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Thermodynamic Study of p-Bromobenzoyl Acetone Complexes from a Temperature Variation Study

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Abstract – The reaction of some transition metal ions like Cu(II), Co(II), Cd(II), Fe(II), Ni(II), Mn(II) and Zn(II) with p-bromo-benzoylacetone (p-BBA) have been carried out pH-metrically in 75% dioxane-water at different temperatures and the ionic strength 0.1 M (NaClO$_4$).

The order of metal ions according to the increasing stability of the complexes is found to be:

Cd < Mn < Co < Zn < Ni < Fe < Cu

The thermodynamic parameters ΔG, ΔH and ΔS have been calculated at 30°C. From these values, it is clear that the interaction between p-BBA and the metal ions is chelation.

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INTRODUCTION

The presence of a β-carbonyl group with proton on the carbon atom allows a keto⇌enol tautomerism to take place (Fig. 1). By the replacement of proton by a metal ion β-ketoenolate complexes are obtained.

Given widespread applications of β-diketones and their derivatives p-Bromobenzoylactone (p-BBA) has been chosen to study the interaction with bivalent metal ions. β-Diketones are commonly used reagents for the solvent extraction of some metal ions like lanthanides.

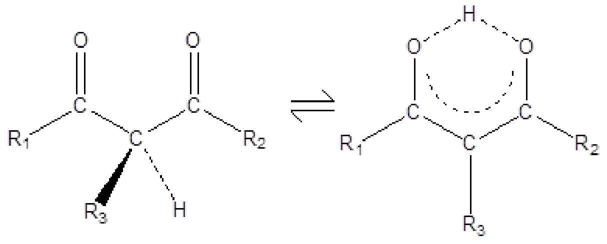
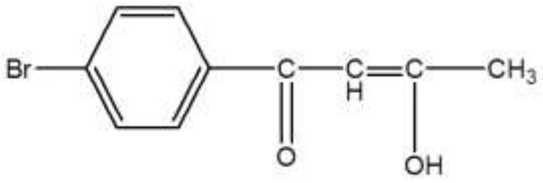


Fig. 1. Keto-enol tautomerism

EXPERIMENTAL

p-Bromoacetophenone (20 g) was mixed with 200ml of ether and 2.5 g of sodium metal. Then 22 g of ethyl acetate was added and the mixture was refluxed for about five hours. Then it was cooled. The residue obtained was dissolved in water and acidified with acetic acid. Light yellow coloured crystals were obtained, recrystallized with alcohol (Fig. 2)



p-Bromobenzoylacetone (pBBA)

The ligand was characterised by elemental analysis, infrared and PMR studies.

The solution of p-Bromobenzoyl acetone (ligand) was prepared in freshly distilled dioxane. The titration was carried out in a 75:25 (V/V) dioxane water mixture. Chemically pure sodium perchlorate was used to maintain the ionic strength. All other chemicals used were of reagent grade. 0.04 M solution of tetramethylammonium hydroxide (TMAH) in 75% (V/V) aqueous dioxane was used as the titrant. Dioxane used was purified by refluxing with sodium metal for about 24 hours and was freshly distilled over sodium before use. The EC-digital pH-meter, model pH 5651 with a combined glass electrode was used for pH measurements. The instrument was standardized by using potassium hydrogen phthalate and phosphate buffers.

pH-titration Procedure

The method of Bjerrum and Calvin et al. as modified by Irving and Rossetti has been used to obtain the values of proton-ligand and the metal-ligand formation constants. For carrying out the studies these solutions with a total volume of 20 ml were titrated against TMAH at 20°, 30°, 40° and 50°C.

(i) 3.0 ml $HClO_4$ (0.02 M) + 1.0 ml $NaClO_4$ (2.0 M) + 0.5 ml K_2SO_4 (0.02 M) + 15 ml dioxan + 0.5 mL H_2O

(ii) 3.0 ml $HClO_4$ (0.02 M) + 1.0 ml $NaClO_4$ (2.0 M) + 0.5 ml K_2SO_4 (0.02 M) + 10 ml ligand (0.01 M) + 5 ml dioxan + 0.5 ml H_2O

(iii) 3.0 ml $HClO_4$ (0.02 M) + 1.0 ml $NaClO_4$ (2.0 M) + 0.5 ml metal ion solution (0.02 M) + 10 ml ligand (0.01 M) + 5 ml dioxan + 0.5 ml H_2O.

RESULTS AND DISCUSSION

The pK_a values were obtained from the plot of log $\bar{n}_H/1-\bar{n}_H$ vs pH. These values are given in table 1.

The $\bar{n}$values obtained lie below 2.0 in all the cases. So only two types of complexes 1:1 and 1:2 are obtained in each case. The concentration of metal ion used was very low (5.0×10^{-4} M) so the possibility of the formation of polynuclear complexes is ruled out.

The number of ligands combining with metal atom depends upon its valency. Each ligand is equivalent to two units so the complexes will have two ligands attached to the metal atom. On complexation a very stable six-membered ring is obtained and the metal atom links the two ends of the ligand through oxygen atoms.

The order of increasing stability constant of the metal complexes is

Cd(II) < Mn(II) < Co(II) < Zn(II) < Ni(II) < Fe(II) < Cu(II).

With the increase in temperature the stability constants and the pK_a values decreases which shows that lower temperature favours the formation of complexes.

Thermodynamic Parameters

The values of the overall changes in free-energy (ΔG), enthalpy (ΔH) and entropy (ΔS) are calculated using these equations-

$$\Delta G = -RT \ln K$$

$$\frac{d \log K}{d(1/T)} = -\frac{\Delta H}{4.57}$$

$$\Delta S = -\frac{\Delta H - \Delta G}{T}$$

The values of ΔG, ΔH and ΔS obtained are given in table 2.

Table 2: Stability constants* of the bivalent metal complexes with p-bromobenzoylacetone at different temperatures and ionic strengths = 0.1 $NaClO_4$

Cation	20°C			30°C		
	log K_1	logK_2	log β_2	log K_1	logK_2	log β_2
Co^{2+}	7.30	6.34	13.64	7.06	6.08	13.14
Cd^{2+}	6.08	4.57	10.65	6.00	4.52	10.52
Zn^{2+}	7.80	6.70	14.50	7.67	6.70	14.37
Cu^{2+}	9.62	7.99	17.61	9.38	7.78	17.16
Fe^{2+}	9.10	7.83	16.93	8.91	7.73	16.64
Mn^{2+}	6.67	3.84	10.51	6.46	3.78	10.24
Ni^{2+}	8.89	6.63	15.52	8.56	6.39	14.95

	40°C			50°C		
	logK_1	log K_2	log β_2	logK_1	log K_2	log β_2
Co^{2+}	6.82	5.96	12.78	6.58	5.78	12.36
Cd^{2+}	5.92	4.47	10.39	5.74	4.47	10.21
Zn^{2+}	7.57	6.70	14.27	7.49	6.62	14.11
Cu^{2+}	9.30	7.63	16.93	9.20	7.54	16.74
Fe^{2+}	8.72	7.59	16.31	8.57	7.55	16.12
Mn^{2+}	6.34	3.68	10.02	6.30	3.60	9.90
Ni^{2+}	8.30	6.27	14.57	8.09	6.16	14.25

* Values obtained by Bjerrums half-integral method.

Table 3: Thermodynamic Parameters for the formation of p-BBA complexes at 30° C

Cation	Free Energy change*			Enthalpy change*			Entropy change**		
	$-\Delta G_1$	$-\Delta G_2$	$-\Delta G$	$-\Delta H_1$	$-\Delta H_2$	$-\Delta H$	ΔS_1	ΔS_2	ΔS
Co^{2+}	9.587	8.562	18.15	9.14	5.712	15.233	1.476	9.405	9.627
Cd^{2+}	8.179	6.411	14.591	5.077	2.176	8.064	10.237	13.976	21.541
Zn^{2+}	10.629	8.583	19.213	6.528	3.264	13.057	13.534	17.554	20.316
Cu^{2+}	12.861	10.879	23.741	9.140	7.030	18.280	12.280	12.702	18.023
Fe^{2+}	12.329	10.658	22.987	8.568	5.484	16.618	12.412	17.075	21.019
Mn^{2+}	9.310	5.169	14.479	5.077	3.264	8.568	13.970	6.287	19.508
Ni^{2+}	11.013	8.887	19.900	10.155	5.077	15.233	2.831	12.574	15.402

* K Cal/mole ** Cal/deg/mole

From the values of the thermodynamic parameters (Table 2) it is concluded that the reactions are exothermic. The values of enthalpy change (ΔH) are negative, so there is release of energy during complex formation. The values of entropy change (ΔS) are positive, so it favours complex formation. Hence the chelation effect is an entropy effect. The higher positive values of entropy are there due to greater availability of coordination sites on the metal ions.

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