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pH METRIC STUDY OF TRANSITION METAL COMPLEXES WITH SUBSTITUTED β–KETO SULPHIDE

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ABSTRACT

A potentiometric studies on some transition metal chelates with substituted β–keto sulphides was carried out according to Calvin–Bjerrum titration technique in 80%(v/v) ethanol water medium at 298.15K and M = 0.1 M ($NaClO_4$). Effect of substitution on pK values is discussed. Stability of transition metal complexes increases in the order Mn < Co < Ni < Cu > Zn. All the chelates follows the relationship log K = a p K + b. The thermodynamic functions for the formation of 1 : 1 complexes have been obtained by temperature coefficient method. The chelates are both enthalpy and entropy stabilized. Crystal field stabilization energies follow the order Ni > Cu > Co.

Key words : pH Metry, β–Keto sulphide, complexes.

INTRODUCTION

Though considerable amount of work has been done earlier in metal complexes of organic ligands[1], the trend of the last two decades is towards the use of biologically active ligands as complexing agents[2]. Sulphur and nitrogen containing organic compounds are well established as medicaments. Sulphonyl / sulphide derivatives are gaining importance due to their wide range of antibacterial activities[3]. Aryl thio substituted acetophenones have been recently reported and found to exhibit passive cutaneous anaphylexis activity[4]. A Perusal of literature reveals that no work has been done on transition metal chelates of substituted β–keto sulphides. In view of the above findings, it was decided to use these compounds as complex forming reagents in the present study. The purpose was to obtain more precise information about the behavior of these ligands in solution and stability constants of their binary complexes.

EXPERIMENTAL

The metal nitrates were obtained from BDH (India) and were of AnalaR grade. The ligands substituted β–keto sulphides were synthesized in this laboratory and their purity was checked by m.p., TLC and IR spectral data. All the required solutions were prepared always afresh in deionized water. The potentiometric titration against carbonate free standard sodium hydroxide were carried out in the thermostated cells, the desired temperature being maintained constant with an accuracy of ± 0.02°c. The ionic strength of the solution was maintained constant at 0.1 M ($NaClO_4$) in all the titrations. The details regarding other chemicals and measurement of pH were the same as those given in earlier papers[5–7]. The substituted β–keto sulphides used in the present study are as:

(i) 2–(Phenyl) mercapto–2'–hydroxy–5'–methyl acetophenone (L_1)

(ii) 2–(4–chlophenyl) mercapto –2– hydroxy –5– methyl acetophenone (L_2)

(iii) 2–(4–methyl phenyl) mercapto –2–hydroxy –5– methyl acetophnone (L_3)

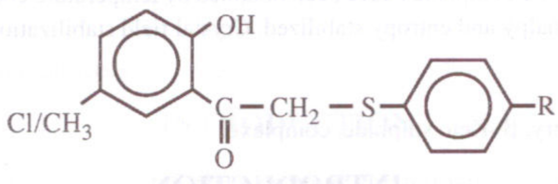
(iv) 2–(phenyl) mercapto) –2– hydroxy –5– chloroacetophenone (L_4)

(v) 2–(4'–Chloro phenyl) mercapto–2'– hydroxy –5'– chloroacetophenone (L_5)

(vi) 2–(4'–methylphenyl) mercapto–2'– hydroxy –5'– chloroacetophenone (L_6)

RESULTS AND DISCUSSION

The general structure of β–keto sulphides is presented as :



where R=H, Cl, CH_3

pK values of β–keto sulphide

Acidity constants of substituted β–keto sulphides at four different temperatures were evaluated by the method of Irving and Rossotti and have been presented in Table 1.

The experimental pK values in 80% (v/v) ethanol – water medium of 2–hydroxy –5–methylacetophenone, 2–hydroxy –5–chloroacetophenone, are also determined under similar conditions and are also given in Table 1.

It was expected that pK values of acetophenone should be lower than the corresponding phenols. The justification for the higher pK values is due to the predominant effect of intramolecular hydrogen bonding between – OH group and $-COCH_3$ group than – M effect of $-COCH_3$ group.

The pK values of β–keto sulphides are lower than their corresponding acetophenones. The overall decrease in the pK values of the ligands is due to electron withdrawing effect exerted by aryl mercapto moiety, which reduces the strength of intramolecular hydrogen bonding and thereby making the ligands more acidic.

Table 1. Formation constants of β–keto sulphides in 80% (v/v) ethanol–water mixtures at different temperatures

μ = 0.1M ($NaClO_4$)

Ligand acids	Temperature (°C)			
	15	25	32	45
L_1	11.01	10.90	10.83	10.71
L_2	10.91	10.80	10.74	10.63
L_3	11.08	10.97	10.89	10.76
L_4	9.82	9.70	9.61	9.50
L_5	8.98	8.93	8.83	8.75
L_6	9.68	9.63	9.56	9.45

Standard deviation in pK values : 0.01 – 0.02

* pK of p–chloroacetophenone 10.90 (0.03)

* pK of p–methylacetophenone 11.80 (0.03)

* Determined in 80% (v/v) ethanol–water medium at 25°C and N = 0.1 ($NaClO_4$).

This effect is markedly observed in the ligand containing chlorine atoms as the only substituent. This is attributed due to the combined electron withdrawing effect of aryl mercapto moiety and that of chlorine atom as substituent in this moiety.

The introduction of the methyl group at para position increases the pK values. This is due to the inductive effect of this group which increases the charge on the phenyl ring; thus opposing the charge transfer from the OH group, which cause stronger bonding of the proton to the oxygen atom. This effect is more pronounced when both the aryl rings has got methyl group as substituent. Thus the pK values of the β–keto sulphides follows the order: $L_3 > L_1 > L_2 > L_4 > L_6 > L_5$.

The enthalpy and the entropy changes involved in dissociation equilibria were obtained by calculating pK values of the ligands at four different temperatures using standard equations and are presented in Table 2. ΔH values are found to be lower than that obtained by Herman[8] or by Ernst[9]. ΔS values for OH dissociation are found to be negative, which indicates the dissociation of H^+ from –OH group is not thermodynamically favored.

Binary chelates

The deviation of metal titration curve was observed in the pH range 4–6 in all the cases. The pH of hydrolysis of the transition metal ion under investigation is more than the pH of complexation. Turbidity appears above pH 7.0. The highest value of $\bar{n}$ in the pH range 4–6 being ~1.0, which indicates that transition metal ions form only 1 : 1 complexes. The transition metal ion coordinate to β–keto sulphides through carbonyl oxygen and phenolic oxygen with the formation of six member 1 : 1 chelate. Formation constant of metal complexes have been evaluated by Irving and Rossotti method[10] and are presented in Table 3.

Table 2. Dissociation constants, free energy, enthalpy and entropy changes in the dissociation equilibria of β–keto sulphides

Temp. = 25 ± 0.1°C μ = 0.1M ($NaClO_4$)

Ligand acids	pK	$+\Delta G$ (kJ/mole)	$-\Delta H$ (kJ/mole)	$-\Delta S$ (kJ/mole)
L_1	10.90	62.24	17.62	267.96
L_2	10.80	61.66	16.44	262.09
L_3	10.97	62.64	18.10	270.93
L_4	9.70	55.38	18.23	240.03
L_5	8.93	50.98	15.32	222.53
L_6	9.63	54.97	23.56	226.66

Table 3. Formation constants of transition metal ions with β–keto sulphides in 80% (v/v) ethanol–water mixture

Temp. = 25 ± 0.1°C μ = 0.1M ($NaClO_4$)

Transition metal ions	β–keto sulphide					
	L_1	L_2	L_3	L_4	L_5	L_6
Mn (II)	6.34	5.76	7.64	5.94	4.66	5.86
Co (II)	6.46	5.91	7.93	6.23	4.98	6.13
Ni (II)	7.23	6.62	8.26	6.53	5.29	6.50
Cu (II)	7.75	7.62	9.25	7.32	6.52	7.26
Zn (II)	7.19	7.12	8.65	6.67	5.80	6.58

Standard deviation of log K values (0.01 – 0.03)

The effect of ligand basicity on metal ligand stability constant have been explained[6] using the relationship $\log K = a\,pK + b$ by several workers[11,12]. The linear relationship between log K and pK have been found to hold for a series of closely related ligands by many workers. The validity of this equation has been examined for present complexes. It is observed from the figure, that all the points falls on or near the straight lines except for the ligand L_3. The values of slope 'Q' obtained for straight line are:

Mn (II)	0.81	Cu (II)	0.81
Co (II)	0.73	Zn (II)	0.70
Ni (II)	0.82		

The effect of substituent in the ligands on the stability of metal ligand complexes as compared to that of proton–ligand complexes will be to a lesser extent if slope is less than one. In the present study, all the slopes are less than one, which is in agreement with Ernst and Meenashi[12].

The value of slopes for Mn (II), Co (II), Ni (II), Cu (II) and Zn (II) complexes observed (less than unity) are also in agreement with the constants of John *et al*[13]. regarding the behavior of ! donors[14]. In all the plots, point corresponding to L_3 deviates far away from the straight line because of the strong basic nature of these ligands, which makes the complexes extra stabilized.

Effect of metal ions on stability constants is generally explained in terms of Irving and Williams's order of stability. The stability values should increase with increase in atomic number. It can be concluded from the plots that the stability of transition metal complexes of β–keto sulphides increases in the order Mn < Co < Ni < Cu > Zn.

The thermodynamic parameters for transition metal complexes with β–keto sulphides were obtained from the data of log K values at four different temperatures listed in Table 2. The value of ΔH obtained for metal complexes of β–keto sulphides follows the order Zn (II) < Cu (II) > Ni (II) > Co (II) > Mn (II). The ΔS values for Cu (II) are relatively higher than for the remaining transition metal ions and follow the order of basicity of ligands. In case of Cu (II) and Ni (II), higher negative ΔH values indicate relatively greater covalent character of the metal ligand bond in these complexes as compared to the other metal ion complexes. Relatively high entropy values in copper complexes may be attributed to Jahn–Teller distortion of the octahedral symmetry in copper, which may result in greater covalent character of the metal ligand bond and consequently greater effective neutralization of cationic and anionic charges. The small values of the ΔH and reasonably good ΔG values results in higher entropy values during complex formation. The entropy effect seems to be predominant over the enthalpy effect in stabilizing the metal chelates of β–keto sulphides.

Calculation of crystal field stabilization energy for metal chelates of β–keto sulphides

The calculation of crystal field stabilization energies for Co (II), Ni (II) and Cu (II) for each β–keto sulphides are carried out by method given by George and MeClure[15]. A typical calculation for L_5 is shown in the Table 4. The difference between ΔH_L values designated as Er for the d^{10} and d^5 configuration which is independent of 'd' orbital splitting is called as transition series contraction energy. The 10 Dq increase reported in the case of all these ligands is of the same order as that obtained for salicylic and substituted salicylic acids[16,17]. This observation is in agreement with the conclusion of George and MeClure that the contribution of oxygen atom is the same no matter whether it is in a water molecule or carboxylate ion or a phenolate ion. The order for crystal field stabilization energy is δH Ni > δH Cu > δH Co. This is in agreement with the observation[18] that Er and crystal field stabilization energy for many complexes are determined solely by the atoms directly bonded to the metal ion, the structure of the rest of the ligand group has far less influence.

The 1 : 1 complex formation of β–keto sulphides with a metal ion results with removal of two water molecules by the ligand from the hydration sphere of the metal ion as: $M(H_2O)_6 + L \rightleftharpoons M(H_2O)_4 L + 2 H_2O$. Water itself functions as a ligand, ΔH values for aquo ion available in the literature and the corresponding 10 Dq values are shown in the Table 4.

Table 4. Calculation of crystal field stabilization energy for Co (II), Ni (II) and Cu (II) complexes of β–keto sulphides
δH and 10 Dq value for Co (II), Ni (II) and Cu (II) complexes with β–keto sulphides

Metal ion		**Mn (II)**	**Co (II)**	**Ni (II)**	**Cu (II)**	**Zn (II)**
Number of d electrons		5	7	8	9	10
ΔG, Kcal / Mole		8.65	8.81	9.86	10.57	9.80
ΔH_c relative to value for Mn (II), KJ/mole		–	0.16	1.21	1.92	1.15
ΔH_H relative to value for Mn (II)		– Literature	43	62	63	47
ΔH_L relative to value for Mn (II)		–	43.16	63.21	64.92	48.15
[n–5/5]Er		–	19	29	38	–
δH		–	24.16	34.21	26.92	–
10 Dq for	L_1	–	12080	9978	15703	–
	L_2	–	12105	9969	16065	–
	L_3	–	12195	8458	15860	–
	L_4	–	12195	9858	15680	–
	L_5	–	12000	9916	16333	–
	L_6	–	12185	9878	15715	–

Dq values are expressed in cm^{-1}

The ratio of crystal field stabilization energy for $M(H_2O)_4 / M(H_2O)_6$ for Cu (II), Ni (II) and Co (II) complexes are 1.26, 1.15 and 1.20, respectively. This indicates a considerable increase in 10 Dq value for Cu (II) in 1 : 1 complexes while much less increase for Co (II) and Ni (II). This extra stabilization of Cu (II) complexes may be attributed to Jahn–Teller distortion usually observed in copper complexes.

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