



Studies on Standard changes in Free energy, Enthalpy & Entropy during Complex Formation of Some Bivalent Metals with Chlorobenzoylthioacetophenone

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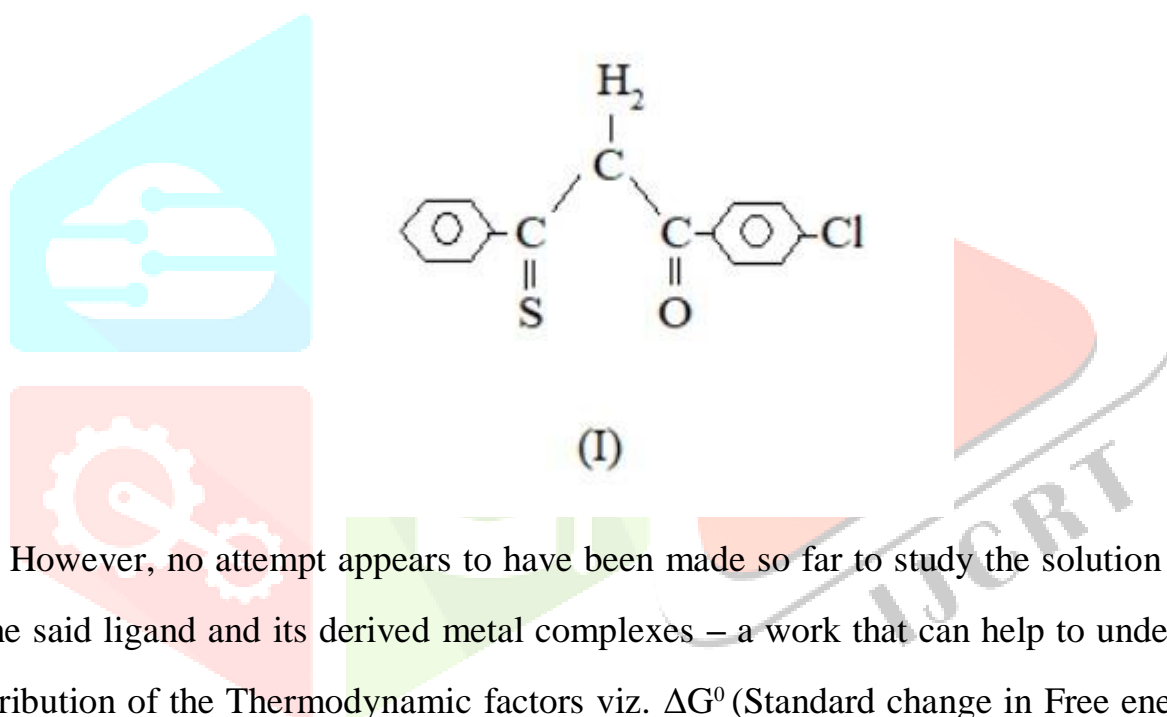
ABSTRACT

The Stability Constants of the complexes of p-chlorobenzoylthioacetophenone with bivalent Manganese, Nickel, Palladium and Platinum at three different temperatures namely 10°C, 20°C and 30°C have been determined potentiometrically using Calvin-Bjerrum Potentiometric technique as modified by Irving and Rossotti. From a knowledge of Overall Stability Constants, standard changes in Free Energy (ΔG^0) at the said temperatures were found out using the Thermodynamic relation, $\Delta G^0 = -2.303 RT \log \beta$. The standard changes in Enthalpy (ΔH^0) accompanying the complex formation reactions were determined with the help of Isobar equation. It was also calculated through Gibbs-Helmholtz equation. The standard changes in Entropy (ΔS^0) accompanying the above complexations were obtained using the Thermodynamic relation, $\Delta G^0 = \Delta H^0 - T\Delta S$. From the data obtained, the thermodynamic factors which contribute towards complex formation have been discussed.

(Key-words : Stability constant, Free energy, Enthalpy & Entropy).

Introduction

The ligand (1) chosen for complexation with some bivalent metal ions of first, second and third transition elements series namely Manganese, Nickel, Palladium and Platinum is p-chlorobenzoylthioacetophenone which belongs to Monothio- β -diketone class of compounds.^{1,2} This ligand behaves as a uninegatively charged bidentate chelating agent after deprotonation through its enol or enethiol form resulting in the formation of a six-membered resonance stabilized ring complex with metal ions.^{1,6} The structure of the said ligand is shown below.



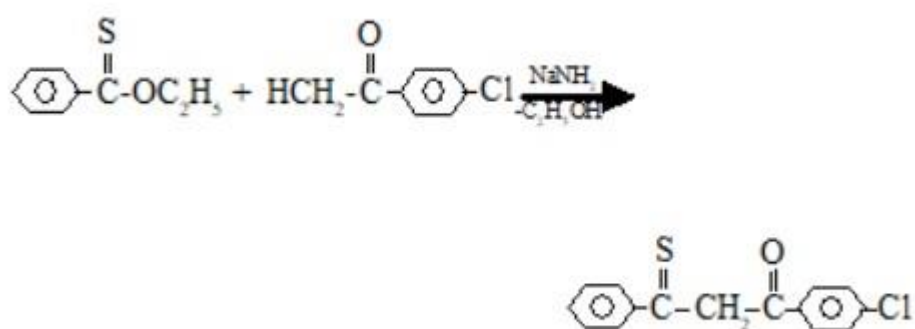
However, no attempt appears to have been made so far to study the solution equilibria of the said ligand and its derived metal complexes – a work that can help to understand the contribution of the Thermodynamic factors viz. ΔG^0 (Standard change in Free energy), ΔH^0 (Standard change in Enthalpy) and ΔS^0 (Standard change in Entropy) towards said complexations when compared with those of its parent ligand i.e. Benzoylthioacetophenone already reported.^{2,3}

In the present communication we report the Stability Constants of the complexes of p-chlorobenzoylthioacetophenone with Manganese, Nickel, Palladium and Platinum (all bivalent) in 75% aqueous dioxan (v/v) at three different temperatures namely 10°C, 20°C and 30°C at a fixed ionic strength of 0.1 M KCl as determined by Calvin-Bjerrum's pH-metric technique and as modified by Irving and Rossotti^{8,9} as well as changes taking place in

Thermodynamic factors namely viz. ΔG^0 , ΔH^0 and ΔS^0 accompanying the above complexation.

EXPERIMENTAL

By the reported method^{4,8}, the said ligand was synthesised by Claisen Condensation of o-ethylthiobenzoate with p-chloroacetophenone in presence of sodamide, and the crude product was recrystallized in ethanol.^{6,7} The synthesis is shown below.



The Ligand (I)

The o-ethylthiobenzoate used in the synthesis of above ligand was obtained from corresponding nitrile.^{3,5}

Primary standard solution of ligand was prepared in dioxan⁵. Aqueous solutions of Metal (II) chlorides were standardized. 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. The temperatures were maintained constant at 10°C, 20°C and 30°C respectively for three different experimental conditions.⁶⁻⁸

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 50ml such that 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^{1,2,3,9,13}

From 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 wherefrom pKa value of ligand or its protonation constant $\left(K_I^H = \frac{1}{K_a} \right)$

was obtained by Half Integral method. i.e. $\text{Log } K_I^H = \text{pKa} = B$ at $\bar{n}_A = 0.5$. This was further

corroborated by Linear Plot of $\text{Log } \frac{\bar{n}_A}{1 - \bar{n}_A}$ versus B.^{11,12}

From the ligand and complex titration curves, the values of \bar{n} and pL were calculated using the appropriate equations.^{7,9,10} Formation curves of the (Metal – Ligand) complexes were drawn by plotting \bar{n} vs pL for each of them. From these curves the stepwise stability constants of each metal complex ($\text{Log } K_1$ and $\text{Log } K_2$) were obtained by Half Integral Method^{9,10} i.e. $\text{Log } K_1 = \text{pL}$ at $\bar{n} = 0.5$ and $\text{Log } K_2 = \text{pL}$ at $\bar{n} = 1.5$. Since the difference

between Log K_1 and Log K_2 values was found to be very small, the same were refined by Least Square Treatment,¹³⁻¹⁷ and the results are reported in Table-1.

Table - 1

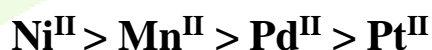
Stepwise and Overall Stability Constant Data of Metal complexes at 10°C, 20°C and 30°C [Medium = 75% Aqueous Dioxan (v/v); $\mu = 0.1$ M KCl]

pKa values of the Ligand at different temperatures :

Log $K_1^H = pKa = 10.92$ at 10°C, Log $K_1^H = pKa = 10.77$ at 20°C, and Log $K_1^H = pKa = 10.68$ at 30°C

Metal Ions	TEMPERATURES								
	10 ± 1° C			20 ± 1° C			30 ± 1° C		
	Log K_1	Log K_2	Log β	Log K_1	Log K_2	Log β	Log K_1	Log K_2	Log β
Ni²⁺	10.59	09.75	20.34	10.37	09.48	19.85	10.31	09.45	19.76
Mn²⁺	09.48	08.79	18.27	09.32	08.69	18.01	09.24	08.55	17.79
Pd²⁺	09.11	08.51	17.62	09.12	08.39	17.51	08.83	08.29	17.12
Pt²⁺	08.93	08.39	17.32	08.77	08.23	17.00	08.63	08.14	16.77

As is clear from the table, the stability constants of Metal complexes follow the trend :



EVALUATION OF ΔG^0

The value of standard change in free energy, ΔG^0 at a given temperature was calculated using the well known Thermodynamic expression, $\Delta G^0 = -2.303 RT \text{ Log } \beta$, where $\Delta G^0 =$ Standard Free energy change accompanying the complex formation reaction, $\beta =$ Overall Stability Constant, T = Temperature, R = Constant.^{7,12,15}

The ΔG^0 values at three different temperatures for each metal complex formed with the said ligand are given in Table 2.

Table – 2

ΔG^0 values of Bivalent Metal Complexes at three different temperatures.

(M = 0.1 M KCl and Medium = 75% aq. Dioxan)

Metal ions	$-\Delta G^0$ (in k Cals/mol)		
	TEMPERATURES		
	10 ± 1^0 C	20 ± 1^0 C	30 ± 1^0 C
Ni II	26.34	26.61	27.40
MnII	23.66	24.15	24.67
PdII	22.82	23.48	23.74
Pt ^{II}	22.43	22.79	23.25

It is, thus, obvious that the decrease in standard free energy is lower at 10^0C than at 20^0C which in turn is lower than those at 30^0C for the chelates of each metal ion.

DETERMINATION OF ΔH^0

The Standard Enthalpy Change, ΔH^0 accompanying the complex formation reaction was determined with the help of following Isobar equation.^{13,14,15}

$$\frac{d \ln \beta}{dT} = \frac{\Delta H^0}{RT^2}$$

The above equation may be rearranged as:

$$\frac{d(\log \beta)}{d(1/T)} = - \frac{\Delta H^0}{2.303 R}$$

Taking $R = 1.987 \text{ Cals. deg}^{-1} \cdot \text{mol}^{-1}$, we have

$$\frac{d(\log \beta)}{d(1/T)} = -\frac{\Delta H^0}{4.576}$$

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 $\log \beta$ as a function of $1/T$ will be equal to $-\frac{\Delta H^0}{4.576}$.

Use of Gibbs–Helmholtz equation^{13,16} was also employed to determine the values of ΔH^0 . These values of ΔH^0 obtainable from the plot of $\log \beta$ vs $1/T$ (Linear Plot method) as well as through Gibbs–Helmholtz equation have been listed in Table-3.

Table -3

ΔH^0 values of Bivalent Metal complexes in K Cals mol⁻¹ (Medium = 75% aqueous dioxan, $\mu = 0.1$ M KCl) at 20°C.

Metal ions	$-\Delta H^0$ (K Cals mol ⁻¹)		
	By Linear Plot Method	By Gibbs-Helmholtz eqn. $t=20\pm 1^\circ\text{C}$	Average values
Ni ⁺⁺	11.58	11.08	11.33
Mn ⁺⁺	09.44	09.35	09.39
Pd ⁺⁺	09.70	10.00	9.85
Pt ⁺⁺	10.85	10.77	10.81

($dT = T_2 - T_1 = 293\text{A} - 283\text{A}$; $T_3 - T_2 = 303\text{A} - 293\text{A}$; $T_2 =$ Desired Tempt.)

The average value obtained by Gibbs–Helmholtz equation under the two different sets of dT has been furnished in the table.

CALCULATION OF ΔS^0

The related values of ΔS^0 (Standard Change in Entropy) were calculated at 20°C using average value of ΔH^0 as mentioned in Table-3.

In the calculation of ΔS^0 , the well know Thermodynamic relationship viz $\Delta G^0 = \Delta H^0 - T\Delta S^0$ was applied.^{13,15} The required ΔG^0 values were utilized from Table-2.

The value of ΔS^0 obtained are listed in Table-4.

Table-4

ΔS^0 values of Bivalent Metal chelates using the average value of ΔH^0 at 20°C

Metal ions	ΔS^0 (Cals deg ⁻¹ . mol ⁻¹) at 20°C
Ni ⁺⁺	52.15
Mn ⁺⁺	50.37
Pd ⁺⁺	46.52
Pt ⁺⁺	40.89

The Standard Change in Entropy associated with the formation of above complexes were calculated at 10°C and 30°C also by making use of ΔH^0 values as obtained by Linear Plot method and are furnished in Table -5.

Table -5

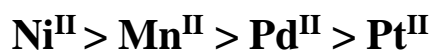
ΔS^0 values of above complexes calculated at 10⁰C and 30⁰C using ΔH^0 values obtainable by LPT (Medium = 75% of Dioxan, $\mu = 0.1$ M KCl)

Metal ions	ΔS^0 (Cals deg ⁻¹ . mol ⁻¹)	
	t=10 ⁰ C	t=30 ⁰ C
Ni ⁺⁺	52.47	52.21
Mn ⁺⁺	50.24	50.26
Pd ⁺⁺	46.36	46.33
Pt ⁺⁺	40.91	40.92

RESULTS & DISCUSSION

From the Thermodynamic relationship, $-RT \ln \beta = \Delta G^0 = H^0 - T\Delta S$, it follows that β increases as ΔG^0 becomes more negative. The value of ΔG^0 becomes more negative when that of ΔS^0 becomes more positive i.e. more positive value of ΔS^0 will lead to a more negative value of ΔG^0 , and hence a more stable metal complex will be formed.¹³⁻¹⁸ 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.^{9,14,15}

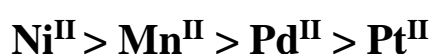
In the present investigation, we find that the Thermodynamic parameters too in conformity with the stability order (mentioned in Table-1) follow the same trend. Thus, at each temperature, the decrease in standard free energy change ($-\Delta G^0$) follows the trend :



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 as well as use of Gibbs–Helmholtz equation gives almost similar values for ΔH^0 for all the complexes of these bivalent metal ions.²²⁻²⁵ The highest value as well as the lowest value are shown by the complexes of Nickel and Manganese respectively which are members of same Transition elements series. However, compared to Palladium, a member of 2nd Transition elements series, Platinum (a member of 3rd Transition elements series) has higher value of ΔH^0 . The average values of ΔH^0 obtainable from Linear Plot method and by utilizing Gibbs–Helmholtz equation for Nickel, Platinum, Palladium and Manganese are 11.33, 10.81, 9.85 and 9.39 respectively in decreasing order as shown in Table - 3.

The negative values of ΔH^0 for each metal complex 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 changes in Entropy (ΔS^0) for these complexes, we find the same pattern as is found in the case of Free energy change. From table-4 containing ΔS^0 values calculated at 20°C for these complexes, it is obvious that the Nickel complex is much entropy stabilized having maximum disorderness. The values of ΔS^0 clearly support the stability order :



This supports the stability order observed in the case of complexes of all the four bivalent metal ions. This can be understood by looking at the values of standard Entropy Change observed for the complexes of Nickel, Manganese, Palladium and Platinum to be 52.15,

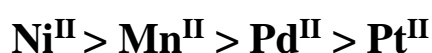
50.37, 46.52 and 40.89 cal/deg/mol when determined by using the average values of ΔH^0 obtainable through LPT as well as Gibbs-Helmholtz equation at 20°C (Table – 4).

Also, we find the same pattern when we calculate the change in Entropy accompanying the above complex formation in the case of said four metals at 10°C & 30°C by making use of values of ΔH^0 obtained by Liner Plot method. These values of ΔS^0 at 10°C are 52.47, 50.24, 46.36 and 40.91 respectively for the complexes of Ni, Mn, Pd & Pt whereas these values are respectively 52.21, 50.26, 46.33, and 40.92 at 30°C.

It can be seen in Table-5. These values of ΔS^0 determined at 10°C & 30°C are almost identical in the case of all the four metal complexes. Also, the value of ΔS^0 obtained at 20°C (furnished in Table-4 are also quite similar to the values obtained at 10°C & 30°C).

Thus, we can say that all the Thermodynamic factors namely Standard Changes in Free energy, Enthalpy and Entropy contribute much in stabilising the metal complexes in each case and at each temperature.

However, there is discrepancy in the values of Standard Change in Enthalpy. It records least value for Manganese complexes as also has lower values for Pd-complexes compared to Pt-complexes. But so far as the values of ΔG^0 and ΔS^0 are concerned, they fully support the stability order shown by the values of Overall Stability Constants obtained according to which the Stability Order of the above four Metal complexes follow the trend:



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