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Effect of Bromine Substituent on Stability Constants of Para-Bromobenzoylthioacetone complexes of some Bivalent Metal ions

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ABSTRACT

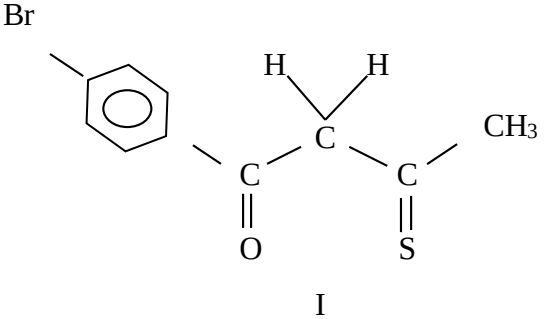
The effect of bromine substituent has been studied by comparing the stability constant data of the complexes of ρ-bromobenzoylthioacetone of Mn^{II}, Co^{II}, Pb^{II}, and Pt^{II} with those of the corresponding complexes of benzoyl thiacetone (the parent ligand). For the stepwise stability constants of the said complexes were determined potentiometrically using Calvin-Bjerrum pH-metric technique as modified by Irving and Rossotti. The order of stabilities of the metal chelates has also been evaluated.

Key Words : Stability Constants, Bivalent metal ions, pH-metric technique, Chelate.

INTRODUCTION :

The present ligand i.e. ρ-bromobenzoylthioacetone belonging to monothio-β-diketone class of compounds behaves as a uninegatively charged bidentate (O,S) chelating agent after deprotonation through its enol or enethiol form creating thereby a six-membered resonance stabilized chelate with the metal ions.[1,2,3] However, no attempt appears to have been made so far to study the solution equilibria of the chelates of the titled ligand (I) with said metal ions – a work that can help to understand the effect of bromine substituent on the stability constants of the metal complexes when compared with those of benzoylthioacetone already reported.[2,3,4]

In the present communication we report the stability constants of the chelates of p-bromobenzoylthioacetone with Manganese, Cobalt, Lead and Platinum all taken in bivalent state in 75% aqueous dioxan (v/v) at a constant temperature of 20^0C and fixed ionic strength of 0.1M KCl as determined by Calvin-Bjerrum's pH-metric technique and as modified by Irving and Rossotti.[4,5] Also reported along with it is the effect of bromine substitution on the acid dissociation constant of the ligand as well as on the stability constants of its derived metal complexes by comparing with those of unbrominated ligand i.e. benzoylthioacetone.



I

Fig-1: ρara-Bromobenzoylthioacetone

(The lignad)

EXPERIMENTAL

The ligand was synthesized by Claisen Condensation of o-ethylthioacetate (II) with p-bromoacetophenone (III) in presence of ethereal suspension of sodamide by the reported method[4] as shown below.

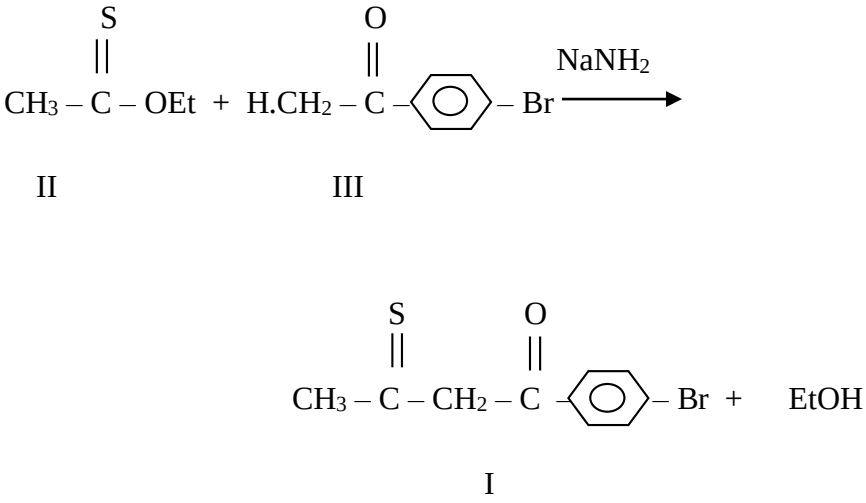
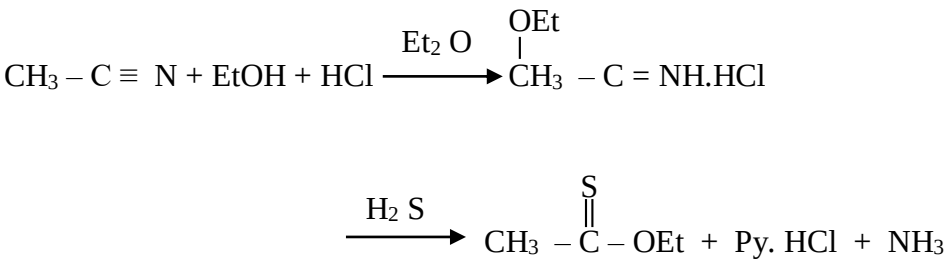


Fig- 2: Synthesis of ρ-bromobenzoylthioacetone

o-Ethythioacetate(II) was synthesized from acetonitrile as shown below.



The crude product was recrystallised from ethanol. The m.pt of the compound was found to be 90^0 (lit.[4] 88-89^0).

Primary standard solution of the ligand was prepared in dioxan. Aqueous solutions of Metal(II) chlorides were standardized.[5,6] 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.

A systronic pH-meter with combined glass and calomel electrodes was used for pH-measurements. The temperature was maintained constant at 30^0C.

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 0.1M 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 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.

From the acid and ligand titration curves, $\bar{n}_A$ values at various B-values were calculated using the appropriate equation.[7,8] A plot of $\bar{n}_A$ against B gave the formation curve of the ligand-proton complex from which pKa of the ligand or its Protonation Constant ($K_1^H = 1/Ka$) was obtained by Half-Integral method,[8] 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.

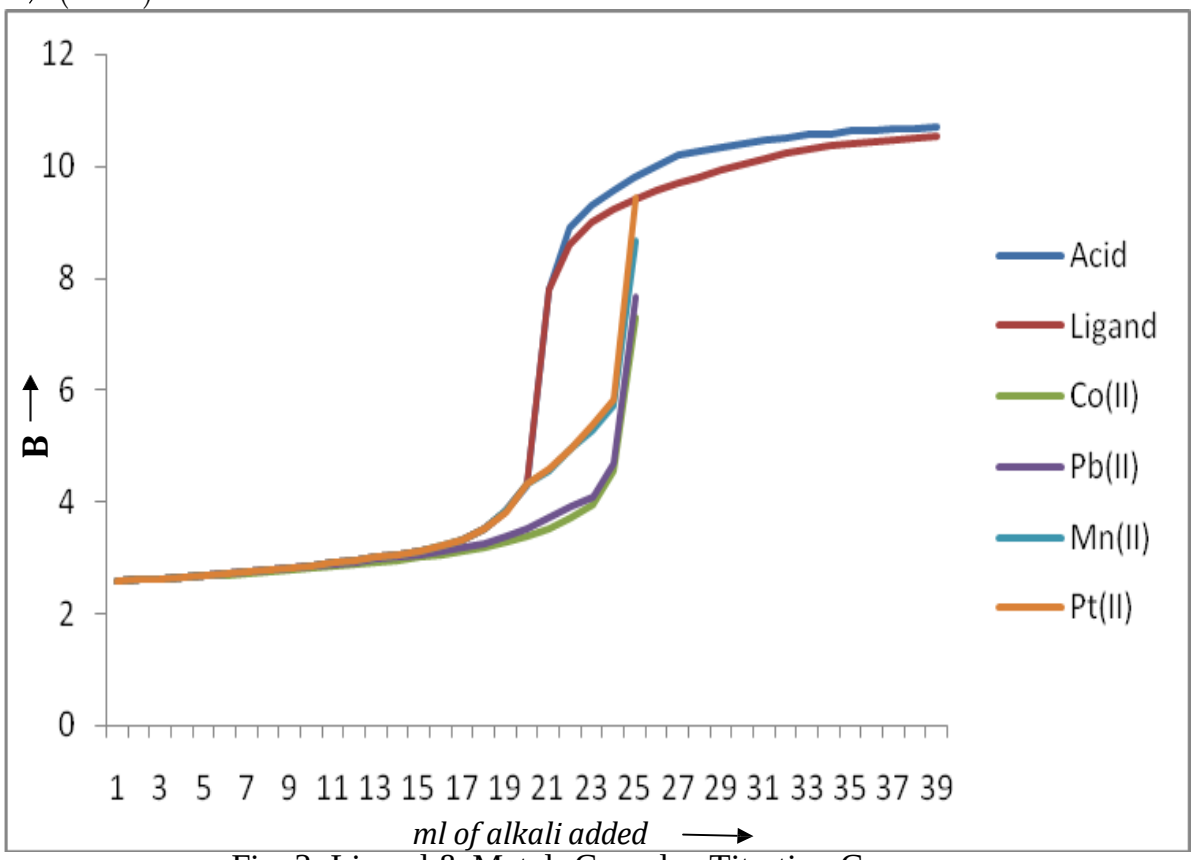


Fig. 3: Ligand & Metal- Complex Titration Curves.

From the ligand and complex titration curves the values of $\bar{n}$ and pL were calculated using the appropriate equation.[7,8,9] 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 (Log K_1 and Log K_2) were obtained by Half-Integral method[9,10] i.e. Log K_1 = pL at $\bar{n}$ = 0.5 and Log K_2 = 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 and the results are reported in Table–1 given below.

Table – 1.

STEPWISE AND OVERALL STABILITY CONSTANT DATA

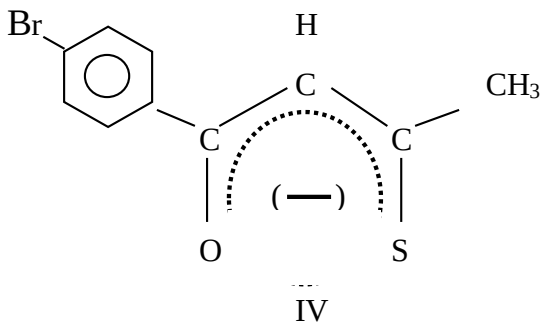
[Tempt.=20±1^{0}C, μ=0.1M KCl, Medium=75% aqueous dioxan (v/v)]

$LogK_1^H$ = pKa = 10.20

Metal ions / *Stability Constants*	$LogK_1$	$LogK_2$	Logβ
Mn^{++}	08.35	07.61	15.96
Co^{++}	10.27	09.50	19.77
Pt^{++}	08.35	07.51	15.86
Pb^{++}	09.86	09.08	18.94

RESULTS AND DISCUSSION

The ligand is known to exist as an equilibrium mixture of tautomeric enol and enethiol forms which interconvert rapidly by intramolecular chelate proton transfer.[3,4,11] However, whether the ligand deprotonates through its enol or enethiol form, the anion (IV) with negative charge delocalized over the whole ion will be essentially the same.



IV

Fig. 4: The Anion

From the figure containing various curves, it is obvious that the separation of ligand titration curve from 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. Thus, while the ligand has a very weak tendency to deprotonate, it has a very strong tendency to coordinate with the metal ion. These facts are also substantiated by very low dissociation constant of the ligand and very high formation constants of its complexes.

The higher value of Ka of the ligand (pKa = 10.20) than that of its parent (pKa =10.43)[2,3,9,12] shows how deprotonation is favoured by the presence of Br-atom at the para-position of the benzoyl ring in p-bromobenzoylthioacetone. This may probably be due to the electronegative nature of bromine, the substituent.

The values of $\bar{n}$ ranging between zero and two indicate the formation of ML_2 type of chelate analogous to the chelates of other monothio-β-diketones reported previously.[2,3,7,13] Very small difference between $LogK_1$ and $LogK_2$ values shows that ML and ML_2 are formed almost simultaneously. The Logβ values of all the metal complexes are slightly less than those of the corresponding complexes of its parent ligand (Mn=16.30, Co=20.17; Pb = 19.38, and Pt = 16.15) which indicate the adverse effect of bromine substituent on the stabilities of the metal chelates. This may be attributed to the steric hinderance posed by the substituent together with increased acidic strength of the ligand.

CONCLUSION

The stability constants of the metal chelates as is obvious from the table follow the trend : **Co^{II} > Pb^{II} > Mn^{II} > Pt^{II}** . Though this sequence differs from the Mellor-Maley series[9,12] which has been found to hold almost universally for oxygen and nitrogen donor ligands or Irving-williams natural order of stability[5,13],it is in conformity with the stability order reported for the chelates of these metals with several other monothio-β-diketones studied so far[2,3,12,13].

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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