



Free energy change values of Monothio- β -diketone complexes of some Bivalent metal ions of 1st & 2nd Transition Series

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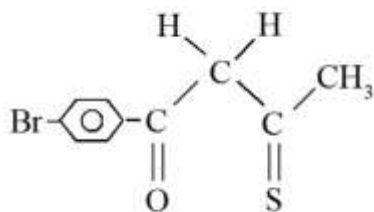
ABSTRACT

The values of Standard Free energy change (ΔG^0) accompanying the complex formation of some bivalent metal ions of first and second transition elements series with two organic ligands of Monothio- β -diketone class were determined at 25°C by knowing the formation constants of these complexes potentiometrically using Calvin-Bejrrum pH-metric technique as modified by Irving and Rossotti. The metal ions taken for the complexation are Cobalt, Copper, Palladium and Cadmium while the ligands belonging to Monothio- β -diketone class of compounds are p-bromobenzoylthioacetone and p-bromobenzoylthioacetophenone designated as Ligand-1 and Ligand-2 respectively. The ΔG^0 values accompanying the above complexation were determined with the help of well known thermodynamic relation viz. $\Delta G^0 = -2.303 RT \log \beta$. The order of stability of these metal complexes as well as free energy change values have been evaluated.

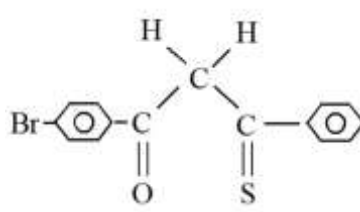
Key-words: Standard Free energy change, Bivalent metal ions, Formation constant, Monothio- β -diketone

Introduction

The two ligands namely p-bromobenzoylthioacetone and p-bromobenzoylthioacetophenone belonging to Monothio- β -diketone class of compounds have been found to be good chelating agents. A number of complexes of monothio- β -diketones with metal ions of different classes have so far been reported¹⁻⁴ and their solution equilibria have also been studied potentiometrically^{5,6}. These ligands behave as uninegatively charged bidentate (O,S) chelating agents after deprotonation through its enol or enethiol form to give six-membered resonance stabilized chelates with metal ions.^{2,3} However, no attempt appears to have been made so far to study the solution equilibria of their derived chelates with said metals – a work that can help to understand the effect of bromine substituent on the formation constants of their derived metal complexes as well as contribution of ΔG^0 accompanying the above complexations in providing the stability when compared with those of their parents i.e. Benzoylthioacetone and Benzoylthioacetophenone already reported.^{3,4} The structures of the two ligands in question are given below.



Ligand -1



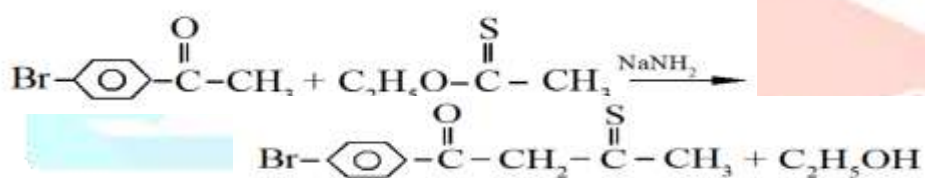
Ligand -2

In the present communication, we report the Stability constants of the complexes of p-bromobenzoylthioacetone and p-bromobenzoylthioacetophenone separately with all the bivalent transition metals taken viz. Cobalt and Copper (of 1st transition series), Palladium and Cadmium (of 2nd transition series) in 75% aqueous dioxan (V/V) at a constant temperature of 25⁰C and at a fixed ionic strength of 0.1M KCl as determined by Calvin-Bejrrum pH-metric technique⁷ and as adopted by Irving and Rossotti.

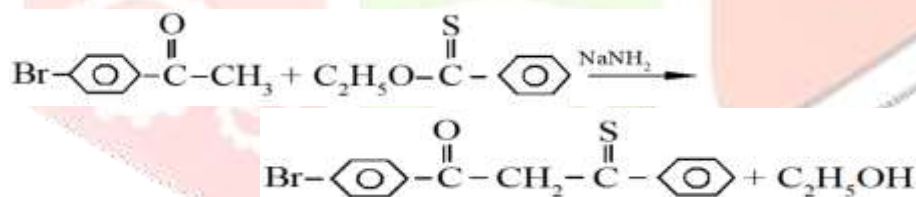
The values of standard change in free energy (ΔG^0) obtained accompanying the above complex formation are also being reported.

EXPERIMENTAL

The ligand-1 and ligand-2 were synthesized by Claisen condensation of p- bromoacetophenone with o-ethylthioacetate and o-ethylthiobenzoate respectively in presence of ethereal suspension of sodamide by reported method⁴. The crude product was recrystallised in ethanol, m.pt. 90⁰ (lit. 88-89⁰) and 130⁰ (lit. 129⁰) for ligand-1 and ligand-2 respectively.

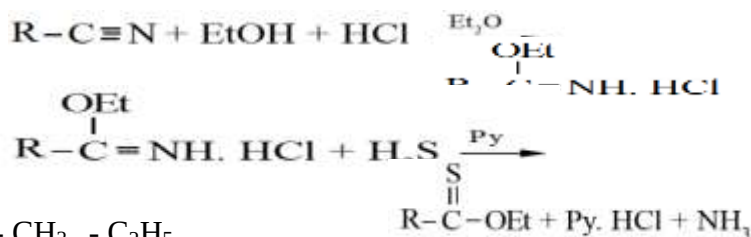


Ligand - 1



Ligand - 2

o-ethylthioacetate and o-ethylthiobenzoate used above may be had from corresponding nitrites as shown below.



Where R = - CH₃, - C₂H₅

All the chemicals were of A.R. Grade. Purified dioxan¹⁰ and double distilled water were used. Primary standard solutions of the ligands were prepared in dioxan. Aqueous solutions of metal (II) chlorides were standardized.¹¹ KOH solution was prepared in CO₂-free conductivity water, and was used to standardize 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 temperature was maintained constant at 25⁰C.

PROCEDURE

The following three mixtures were prepared :

- (i) 5 ml 0.4 M HCl + 5 ml M KCl
- (ii) Mixture (i) + 5 ml 0.02 M Ligand solution, and
- (iii) Mixture (ii) + 5 ml 0.004 M Metal ion solution

Total volume in each case was maintained 50 ml such that the dioxan volume remained 70% and 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 readings) 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^{1,2,3}

From the acid and ligand titration curves, the $\bar{n}_A$ values at various B-values were calculated using the appropriate equation.¹⁰ 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 the number of dissociable protons per ligand molecule (Y) was taken to be equal to one in the above calculation.^{7,11}

The $\bar{n}_A$ values increase with increase in B values showing thereby increase in the degree of dissociation of the ligand. A plot of $\bar{n}_A$ against B gave the Formation Curve of the Ligand-Proton complex wherefrom pKa of the ligand or its protonation constant $\left(K_I^H = \frac{1}{K_a}\right)$ was obtained by Half - Integral method. i.e. Log

$K_I^H = pKa = B$ 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.^{11,12}

From the ligand and complex titration curves, the values of $\bar{n}$ and pL were calculated using the appropriate equations.^{6,10} Formation Curves of the Metal – Ligand complexes were drawn by plotting $\bar{n}$ vs pL for each of the complexes formed. From these curves the stepwise stability constants of each metal complex (Log K₁ and Log K₂) were obtained by Half Integral Method. i.e. Log K₁ = pL at $\bar{n} = 0.5$ and Log K₂ = pL at $\bar{n} = 1.5$. Since the difference between LogK₁ and LogK₂ values was found to be very small, the same were refined by Least Square Treatment, and the results are reported in Table-1 given below.

Table - 1

Stepwise and Overall Stability Constant data of the Metal Complexes [Temp. = 25⁰, μ = 0.1M KCl, Medium = 75% aq. dioxan(v/v)]

[Log K_I^H = pKa = 10.12 (Ligand -1); Log K_I^H = pKa = 10.72 (Ligand -2)]

Metal Ions	Ligand -1			Ligand - 2		
	LogK ₁	LogK ₂	Log β_2	LogK ₁	LogK ₂	Log β_2
Cu ^{II}	10.22	09.63	19.85	10.52	09.75	20.27
Co ^{II}	09.86	09.20	19.06	10.39	09.48	19.87
Pd ^{II}	08.42	07.60	16.11	08.98	08.49	17.47
Cd ^{II}	08.36	07.59	15.95	08.79	08.24	17.03

Thus, the Stability Constants of the metal complexes in the case of both the ligands follow the order : Cu^{II} > Co^{II} > Pd^{II} > Cd^{II}

Evaluation of ΔG^0

The value of standard change in free energy in the case of formation of each complex was calculated using the following well known thermodynamic relation,

$$\Delta G^0 = -2.303RT \text{ Log} \beta$$

Where, ΔG^0 = Standard Free energy change accompanying the complex formation reaction.

β = Overall stability constant of the metal complex

R = Gas constant = 1.987 cals deg⁻¹mol⁻¹

T = Temperature on absolute scale.

The ΔG^0 values at 25⁰C for each metal complex formation with the titled ligands are given in table – 2

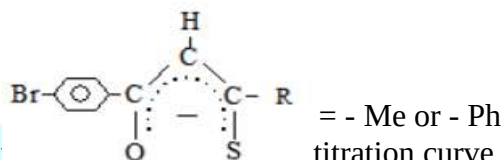
Table – 2

ΔG^0 values of bivalent metal complexes in Kcals. mol⁻¹ at 25⁰C
(μ = 0.1M KCl, Medium = 75% aq. dioxan)

Metal ions	ΔG^0 (in Kcals./mol)	
	Ligand - 1	Ligand - 2
Cu ^{II}	27.06	27.64
Co ^{II}	25.99	27.09
Pd ^{II}	21.96	23.82
Cd ^{II}	21.75	23.22

RESULTS & DISCUSSION

Each ligand in the present investigation is known to exist as an equilibrium mixture of tautomeric enol and enethiol forms which interconvert rapidly by intramolecular chelate proton transfer.²⁻⁶ However, whether the ligand deprotonates through its enol or enethiol form, the anion (3) with negative charge delocalized over the whole ion will be essentially the same.



The separation of ligand titration curve (in the case of both ligands) begins only at pH > 7 and that it shifts to the right. But the separation of complex titration curve from the ligand titration curve (in the case of both ligands) begins at pH ≤ 4 depending on the nature of the metal ion taken. These facts reveal that while the ligands have a very weak tendency to deprotonate, they have a very strong tendency to coordinate with the metal ions. This is well supported by the very low dissociation constant value of the ligands and very high formation constants of their complexes. The higher value of Ka of the ligand-1 (pka = 10.12) than that of its parent (pka = 10.40, 10.43)^{2,3} shows how deprotonation is favoured by the presence of Br-atom at the para - position of the benzoyl ring of the ligand. Similarly, value of Ka of ligand-2 (pka = 10.72) is greater than that of its parent (pka = 11.14, 11.40)^{2,3}. This may be probably due to the electronegative nature of the substituent.

The values of n range between zero and two indicating the formation of ML₂ type of chelate analogous to the chelates of other monothio- β -diketones reported previously.^{2,3} Very small difference between log K₁ and log K₂ values show that ML and ML₂ are formed almost simultaneously rather successively. The log β_2 values of all the chelates are slightly less than those of the corresponding chelates of its parent (Cu = 20.17, Co = 19.49, Pd = 16.53, Cd = 16.18)² in the case of ligand-1. Similar pattern is shown by the metal complexes in the case ligand-2 (Cu = 20.42, Co = 19.11, Pd = 17.74, Cd = 17.17)². This indicates the adverse effect of bromine substituent on the stabilities of the metal chelates. This may be attributed to the steric hinderance posed by the substituent together with increased acidic strength of the ligand.

The stability order of the metal chelates in present investigation though differs from the Mellor Maley Series¹² which has been found to hold almost universally for oxygen and nitrogen donor ligands or Irving-Willam natural order of stability, 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}

Very large decrease in free energy during the complex formation reaction as is evident from table-2 is indicative of very high stabilities of the metal chelates. The negative ΔG^0 values of the metal chelates at the given temperature in the case of both the ligands follow the trend : Cu (II) > Co (II) > Pd (II) > Cd, which are in the same order as the overall stability constants of these metal chelates follow. Thus, all the complexes are free energy stabilized. It is also obvious from the table that the decrease in standard free energy is higher in the case of ligand-2 than in the case of ligand -1 for each metal complex. Thus, the stability of complexes formed out of Ligand-2 is higher than those derived from Ligand-1 which is well supported by the overall stability constant values of the complexes formed with the two ligands. The overall stability constant values of complexes of Copper, Cobalt, Palladium and Cadmium derived from Ligand-2 are respectively 20.27, 19.87, 17.47 and 17.03 log units which are higher than those of complexes of these metals derived from Ligand-1. These values are respectively 19.85, 19.06, 16.11 and 15.95 respectively. it may be seen in Table-1.

Thus, the Free energy change values associated with the formation of these complexes support the overall stability constant values of these complexes.

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