

Studies on Solution Equilibria of Chlorobenzoylthioacetone and derived Metal Chelates

¹Dr. Rahul Anand & ²Dr. Puja Anand

1. Asstt. Professor, Dept. of Chemistry, Araria College, Araria (Bihar)

2. P.G. Chemical Research Laboratory, J.P. University, Chapra (Bihar)

ABSTRACT

The stepwise and overall stability constants of the complexes of *p*-Chlorobenzoylthioacetone with bivalent transition metal ions namely Fe^{+2} , Ni^{+2} , Cu^{+2} , and Hg^{+2} have been determined potentiometrically at 15°C and 25°C using Calvin-Bjerrum pH-metric technique as modified by Irving and Rossotti. The effect of Chlorine substituent at para position of benzoyl ring of the ligand has been studied by comparing the stability constant data of the complexes with those of the corresponding complexes of Benzoylthioacetone. *p*-Chlorobenzoylthioacetone, the organic ligand chosen for the complexation with bivalent metal ions in the present investigation belongs to Monothio- β -diketone class of compounds. The order of stabilities of the metal complexes formed has been evaluated and is reported here.

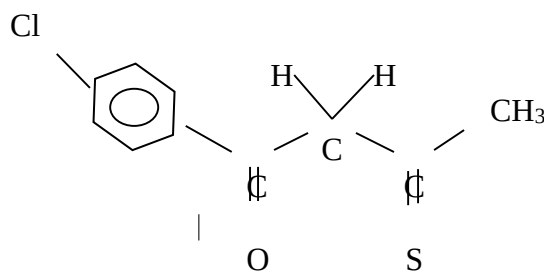
Key Words : Stability Constants, Chlorobenzoylthioacetone, Potentiometric technique, Chelate.

INTRODUCTION :

The ligand taken in the present investigation is *p*-chlorobenzoylthioacetone which belongs to monothio- β -diketone class of compounds and has been found to be a good chelating ligand. A number of complexes of this class of ligands with different metal ions have so far been reported¹⁻⁶ and their solution equilibria have also been studied potentiometrically²⁻⁴. Monothio- β -diketones behave as uninegatively charged bidentate (O,S) chelating agent after deprotonation through its enol or enethiol form thereby forming a six-membered resonance stabilized complex with various metal ions.^{2,3}

However, no attempt appears to have been made so far to study the solution equilibria of the titled ligand i.e. *p*-chlorobenzoylthioacetone (1) and its derived metal chelates – a work that can help to understand the effect of Chlorine substituent on the acid dissociation constant of the ligand and stability constants of its derived metal complexes when compared with those of its parent i.e. Benzoylthioacetone already reported.^{2,7,8}

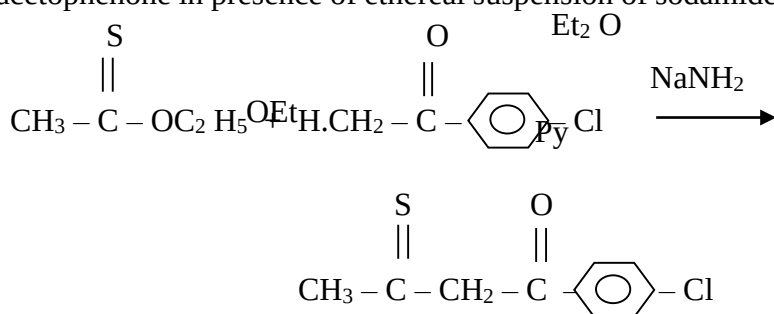
The structure of the ligand (1) i.e. *p*-Chlorobenzoylthioacetone chosen for our present research work is shown below.



In the present communication, we report the stability constants of the complexes of *p*-chlorobenzoylthioacetone with Iron, Nickel and Copper, the transition metals of 1st series as well as Mercury of 3rd series, all bivalent in 75% aqueous dioxan (v/v) at a two different temperatures viz 15°C and 25°C and at a fixed ionic strength of 0.1M KCl as determined by Calvin-Bjerrum PH-metric technique and as modified by Irving and Rossotti^{8,9}.

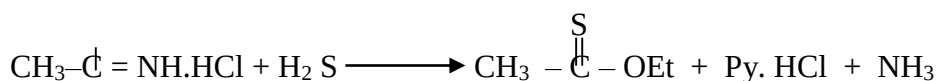
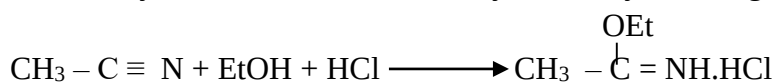
EXPERIMENTAL

The titled ligand was synthesized by Claisen Condensation of o-ethylthioacetate with p-chloroacetophenone in presence of ethereal suspension of sodamide by the reported method⁴ as shown below.



p-Chlorobenzoylthioacetone

The o-Ethythioacetate used above may be had by folloeing way.



All the chemicals were of A.R. grade. Purified dioxan and double distilled water were used. Primary standard solution of the ligand was prepared in dioxan. Aqueous solution of Metal (II) chlorides were standardised⁹. KOH solution was prepared in CO₂-free conductivity water and used to standardise HCl solution. KCl solution was prepared in 1:1 dioxan-water medium and was used to maintain the desired ionic strength. A systronic pH-meter with combined glass and calomel electrodes was used for pH-measurements. The tempt. was maintained constant at 15°C and 25°C for the two sets of experiments.

Procedure

Following three mixtures were prepared :

1. 5ml 0.4 M HCl + 5 ml KCl
2. Mixture (i) + 5ml 0.02 M Ligand solution, and
3. Mixture (ii) + 5ml 0.004 M metal ion solution.

Total volume in each case was maintained 50ml such that the dioxan volume remained 70 % and the ionic strength was kept at 0.1 M KCl. The mixtures were titrated (in duplicate) against 0.2 M KOH solution and the pH was measured in O₂-free nitrogen atmosphere. The B-values (pH-meter reading) and the volume of alkali added was plotted in each case and referred to as (i) Acid- (ii) Ligand- and (iii) Complex Titration curves respectively.

From the Acid and Ligand Titration curves, the values of $\bar{n}_A$ at various B-values were calculated using the appropriate equation. Since the ligand is monoprotic due to the presence of an –OH or –SH group in its enol or enethiol form respectively, and there is no basic group to take up proton(s), hence number of dissociable protons per ligand molecule (Y) was taken to be equal to one in the above calculation.

$\bar{n}_A$ values increase with increase in B-values showing thereby an increase in the degree of dissociation of the ligand. A plot of $\bar{n}_A$ against B gave the Formation curve of Ligand-Proton complex. From this curve, pka value of the ligand i.e. its Protonation Constant ($K_I^H = 1/K_a$) was obtained by Half-Integral method i.e.

$\text{Log}K_I^H = pK_a = B$ at $\bar{n}_A = 0.5$. This was further corroborated by Linear Plot of $\text{Log} \frac{\bar{n}_A}{1-\bar{n}_A}$ vs B.

From the Ligand- and Complex Titration curves, the values of $\bar{n}$ and pL were calculated using the appropriate equations. Formation curves of the Metal-Ligand complexes were drawn by plotting $\bar{n}$ vs pL for each of them. From these curves, stepwise formation constants of each metal complex (Log K_1 and Log K_2) were obtained by Half-Integral method i.e. Log K_1 = pL at $\bar{n}$ =0.5 and Log K_2 = pL at $\bar{n}$ =1.5 Since the

difference between Log K_1 and Log K_2 values was found to be very small, hence the same were refined by Least square treatment, and the results are reported in Table-1 given below

Table-1

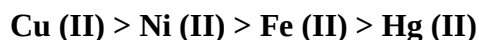
Observed Stepwise and Overall stability constant data of Metal complexes

Log K_1^H = pKa = 10.22 at 15°C, Log K_1^H = pKa = 10.11 at 25°C

[μ = 0.1 M KCl Medium = 75% Aqueous dioxan (v/v)]

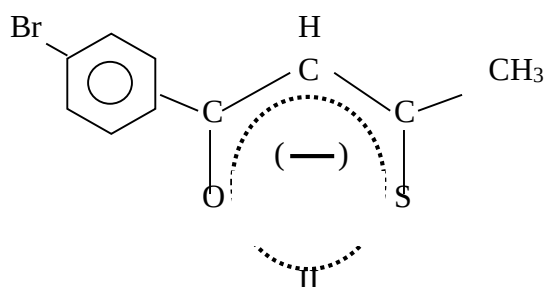
Metal ion	Temperature					
	15 ± 1°C			25 ± 1°C		
	Log K_1	Log K_2	Log β	Log K_1	Log K_2	Log β
Cu²⁺	10.28	09.60	19.88	10.16	09.53	19.69
Ni²⁺	09.88	09.20	19.08	09.78	09.12	18.90
Fe²⁺	08.75	07.96	16.71	08.61	07.92	16.63
Hg²⁺	08.41	07.60	16.01	08.29	07.55	15.84

From the above table, it is obvious that overall stability constants of all the four metal complexes are greater at 15°C than what these are at 25°C. The highest value is shown by Copper (II) whereas the bivalent Mercury ion, a member of 3rd Transition series shows comparatively least value, and this least value in the case of Hg²⁺ ion is found at both the temps. The stability order, thus, follows the trend:



Results & Discussion

The ligand in our present work exists as an equilibrium mixture of tautomeric enol and enethiol forms getting rapidly interconverted through intramolecular chelate proton transfer.²⁻⁶ However, whether the ligand deprotonates through enol or enethiol form, the anion obtained with negative charge delocalized over the whole ion will nevertheless be the same. The anion (II) is shown below :



From experimental results, it is quite clear that the separation of ligand titration curve from the acid titration curve begins only at pH>7 and that it shifts to the right. But the separation of complex titration curve from the ligand titration curve begins at pH>4 depending on the nature of metal ion with which complexation is to be taken place.

Thus, while the ligand has a very weak tendency to deprotonate, it has a very strong tendency to coordinate with metal ions. This truth is also substantiated by very low dissociation constants of the ligand and very high formation constants of its complexes. It is imperative to note here that the pka values of ligand are 10.22 and 10.11 respectively at 15°C and 25°C. These values of the ligand, p-chlorobenzoylthioacetone are higher than its parent compound i.e. Benzoylthioacetone at both the said temperatures as is evident from the literature^{4,5}.

The higher values of pKa of the ligand than its parent compound at both the temperatures show how deprotonation is favoured by the presence of chlorine atom at para position of benzoyl ring of the ligand. This may probably be due to the electronegative nature of the substituent, chlorine

The values of $\bar{n}$ range between zero and two indicating thereby the formation of ML₂ type of ring complexes analogous to the chelates of other Monothio-β-diketones reported previously^{5,6,10} Very small differences between Log K_1 and Log K_2 values show that ML and ML₂ are formed in quick succession.

The Overall stability constant ($\text{Log}\beta$) values of all the chelates are slightly less than those of corresponding chelates of parent ligand indicating thereby the adverse effect of chlorine substituent on the stabilities of the metal complexes. This may probably due to steric hindrance posed by the substituent together with increased strength of the ligand.

The stability constants of the metal chelates follow the trend: $\text{Cu}^{\text{II}} > \text{Ni}^{\text{II}} > \text{Fe}^{\text{II}} > \text{Hg}^{\text{II}}$ at both the temperatures (Table-1). Thus, the stability order of the said complexes in our present investigation in the case of both the temperatures follows the same trend i.e. $\text{Cu (11)} > \text{Ni (11)} > \text{Fe(11)} > \text{Hg(II)}$. This trend is in conformity with the stability order reported for the complexes of these metals with several other monothio- β -diketones (ligands) studied so far¹⁻⁷.

The overall stability constant values of the metal complexes decrease with increase in temperature. This trend is shown by all the metal ions used in complexation. The $\text{Log}\beta$ value, for example, in the case of Copper-complex is 19.88 at the lower temperature of 15°C whereas at 25°C it is 19.69 i.e. it has lesser value than what it has at 15°C. The difference in the $\text{Log}\beta$ values at the two temps, thus comes to be 0.19 log unit. Exactly same pattern is followed by other metal complexes also. This clearly suggests that low temp. is favourable for complex formation. The decrease in the stability of the metal complexes with increase in temp. is in agreement with decrease in pK_a values of the ligand with rise in temp. as described earlier.

In all the complexes formed above, LogK_2 value is lesser than logK_1 value which is in consistence with the results obtained with complexes of other ligands of this class. The difference between LogK_1 and LogK_2 values at 15°C in the case of Copper and Nickel-complexes is exactly equal being 0.68 Log unit whereas this difference in the case of Fe-complex is higher being 0.79 unit and in the case of Hg-complex it is still higher i.e. 0.81 unit.

However, at 25°C this difference of LogK_1 and LogK_2 values has a regular increasing pattern as we move from Cu- to Hg-complexes. The differences being 0.63, 0.66 and 0.69 units in the case of Cu-, Ni- and Fe-complexes respectively. Thus, a regular increase of 0.03 unit is to be found in the said values of three complexes of first transition metal series. So far as Hg-complex is concerned, this difference comes to be 0.74 unit. It is to be noticed that in the case of Hg-complex at both the temperatures, the difference between LogK_1 and logK_2 value is higher compared to those of other three chelates of 1st transition series. This means, Mercury has some peculiar behavior towards the present ligand for complexation.

Finally, the stability order of the complexes of the ligand chosen with four bivalent metal ions taken in the present investigation although differs from the Mellor-Maley series¹² which has been found to hold almost universally for oxygen and nitrogen donor ligands, it is in conformity with the stability order reported for the chelates of these metals with several other monothio- β -diketones studied so far^{2,8}.

DECLARATION

It is declared that all ethical guidelines have been properly followed during this work, and there is no conflict of interest with anyone.

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