



Studies on Stability Constants of Fluorobenzoylthioacetophenone complexes of Ni(II), Mn(II), Cd(II) and Hg(II) at three different temperatures

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ABSTRACT

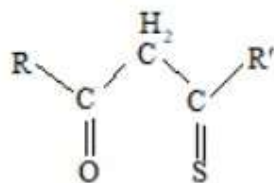
The stepwise and overall stability constants of the complexes of p-fluorobenzoylthioacetophenone with Nickel (II), Manganese (II), Cadmium (II) and Mercury (II) have been determined potentiometrically using Calvin-Bjerrum Potentiometric technique as modified by Irving and Rossotti. The effect of Fluorine substituent on the solution equilibria of ligand as well as on the stabilities of complexes formed has been studied. The order of stabilities of the metal complexes has been discussed.

(key words : Stability constants, Potentiometric technique, Solution equilibria)

Introduction

The ligand chosen for the present research work belongs to Monothio- β - diketone class. This organic compound behaves as uninegatively charged bidentate (O,S) chelating ligand after deprotonation through its enol or enethiol form in order to form a six membered resonance stabilized chelate with metal ions, especially the bivalent transition metal ions.

A number of complexes of Monothio- β -diketones (I; thioxo form) with metal ions of different classes have so far been reported¹⁻⁶ and their solution equilibria have also been studied.²⁻⁴ The general structural formula of Monothio- β -diketones is presented below.

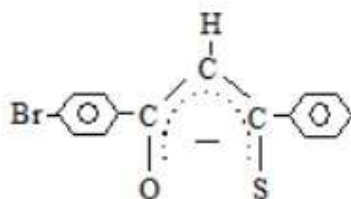


It is para-fluorobenzoylthioacetophenone, the ligand of our present work.

The solution equilibria of so many substituted Monothio- β -diketones have been studied. However, no attempt appears to have been made so far to study the solution equilibria of this ligand and its derived metal complexes – a work that can help to understand the effect of fluorine substituent on the stability constants of complexes of some bivalent metal ions viz. Ni (II), Mn(II), Cd(II) and Hg (II) belonging to first, second and third Transition metal series derived from the said ligand i.e. para-fluorobenzoylthioacetophenone when compared with those of its parent ligand i.e. Benzoylthioacetophenone as also the chelating ability of the ligand chosen.

Monothio- β -diketones are known to exist as an equilibrium mixture of tautomeric enol and enethiol forms which interconvert rapidly by intramolecular chelate proton transfer^{2,5,6} However, whether the ligand deprotonates through its enol or enethiol form, the anion produced having the negative charge delocalized throughout the whole ion will essentially be the same.

This is shown below.

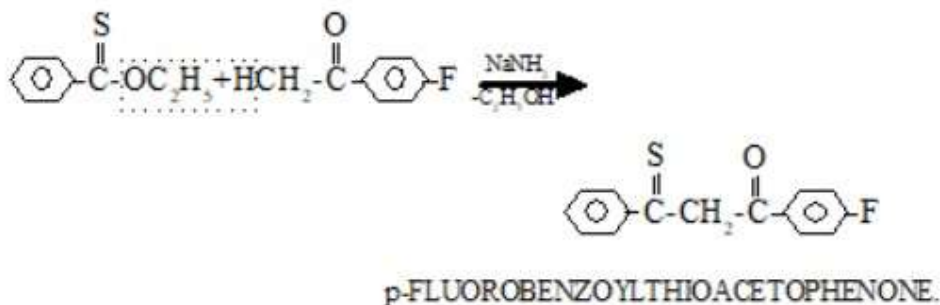


In the present communication, we report the stepwise as well as the overall stability constants of the chelates of p-fluorobenzoylthioacetophenone with Nickel, Manganese, Cadmium and Mercury (all bivalent) in 75% aqueous dioxan at three different temperatures namely 10°C, 20°C and 30°C and at a fixed ionic strength of 0.1M KCl as determined by Calvin-Bjerrum pH-metric technique⁷ and as modified by Irving and Rossotti.⁸

EXPERIMENTAL

By the reported method⁴, the ligand was synthesised by Claisen Condensation as shown below.

Syntheses of p-fluorobenzoylthioacetophenone.



The crude product was recrystallized in ethanol at m.pt. 130°C (lit. 129°C). The O-ethylthiobenzoate used in the preparation of the above ligand was obtained from corresponding nitrile.

Primary standard solution of the ligand was prepared in dioxan^{8,9}. 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 temperature were maintained constant at 10°C, 20°C and 30°C for the three observations.

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 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^{1,2,3}.

From the acid and ligand titration curves, the values of \bar{n}_A 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 protons, hence the value of the number of dissociable protons per ligand molecule (Y) was taken to be equal to one in the above calculation.

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 $\left(K_1^H = \frac{1}{K_a} \right)$ was

obtained by Half Integral method. i.e. $\text{Log } K_1^H = \text{pKa} = B$ at $\bar{n}_A = 0.5$. This was further

corroborated by Linear Plot of $\text{Log } \frac{\bar{n}_A}{1 - \bar{n}_A}$ 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 them. From these curves, the stepwise stability

constants of each metal complex i.e. $\text{Log } K_1$ and $\text{Log } K_2$ were obtained by Half Integral method. 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 $\text{Log } K_1$ and $\text{Log } K_2$ 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

Observed Stepwise and Overall Stability Constant Data of Metal

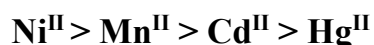
Complexes of four Bivalent Metal ions at 10°C, 20°C and 30°C.

[$\text{Log } K_1^H = \text{pKa} = 10.77$ (at 10°C), 10.60 (at 20°C) & 10.52 (at 30°C)]

(Medium = 75% aqueous dioxan, $\mu=0.1\text{M KCl}$)

Metal Ion	TEMPERATURES								
	10 ± 1° C			20 ± 1° C			30 ± 1° C		
	LogK ₁	LogK ₂	Log β	LogK ₁	LogK ₂	Log β	LogK ₁	LogK ₂	Log β
Ni ²⁺	10.47	09.43	19.90	10.21	09.38	19.59	10.18	9.31	19.49
Mn ²⁺	09.57	08.63	17.95	09.18	08.52	17.70	09.03	8.40	17.43
Cd ²⁺	08.94	08.35	17.29	08.76	08.16	16.92	08.59	8.05	16.64
Hg ²⁺	08.72	08.26	16.98	08.63	08.06	16.69	8.39	7.89	16.28

From the table, it is obvious that the stability constants of Metal complexes follow the trend :



It is also obvious that the overall stability constants of all the four metal chelates are greater at 10±1°C than what are these at 20±1°C which in turn are greater than those at 30±1°C. The highest value is shown by the complex of Nickel (II) whereas the complex of bivalent Mercury ions, a member of third transition elements series shows comparatively least value, and this is found at all the three temperatures.

RESULTS & DISCUSSION

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

Thus, while the ligand has a very weak tendency to deprotonate, it has a very strong tendency to coordinate the metal ions. This truth is also substantiated by very low dissociation constant of the ligand and very high formation constants of its complexes. It is imperative to note down here that the pK_a values of the ligand are 10.77, 10.60 and 10.52 respectively at $10 \pm 1^\circ\text{C}$, $20 \pm 1^\circ\text{C}$ and $30 \pm 1^\circ\text{C}$.

The important facts and noteworthy points coming out of the present research work may be listed below.

1. The pK_a value of the ligand was observed to be 10.77 at 10°C which is higher in the case of its parent compound. Similarly, the pK_a value of the ligand (p-fluorobenzoylthioacetophenone) has been observed in the present observation to be 10.60 at 20°C which is higher than that of benzoylthioacetophenone as is evident from the literature. Likewise, the same has been found equal to 10.52 at 30°C which is higher than that of its parent Monothio- β -diketone.

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

2. The values of \bar{n} range between zero and two indicating thereby the formation of ML_2 type of ring complexes analogous to the chelates of other monothio- β -diketones

reported previously. Very small difference between $\text{Log } K_1$ and $\text{Log } K_2$ values shows that ML and ML_2 are formed in very quick succession.

3. The $\log \beta$ values i.e. the Overall stability constant values of all the chelates are slightly less than those of the corresponding chelates of their parents indicating thereby the adverse effect of fluorine substituent on the stabilities of the metal complexes.

This may be probably due to the steric hinderance posed by the substituent together with increased strength of the ligand.

4. The stability constants of the metal chelates follow the trend: $\text{Ni}^{\text{II}} > \text{Mn}^{\text{II}} > \text{Cd}^{\text{II}} > \text{Hg}^{\text{II}}$ at all the three temperatures. This is obvious from Table-1.

Thus, the stability order of the complexes of the above metals in our present investigation at all the three temperatures is as follows:



The above trend is in conformity with the stability order reported for the complexes of these metals with several other monothio- β -diketones studied so far.

5. A comparison of the stability data of the present investigation with stability data of the previous work with the parent monothio- β -diketones reported so far clearly reveals that the overall stability constants of all the four metal chelates at 10°C are less than the respective metal chelates derived from benzoylthioacetophenone, the parent ligand.

Likewise, the overall stability constants of all the metal chelates at 20°C and 30°C also follow the same trend i.e. their $\log \beta_2$ values are less than those derived from the parent ligand which does not contain fluorine substituent in benzoyl ring .

This amply reflects that the substitution by fluorine in the para position of the benzoyl ring in the ligand decreases the stability of the derived metal chelates.

6. The above said decrease in the stability of the chelates may be probably due to the steric hinderance caused by the fluorine substituent as mentioned earlier.

The reason for the lower values of the overall stability constants may also be due to the increased acidic strength of the ligand as is obvious from the $\text{Log } K_1^H$ values of the ligand. These values are 10.77, 10.60 and 10.52 at 10°C , 20°C and 30°C respectively as mentioned earlier observed in the present investigation.

7. In our present investigation, the overall stability constant values of the metal complexes are less at higher tempt than at the lower temperature in the case of each metal complex which amply supports that the ligand has lower pka value at higher temperature. This is so far true also.
8. 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 log β value, for example in the case of Nickel complex is 19.90 at the lower tempt. 10°C whereas at 20°C it is 19.59 i.e. it has lesser value than what it has at 10°C . The difference in the log β values at the two tempts. thus comes to be 0.23 log unit. Again the log β value at 30°C is 19.49 which is still lower by 0.10 log unit when compared to its value at 20°C which is equal to 19.59. Exactly same pattern is followed in the case of other Metal complexes which is obvious by looking at the data furnished in the table.

This clearly suggests that the low temperature is favourable for the complex formation. The decrease in the stability of the metal chelates with increase in tempt is in agreement with the decrease in pKa values of the ligand with rise in tempt as described earlier.

9. In all the complexes formed above, the $\log K_2$ value is lesser than $\log K_1$ value which is in consistence with the results obtained for complexes of other ligands of this class. The difference between $\log K_1$ and $\log K_2$ values at different temperatures for different metal complexes are different. This difference in the case of Nickel complex at 10°C being 1.04 log unit is the highest whereas this difference in the case of Mercury is the lowest being equal to 0.49 log unit at the same tempt. i.e. at 10°C . At all the three temperatures this difference between $\log K_1$ and $\log K_2$ has been found greater in the case of Ni-Complexes compared to other metal complexes. This difference has been found equal to 1.04, 0.83 and 0.87 log units at 10°C , 20°C & 30°C respectively. This difference in the case of Hg-Complexes at all the three temperatures are almost of the same range. The same thing is observed in the case of Cadmium complexes.

Except in the case of Ni-complex, the difference in the values of $\log K_1$ & $\log K_2$ at 20°C range between 0.57 to 0.66 log units. Same pattern is to be found at 30°C in other three metal complexes except Nickel. The value ranges between 0.50 to 0.63 log units. For Hg complex, it is 0.50 log unit whereas for Cd- & Mn-Complexes it is respectively 0.54 and 0.63 log units.

Thus, Nickel has some peculiar behaviour towards the present ligand during complexation.

10. Importantly, the sequence of stability order of the metal chelates obtained in the present investigation with the ligand chosen is in conformity with the Mellor-Malley series which has been found to hold almost universally for oxygen and nitrogen donor ligands or Irving-William natural order of stability.

It is also in conformity with the stability order reported for the chelates of these metals with several other Monothio- β -diketones reported so far.^{2,8,11,12}

11. And finally, the complexes of this ligand in general have good biological and medicinal action on various diseases of animals and plants. These complexes have extensive use in the treatment of Breast Cancer. These have good⁵ Therapeutic use there.

Besides, these have adverse effects on the growth of some micro organisms including bacteria and fungus harmful for tropical plants.

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