Studies on Stability Constants of p-Bromobenzoylthioacetophenone Complexes of Mn(II), Fe(II), Co(II) and Ni(II) at Two Different Temperatures

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Abstract

The stepwise and overall stability constants of the complexes of p-bromobenzoylthioacetophenone with Manganese (II), Iron (II), Cobalt (II) and Nickel (II) have been determined potentiometrically using Calvin-Bjerrum potentiometric technique as modified by Irving and Rossotte. The effect of bromine substituent on the solution equibria 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.

Keywords: Stability Constants, Potentiometric Technique, Solution Equilibria

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Introduction

The ligand chosen for the present research work belongs to monothio-β-diketone class. This organic ligand 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 reported[1-6] and their solution equilibria also studied.[2-4]
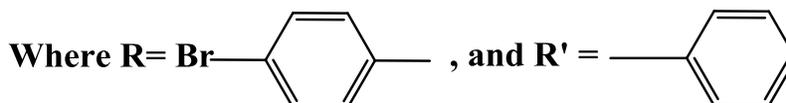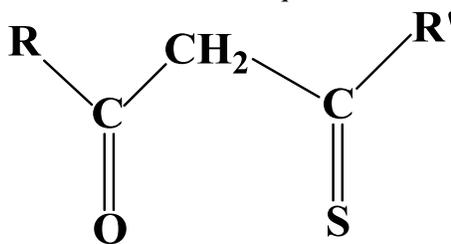
However, no attempt appears to have been made so far to study the solution equilibria of this ligand and its derived metal complexes –a work that can help to understand the effect of bromine substituent on the stability constants of complexes of some bivalent metal ions viz. Mn(II), Fe(II), Co(II) and Ni(II) belonging to first transition metal series derived from the said ligand i.e. para-

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Bromobenzoylthioacetophenone 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.
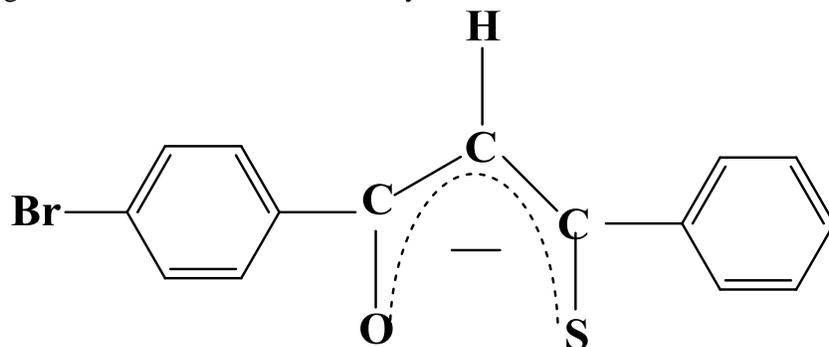

In the present communication, we report the stepwise as well as the overall stability constants of the chelates of p-bromobenzoylthioacetophenone with manganese, iron, cobalt and nickel (all bivalent) in 75% aqueous dioxan at two different temperatures namely 15˚C and 25˚C and at a fixed ionic strength of 0.1 (M) KCl as determined by Calvin-Bjerrum pH-metric technique[7] as modified by Irving and Rossotti.

Experimental work

By the reported method[4], the ligand was synthesized by Claisen condensation as shown below.

Synthesis of p-bromobenzoylthioacetophenone
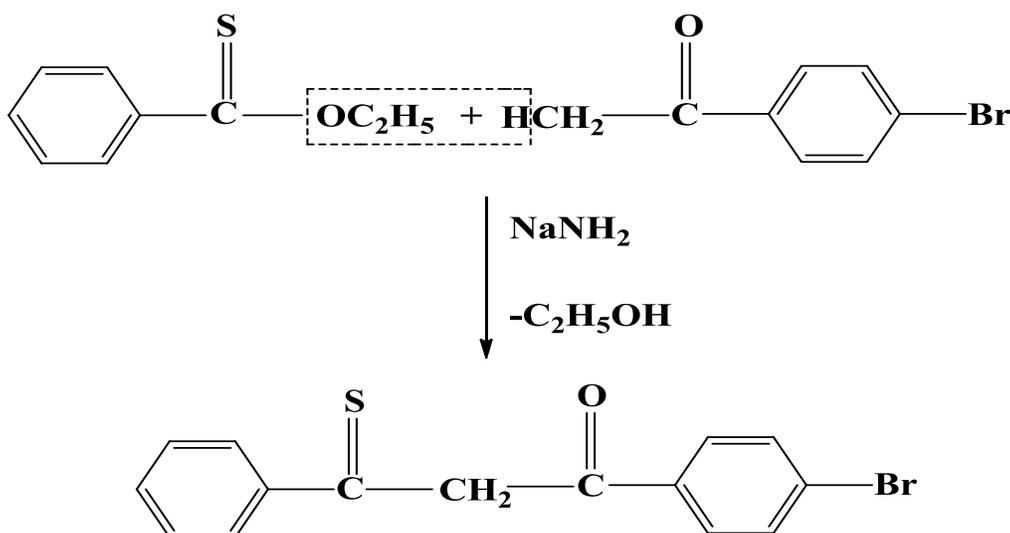
p-Bromobenzoylthioacetophenone

The crude product was recrystallised in ethanol at m.pt. 130˚C (lit. 129˚) . The O-ethyl thiobenzoate 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 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 for the two observations.

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 β-values (pH-meter reading) and the volume of alkali added (B) was plotted[6,7] 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 $\overline{n_A}$ at various B-values were calculated using the appropriate equation.[10] Since the ligand is monoprotonic due to the presence of an –OH or –SH group in its enol or enethiol form[2] respectively and there is no basic group to take up proton(s), 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 $\overline{n}_A$ values increase with increase in B-values showing thereby increase in the degree of dissociation of the ligand. A plot of 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 $\overline{n_A}$ = 0.5. This was further corroborated by linear plot of Log $\overline{n_A}/\overline{1}$-$n_A$ vs B

From the ligand and complex titration curves the values of $\overline{n}$ and pL were calculated using the appropriate equations[6,10]. Formation curves of the metal-ligand complexes were drawn by plotting $\overline{n}$ vs pL for each of them. From these curves, the stepwise stability constants of each metal complex ($LogK_1$ and $LogK_2$) were obtained by half-integral method i.e. Log K_1 = pL at $\overline{n}$ = 0.5, and $LogK_2$ = pL at $\overline{n}$ = 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** given below.

Table 1: Observed Stepwise and Overall stability Constants Data of the Metal Complexes at 15˚C and 25˚C for all the four Bivalent Metal ions taken [$LogK_1^H$ = pKa = 10.69 (at 15˚C) & 10.60 (at 25˚C)] (Medium = 75% aqueous dioxan, μ = 0.1(M) KCl)

Metal ions	TEMPERATURES					
	15 ±1˚C			25±1˚C		
	$LogK_1$	$LogK_2$	Logβ	Log K_1	$LogK_2$	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

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From the table, it is obvious that the stability constants of the metal complexes follow the trend: $Ni^{II} > Co^{II} > Fe^{II} > Mn^{II}$.

It is also obvious that the overall stability constants of all the four metal chelates are greater at 15 ±1˚C than what are these at 25±1˚C. The highest value is shown by Nickel(II) whereas the bivalent Manganese ion, a member of same transition series shows comparatively least value, and this is found at both the temperatures.

Results and Discussion

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

Thus, while the ligand has a very weak tendency to deprotonate, it has a very strong tendency to coordinate with metal ions. This fact is also substantiated by a very low dissociation constant of the ligand and very high stability constants of its complexes. It is imperative to note that the pKa values of the ligand are 10.69 and 10.60 respectively at 15±1˚C and 25±1˚C.

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

1.   The pKa value of the ligand was observed to be 10.69 at 15˚C which is higher than in the case of its parent compound. Similarly, the pKa value for the ligand (p-bromobenzoylthioacetophenone) has been observed in the present observation to be 10.60 at 25˚C which is higher than its parent compound i.e. Benzoylthioacetophenone as is evident from the literature.

The higher values of pKa of the ligand than its parent compound at both the said temperatures show how deprotonation is favoured by the presence of bromine atom at the para position of the benzoyl ring in the ligand. This may be probably due to the electronegative nature of the substituent, bromine.

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 $logK_1$ and $logK_2$ values shows that ML and ML_2 are formed in very quick succession.

3.   The Logβ values i.e. the Overall stability constant values of all the chelates are slightly less than those of the corresponding chelates of their parent ligand indicating thereby the adverse effect of bromine substituent on the stabilities of the metal complexes.

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

4.   The stability constant of the metal chelates follow the trend: $Ni^{II} > Co^{II} > Fe^{II} > Mn^{II}$ at both the temperatures. This is obvious from **Table-1**. Thus, the stability order of the complexes of the above metals in our present investigation in the case of both the temperatures is as follows:

$$Ni^{II} > Co^{II} > Fe^{II} > Mn^{II}$$
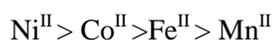
The above trend is in conformity with the stability order reported for the complexes of these metals with several other monothio-β-diketones studied so far.

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 overall stability

constants of all the four metal chelates at 25˚C are less than the respective metal chelates derived from Benzoylthioacetophenone.

Likewise, the overall stability constants of all the metal chelates at 15˚C also follow the same trend i.e. their logβ values are less than those derived from the parent ligand which does not contain Br-atom, the substituent in benzoyl ring.

This simply reflects that the substitution by bromine at 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 hindrance caused by bromine substituent as mentioned elsewhere.

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 $logK_1^H$ values of the ligand. These values are 10.69 and 10.60 at 15˚C and 25˚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 temperature than at the lower temperature in the case of each metal complex which amply supports the fact 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 with the ligand chosen. The logβ value, for example, in the case of Nickel-complex is 20.08 at the lower temperature 15˚C whereas at 25˚C it is 19.85. The difference in the log β value at the said two temperatures thus comes to be 0.23 log unit. Exactly same pattern is followed by in the case of other ions 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 temperature is in agreement with the decrease in pKa values of the ligand with rise in temperature as described earlier.

9.   In all the complexes formed above, the $LogK_2$ value is lesser than $LogK_1$ which is in consistence with the results obtained with complexes of other ligands of this class so far. The difference between $LogK_1$ and $LogK_2$ values at 15˚C in the case of all the metal chelate is nearly equal except for Ni-Complex. This difference in the case of Ni-Complex at 15˚C is equal to 0.74 whereas this difference in the case of Cobalt, Iron and Manganese complexes are respectively 0.46, 0.45 and 0.45 log units.

Conclusion

It was demonstrated that same patterns is followed by the metal chelates of the said metal ions at the other temperatures in exhibiting the difference between the values of $LogK_1$ and $Log K_2$ except again in the case of Ni-complex where this difference is of 0.89 unit at 25˚C. The difference at 25˚C in the case of other three metal chelates lies between 0.47 unit to 0.51 unit. Thus, Nickel has some peculiar behavior towards the present ligand during complexation.

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[10] which has been found to hold almost universally for oxygen and nitrogen donor ligands or Irving-William natural order of stability.

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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] And finally, the complexes of these 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 good[5] therapeutic use there.

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

Acknowledgement

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