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A Study on Thermodynamic Changes during Complexation of p-Bromobenzoylthioacetophenone with Some Bivalent Metals of First Transition Series

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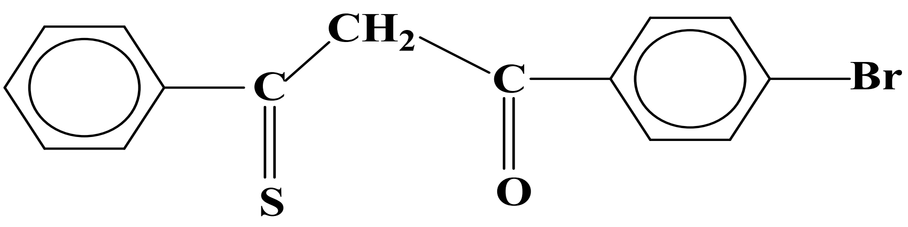
Abstract

The formation constants of complexes of p-bromobenzoylthioacetophenone with some bivalent metal ions of first transition elements series at two different temperatures namely 15˚C and 25˚C have been determined potentiometrically using Calvin-Bjerrum potentiometric technique as modified by Irving and Rossotti. From a knowledge of overall formation constants, standard change in free energy at the said temperatures were found out using the thermodynamic relation, $\Delta G^\circ = -2.303RT\log\beta$. The standard enthalpy changes (ΔH°) accompanying the complex formation reactions were determined with the help of Isobar equation. The standard entropy changes, ΔS° accompanying the above complexation were obtained using the relation $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$. From the data obtained, the thermodynamic factors which contribute towards complex formation have been discussed.

Keywords: Formation Constants, Free Energy, Enthalpy & Entropy effect**.**

Introduction

The ligand (1) chosen for complexation with bivalent metal ions of first transition elements series namely Manganese, Ferrum, Cobalt and Nickel is p-bromobenzoylthioacetophenone which belongs to Monothio-β-diketones class.[1,2] This ligand behaves as a uninegatively charged bidentate chelating agent after deprotonation through the enol or enethiol form resulting in the formation of a six-membered resonance stabilized ring with metal ions.[1,3] The structure of the said ligand is shown below.



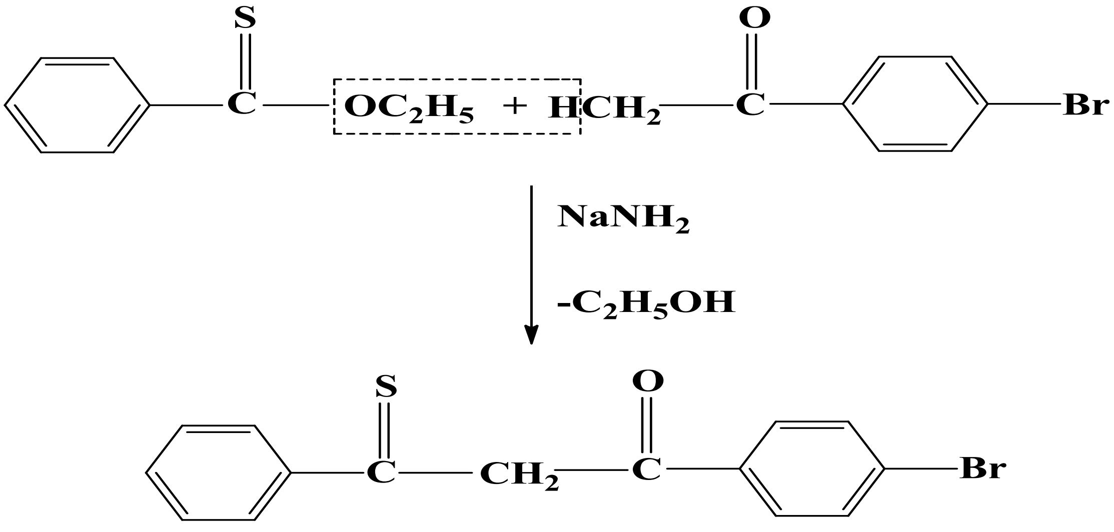
(I)

However, no attempt appears to have been made so far to study the solution equilibria of the said ligand and its derived metal complexes—a work that can help to understand the contribution of the thermodynamic factors viz. ΔG˚ (Standard change in free energy), ΔH˚(Standard change in Enthalpy) and ΔS˚ (Standard change in Entropy) towards said complexations when compared with those of its parent ligand i.e. Benzoyl thioacetophenone already reported.

In the present communication we report the Formaation constants of the complexes of p-bromobenzoylthioacetophenone with Manganese, Iron, Cobalt and Nickel (all bivalent) in 75% aqueous dioxan (v/v) at two different temperatures 15˚C and 25˚C at a fixed ionic strength of a 0.1(M) KCl as determined by Cavin-Bjerrum's pH-metric technique and as modified by Irving and Rossotti[4,5,6] as well as thermodynamic factor viz. ΔG˚, ΔH˚ and ΔS˚ accompanying the above complexation.

Experimental

By the reported method[4,5] the said ligand was synthesized by Claisen condensation of O-ethylthiobenzoate with p-bromoacetophenone in presence of sodamide, and the crude product was recrystallized in ethanol, m.pt. 130˚C (lit. 129˚C)[3,7]. The synthesis is shown below



p-Bromobenzoylthioacetophenone

The Ligand (I)

The O-ethylthiobenzoate used in the synthesis of above ligand was obtained from corresponding nitrile.[4,8] Primary standard solution of ligand was prepared in dioxan.[4] Aqueous solution of Metal(II) chlorides were standardized. KOH solution was prepared in CO_2-free conductivity water and 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 15˚C and 25˚C respectively for two different experimental conditions.

Procedure

The following three mixtures were prepared

(i) 5 ml 0.4(M) HCl + 5 ml 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 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 O_2-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.[1,2,6,8,9]

From the acid and ligand titration curves, $\bar{n}_A$ values at various B-values were calculated using the appropriate equation. A plot of $\bar{n}_A$ against B gave the formation curve of the ligand-proton complex form which pKa of the ligand or its protonation constant (K_1^H = 1/Ka) was obtained by Half-integral method i.e. Log K_1^H = pKa = B at $\bar{n}_A$ = 0.5. This was further corroborated by linear plot of Log $\bar{n}_A/1-\bar{n}_A$ vs B.[10,11] From the ligand and complex titration curves the values of $\bar{n}$ and pL were calculated using the appropriate equations[6,7,12]. Formation curves of (Metal-Ligand) complexes were drawn by plotting $\bar{n}$ vs pL for each of them. From these curves, stepwise stability constants of each metal complex (LogK_1 and LogK_2) were obtained by half-integral method[7,12] i.e. Log K_1 = pL at $\bar{n}$ = 0.5, and LogK_2 = pL at $\bar{n}$ = 1.5. Since the difference between LogK_1 and LogK_2 values was found to be very small, the same were refined by least square treatment and the results are reported in **Table-1**.

Table 1: Stepwise and Overall stability Constants Data of the Metal Complexes at 15˚C and 25˚C.
Medium = 75% Aqueous Dioxan(v/v), μ = 0.1(M) KCl.
pKa value of the ligand:
Log K_1^H = pKa = 10.69 at 15˚C
Log K_1^H = pKa = 10.60 at 25˚C

Metal ions	**TEMPERATURES**					
	15 ±1˚C			**25±1˚C**		
	LogK₁	**LogK₂**	**Logβ**	**Log K₁**	**LogK₂**	**Logβ**
Ni^{2+}	10.41	09.67	20.08	10.37	09.48	19.85
Co^{2+}	09.57	09.11	18.68	09.50	08.99	18.49
Fe^{2+}	08.91	08.46	17.37	08.48	08.37	17.21
Mn^{2+}	08.71	08.26	16.97	08.68	08.18	16.86

As is clear from the table, the stability constants of the metal complexes follow the trend: $Ni^{II} > Co^{II} > Fe^{II} > Mn^{II}$.

Evaluation of ΔG˚

The value of standard change in free energy, ΔG˚ at a given temperature was calculated using the well known thermodynamic expression, ΔG˚ = -2.303RTlogβ, where ΔG˚= standard free energy change accompanying the complex formation reaction, β = overall formation (stability) constant, T = temperature, and R = constant.

The ΔG˚ values at two different temperatures for each metal complex formation with the said ligand are given in **Table 2.**

Table 2: ΔG˚ Values of Bivalent Metal Complexes at two Different Temperatures. (μ = 0.1(M) KCl and Medium = 75 % Aqueous Dioxan.)

Metal ions	**-ΔG˚ (in Kcal mol^{-1})**	
	Temperatures	
	15±1˚C	**25±1˚C**
Ni^{2+}	26.46	27.06
Co^{2+}	24.61	25.21
Fe^{2+}	22.89	23.46
Mn^{2+}	22.36	22.99

It is, thus obvious that the decreases in standard free energy is higher at 25˚C than at 15˚C in the case of chelate of each metal ion.

Determination of ΔH˚

The standard change in enthalpy, ΔH˚ accompanying the complex formation reaction was determined with the help of following Isobar equation.[9,13,14]

$$d\ln\beta/dT = \Delta H^{\circ}/RT^2$$

The above equation may be rearranged as $d(\log\beta)/d(1/T) = -\Delta H^{\circ}/2.303R$
Taking R = 1.987 calsdeg^{-1}mol^{-1}, we have $d(\log\beta)/d(1/T) = -\Delta H^{\circ}/4.576$

According to this equation, the gradient of the tangent drawn at the point corresponding to any temperature on the curve obtained by plotting the values of Logβ as a function of 1/T will be equal to -ΔH˚/4.576.

Use of Gibbs-Helmholtz[9,15] equation was also employed to determine the values of ΔH˚. These values of ΔH˚ obtainable from the plot of Logβ vs. 1/T (Linear plot method) as well as utilizing Gibbs-Helmholtz equation have been listed in **Table 3**.

Table-3: ΔH˚ Values of Bivalent Metal complexes in Kcal mol^{-1} (Medium = 75 % Aqueous Dioxan and μ = 0.1(M) KCl) at 25˚C

Metal ions	**-ΔH˚ (Kcal/mol)**		
	By Linear Plot Method	**Using Gibbs-Helmholtz Equation at 25˚C**	**Average Value**
Ni^{2+}	08.30	09.18	08.74
Co^{2+}	06.87	07.33	07.10
Fe^{2+}	06.50	06.47	06.48
Mn^{2+}	06.08	04.21	05.14

($dT = T_2-T_1$ = 298K-288K), T_2 = Derived temperature.

Calculation of ΔS˚

The related values of ΔS˚ (standard change in entropy) were calculated at 25˚C using average value of ΔH˚ as mentioned. in **Table 3**.

In the calculation of ΔS˚, the well known thermodynamic relationship viz. ΔG˚= ΔH˚- TΔS˚ was applied.[9,14] The required ΔG˚ values were utilized from **Table 2**. The values of ΔS˚ obtained are listed in **Table 4**.

Table 4: ΔS˚ Values of Bivalent Metal Chelates Using Average Value of ΔH˚ at 25˚C

Metal ions	ΔS˚(Caldeg^{-1}mol^{-1}) at 25˚C
Ni^{2+}	63.28
Co^{2+}	60.77
Fe^{2+}	56.97
Mn^{2+}	59.89

The standard change in entropy associated with the formation of above complexes were calculated also at 15˚C also by making use of ΔH˚ values as obtained by linear plot method and are furnished in **Table 5.**

Table 5: ΔS˚ Values of Bivalent Metal Chelates at 15˚C

Metal ions	ΔS˚(Caldeg^{-1}mol^{-1}) at 15˚C
Ni^{2+}	63.05
Co^{2+}	61.59
Fe^{2+}	56.90
Mn^{2+}	56.52

Results and Discussion

From the thermodynamic relationship ΔG˚ = -RTlnβ = ΔH˚- TΔS˚, it follows that β increases as ΔG˚ becomes more negative. The value of ΔG˚ becomes more negative when that of ΔS˚ becomes more positive i.e. more positive value of ΔS˚ will lead to a more negative value of ΔG˚ and hence a more stable complex will be formed. Also, greater the amount of heat released in a reaction, more stable will be the reaction product. The entropy of a system is a measure of degree of disorderness or randomness of the system. The greater the amount of this disorder produced in the product, the greater will be the value of entropy during the reaction and hence greater will be the stability of products (complexes) formed.[6,13,14]

In the present investigation, we find that the thermodynamic parameters too in conformity with the stability order (mentioned in **Table 1**) follow the same trend. Thus, at each temperature, the decrease in standard free energy change (-ΔG˚) follows the trend: Ni^{II} > Co^{II} >Fe^{II} > Mn^{II}. This can be seen in **Table 2**. Thus, the complexes formed are free energy stabilized.

So far as standard change in enthalpy is concerned, linear plot method gives a successive decreasing value of ΔH˚. But the use of Gibbs-Helmholtz equation for calculating ΔH˚, although follows the same pattern, gives much less value for manganese complex. It comes to be just 4.21 Kcalmol^{-1}. But overall the enthalpy factor supports the above stability order.

The negative values of ΔH˚ for each metal complexes as listed in **Table 3** signifies that complex formation reactions are exothermic in nature. Thus, all the complexes formed so far are all enthalpy stabilized.

In the case of standard change in entropy (ΔS˚) for these complexes, we find the same pattern as is followed by above said two thermodynamic factors. From **Table 5** containing ΔS˚ values calculated at 15˚C for these complexes, it is obvious that the nickel complex is much entropy stabilized having maximum disorderness. The values of ΔS˚ clearly support the stability order $Ni^{II} > Co^{II} > Fe^{II} > Mn^{II}$.

However, the values of ΔS˚ obtained at 25˚C involving the use average value of ΔH˚ show a sudden rise for Mn-complex (**Table 4**). In fact, it is the comparatively much lower value of ΔS˚ in the case Fe-complex which makes the value of ΔS˚ for Mn-complex appear higher than that of Fe-Complex.[5,12,16,17,18]

However, at the same temperature i.e. at 25˚C when the values of ΔS˚ were determined using the values of ΔH˚ obtainable from linear plotting (which are 08.30, 06.87, 06.50 and 06.08 in Kcal/mol respectively for bivalent nickel, cobalt, iron and manganese ions as contained in Table 3), it (ΔS˚) came out to be 62.95, 61.54, 56.91 and 56.74 calsdeg^{-1}mol^{-1} respectively for Ni, Co, Fe and Mn-complexes as $Ni^{II} > Co^{II} > Fe^{II} > Mn^{II}$.

This exactly follows the order discussed above. Thus, we can say that all the complexes formed are free energy, enthalpy and entropy stabilized.

The ΔS˚ values in calsdeg^{-1}mol^{-1} at 25˚C determined by both ways i.e. by using ΔH˚ values obtained from linear plot method as well as by using ΔH˚ obtainable from Gibbs-Helmholtz equation, for the sake of convenience are shown below.

We find that it is the much lower value of ΔH˚ in the case of Mn-complex obtainable by the use of Gibbs-Helmholtz equation which makes all the discrepancies. Regarding this, it can be said that CFSE value comes to be minimum for Mn^{2+} ion. Irving-William order says that complex of Mn is less stable.[4,6,16,17,18]

Table 6: ΔS˚ Values at 25˚C for all the Metal Complexes by Using ΔH˚ Values Obtainable from Both Methods

Metal ions	**ΔS˚(Caldeg^{-1}mol^{-1})**	
	Using ΔH˚ value by linear plot method	**Using ΔH˚ value by Gibbs-Helmholtz equation**
Ni^{2+}	62.95	60.00
Co^{2+}	61.54	60.00
Fe^{2+}	56.91	57.01
Mn^{2+}	56.74	63.02

It is imperative and significant as well to know here that the complexes of this ligand in general have good biological and medicinal action on various diseases of animal and plants.[9,10,19] These complexes have extensive use in the treatment of breast cancer.[11,16] These have good therapeutic use there. Besides, these have adverse effect on the growth of some microorganisms including bacteria and fungus harmful for tropical plants.[9,11,20]

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