide

T°L =Normality of Sodium hydroxide

E°=Initial concentration of free acid(HNO_3).

Y=Number of dissociable protons from ligand.

$(V_2-V_1)=\Delta V$=Volumes of alkali consumed by acid and ligand On the same pH

The pKa values for both systems were calculated by half integral caluculation which are presented in Table 1.

Table 1. Proton-Ligand Stability Constants

System	pK
Ligand-1: 1-(2"-Hydroxy-3"-nitro-5"-methylphenyl)-3-(3'-nitrophenyl)-2-propen-1-one	7.89
Liagnd-2: 1-(2"-Hydroxy-3"-nitro-5"-methylphenyl)-3-(3'4'-methylene dioxyphenyl)-2-propen-1-one	8.37

Table 2. Metal-Ligand Stability Constants(Log K)

System	Metal-ligand stability constant	
	log K_1	Log K_2
Ligand-1 Co(II)	8.17	7.90
Ligand-1 Cu(II)	8.71	7.45
Ligand-1 Zn(II)	8.29	7.37
Ligand-1 Ni(II)	8.11	7.21
Ligand-II Co(II)	9.19	8.35
Ligand-II Cu(II)	8.77	8.11
Ligand-II Zn(II)	8.89	8.03
Ligand-II Ni(II)	8.07	7.91

IV. CONCLUSION

It is observed from the titration curves between (acid+ligand) and (acid+ligand+metal) for all the systems that the deviation between the curves is found to be at about pH 1.7. This indicates the commencement of complex formation from this pH. During the titarion process, solution colour is changed from light to brown to dark brown. This also shows the formation of complex between ligand and metal ion.

It could also be seen from Table-1 that the order of pK values of the ligands is found to be as:
pK ligand 1<pK ligand 2 this may be due to the fact of the presence of two nitro(-NO_2) as the electron withdrawing groups in ligand 1in two phenyl rings. The electron withdrawing group reduces the pK values of the ligand 1.

It is oberserved from Table 2 that the difference between the values of log K_1 and log k_2 is suffieciently large. This indicates the stepwise complex formation between ligand and metal ions. The values of metal-ligand stability constants (log K_1 and log K_2) are greater of Cu(II) complexes that Co(II) and Zn(II) complexes. It means Cu(II) forms more stable complexes than the complexes of Co(II) and Zn(II) with ligand 2 but less stable in case of ligand 1.

V. ACKNOWLEDGEMENT

Thanks to Prncipal Nanasaheb Y. N. Chavan Arts, science and Commerce College, Chalisgaon for providing necessary laboratory facilities and valuable support in this work.

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