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Studies On Standard Change In Free Energy Accompanying Complexation Of Bromobenzoylthioacetophenone With Some Divalent Transition Metals

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ABSTRACT

The stability constants of the complexes of p-Bromobenzoylthioacetophenone with some divalent transition metals namely Nickel, Copper, Zinc and Cadmium have been determined at three different temperatures potentiometrically. The ligand belongs to Monothio-β-diketone class of compounds. The Stepwise and Overall Stability Constants of the complexes synthesized have been determined. From a knowledge of overall stability constants, Standard change in Free energy accompanying the said complexation at all the three temperatures have been determined using the appropriate thermodynamic equation. The changes in Free energy contributing towards complex formation as also the stability of the complexes formed have been properly studied.

Key-words : p-Bromobenzoylthioacetophenone, Potentiometric Titration, Overall Stability constant, Standard change in Free energy.

INTRODUCTION

The ligand chosen for complexation with bivalent Ni. Cu, Zn and Cd is Para-Bromobenzoylthioacetophenone. This is a uninegatively charged bidentate chelating ligand. After deprotonation through its enol or enethiol form it forms a six-membered resonance stabilized chelates with metal ions.[1,6] However, no attempt appears to have been made so far to study the solution equilibria of this ligand and its derived metal complexes as also the standard changes in free energy accompanying the said complex formation – a work that can help to understand the effect of bromine substituent on the chelating ability of the ligand as also the contribution of standard change in free energy (ΔG^0), a significant thermodynamic factor towards said complexations.

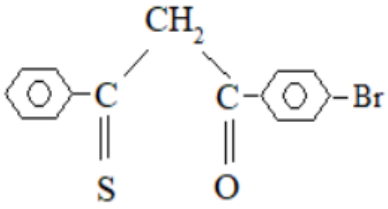

Fig1: p-Bromobenzoylthioacetophenone

In the present communication, we report the stability constants of the complexes of para-Bromobenzoylthioacetophenone with nickel, copper, zinc and cadmium (all bivalent) at three different temperatures viz 10^0C, 20^0C and 30^0C at a fixed ionic strength as determined by Calvin-Bjerrum Potentiometric titration[4,7] as well as standard change in Free energy associated with above complexations.

EXPERIMENTAL

The said ligand was synthesized by Claisen Condensation of o-ethylthiobenzoate with p-bromoacetophenone in presence of sodamide, and the crude product was recsystallised in ethanol.[3,5]

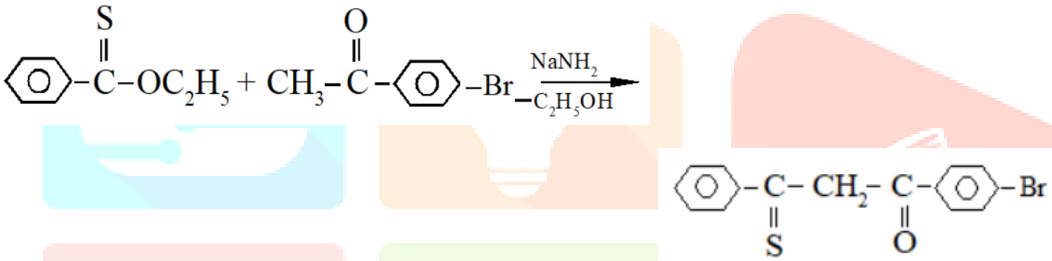

Fig 2 : Synthesis of p-Bromobenzoylthioacetophenone

Primary standard solution of ligand was prepared in dioxan.[5] Aqueous solution of Metal (II) chlorides were standardized. KOH solution was prepared in CO_2 - 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. The temperatures were maintained constant at 10°C, 20°C & 30°C respectively for three different experimental condition.

PROCEDURE

The following three mixtures were prepared for potentiometric titration :–

(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 50ml so that the volume of dioxan could remain 70% and the ionic strength as 0.1 M KCl. The mixtures were titrated against 0.2 M KOH solution, and the pH was measured in oxygen-free nitrogen atmosphere. B-values (pH-meter readings) and the volume of alkali

added was plotted in each case to get (i) Acid, (ii) Ligand, and (iii) Complex Titration Curves respectively[4,5,6]

Values of $\bar{n}_A$ at various pH-meter readings were calculated from acid and ligand titration curves using appropriate equation. A plot of $\bar{n}_A$ vs B gave Formation curve of Ligand-Proton complex. From this curve, pKa value of ligand i.e. Protonation Constant of ligand was obtained by Half-Integral method[5,9]. Likewise, values of $\bar{n}$ and pL were calculated from Ligand and Complex titration curves through appropriate equations.[7,8,9] Formation Curves of the complexes were drawn by plotting $\bar{n}$ vs pL for each complex. From these curves, stepwise and overall stability constants for each complex were obtained through Half-Integral Method ($LogK_1$=pL at $\bar{n}$=0.5 and $LogK_2$=pL at $\bar{n}$=1.5). The results are furnished in Table-1

Table - 1

Stepwise & Overall Stability Constants Data of the Complexes

[μ=0.1MKCl, Medium = 75% aqueous dioxan (v/v)]

Metal Ions	TEMPERATURES								
	10 ± 1⁰ C			20 ± 1⁰ C			30 ± 1⁰ C		
	$LogK_1$	$LogK_2$	Logβ	$LogK_1$	$LogK_2$	Logβ	$LogK_1$	$LogK_2$	Logβ
Cu^{++}	10.69	09.84	20.53	10.55	09.73	20.28	10.47	09.68	20.15
Ni^{++}	10.65	09.65	20.30	10.40	09.54	19.94	10.36	09.47	19.83
Zn^{++}	09.75	08.97	18.72	08.93	08.43	17.36	08.87	08.39	17.26
Cd^{++}	08.99	08.44	17.43	08.88	08.31	17.19	08.72	08.18	16.90

As is obvious from the Table, Stability Constants of Metal complexes formed follow the trend : **Cu^{II} > Ni^{II} > Zn^{II} > Cd^{II}**

Determination of ΔG^0 :

With the help of Overall Stability Constant values of the metal complexes furnished in Table-1, the value of Standard Change in Free energy (ΔG^0) at a given temperature was determined using the Thermodynamic relation, $\Delta G^0 = -2.303RT\log\beta$, where β= Overall Stab. Const., T= Tempt. & R= Constant.

The ΔG^0 values obtained at three different temperatures for each metal complex are arranged in Table-2 given below.

Table – 2

Values of Standard Free Energy Change (ΔG^0) of Complexes

[μ=0.1MKCl, Medium = 75% aqueous dioxan (v/v)]

Metal Ions	$-\Delta G^0$ (K Cals/mol)		
	10^0C	20^0C	30^0C
Cu^{++}	26.58	27.19	27.93
Ni^{++}	26.28	26.73	27.49
Zn^{++}	24.24	23.27	23.93
Cd^{++}	22.57	23.04	23.43

Thus, at each temperature, the decrease in Standard change in free energy (ΔG^0) follows the trend : **Cu^{II} > Ni^{II} > Zn^{II} > Cd^{II}**

RESULTS & DISCUSSION

In the present investigation, we find that the decrease in Standard Free energy is higher at 20^0C for all compexes formed than at 10^0C except in the case of Zinc complex whose values at 10^0C and 20^0C are respectively 24.24 & 23.27 KCals/mol. Likewise, the decrease in Free energy is higher at 30^0C than at 20^0C in the case of each metal complexe formed. This may be seen in Table-2 containing Free energy change data.

Also, the decrease in Free energy associated with the formation of complexes of these metal ions has a regularity which can be understood by looking at the values obtained furnished in Table-2. For illustration, ΔG^0 values at 10^0C for the complexes of bivalent Cu, Ni, Zn & Cd are respectively 26.58, 26.28, 24.24 & 22.57 K Cals. mol^{-1} supporting the values of overall stability constants obtained for these metal complexes. Likewise, Standard changes in Free energy (ΔG^0) values at 20^0C and 30^0C also have similar trends. At 20^0C, these values for the complexes of Cu, Ni, Zn & Cd are respectively 27.19, 26.73, 23.27 & 23.04 K Cals.mol^{-1} whereas these values for the said complexes at 30^0C are 27.93, 27.49, 23.93 & 23.43 K Cals.mol^{-1} respectively. These values are furnished in Table-2.

At each temperature, it may be noticed that ΔG^0 values go on decreasing from Cu- to Cd-complexes which support the stability order of these metal complexes. Thus, the decrease in Free energy in conformity with the Stability Order follows the same trend.

CONCLUSION

From thermodynamic expression, $-RT\ln\beta=\Delta G^0$, it follows that β increases as ΔG^0 becomes more negative; and more negative value of ΔG^0 leads to a more stable complex.

In the present investigation, we find that the Standard changes in Free energy in conformity with the stability order (Table-1) also follow the same trend. Hence, at each temperature the decrease in Standard Free energy change ($-\Delta G^0$) follows the trend : **$Cu^{II} > Ni^{II} > Zn^{II} > Cd^{II}$**

Thus, the complexes formed are free energy stabilized. This supports the stability order observed in the case of all the four bivalent metal complexes.

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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