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Transition Metal Complexes of Some Substituted Chalcones

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The present paper reports the synthesis of a series of chalcones derived from 2-hydroxy/5′-chlorophenyl acetophenones and *p*-nitromethyl benzoic acid and benzaldehyde. The ligands synthesized were studied with regard to complex formation with V(II), Cr(II), Mn(II) and Fe(II).

INTRODUCTION

In view of the analytical, biological[1,2], industrial and manifold uses of chalcone complexes with metals, a study of their stability is an important factor in determining the effectiveness of these chelates in the above mentioned fields. Chalcones also exhibt germicidal,[3] bactericidal,[4] fungicidal[5] and carcinogenic activities. The exhaustive literature survey revealed that stability constants of complexes of these chalcones with transition metal ions have so far not been reported and hence a study of their binary complexes with transition metal ions like V(II), Cr(II), Mn(II) and Fe(II) was undertaken.

EXPERIMENTAL

All the chemicals such as phenol, NaOH, acetic anhydride, aluminium chloride, hydrochloric acid, pyridine, ethanol, transition metal salts, $HClO_4$, $NaClO_4$ etc. were of analytical grade. The concentrations of metal ions in the solutions were determined by standard procedures.[6–9]

Preparation and characterisation of chalcones

o-Hydroxy acetophenones which are the starting material for the preparation of chalcones were prepared by Fries migration reaction of phenol and chlorophenol. These were turned to β-diketones by Baker-Venkatraman transformation. Finally the chalcones were prepared by condensing aldehydes with β-diketones in basic medium. They were characterised by physical methods such as melting points and infrared spectroscopy.

The determination of stability constants of binary complexes from the experimental data consists of three steps:

Step 1: Titration of $HClO_4 + NaClO_4$ in 60% ethanol against the standard NaOH solution and construction of curve (A).

Step 2: Titration of $HClO_4 + NaClO_4 +$ ligand in 60% ethanol and construction of a plot (A + R) .

Step 3: Titration of $HClO_4 + NaClO_4 +$ ligand + metal ion in 60% ethanol and plotting of a curve (A + R + M).

The ionic strength of each solution was maintained constant at 0.1 M by addition of $NaClO_4$ solution.

RESULTS AND DISCUSSION

For the sake of convenience, these chalcones (Fig. 1) are divided into two groups.

Group A: Those which are derived from *o*-hydroxyacetophenone, *e.g.*,

(R_1) = 1-(2′-hydroxyphenyl)-2-(4′-nitrobenzoyl)-3-(phenyl)-2-propene-1-ones,

(R_2) = 1-(2′-hydroxyphenyl)-2-(4′-methylbenzoyl)-3-(phenyl)-2-propene-1-ones,

(R_3) = 1-(2′-hydroxyphenyl)-2-(4′-methylbenzoyl)-3-(4′-methoxyphenyl)-2-propene-1-ones.

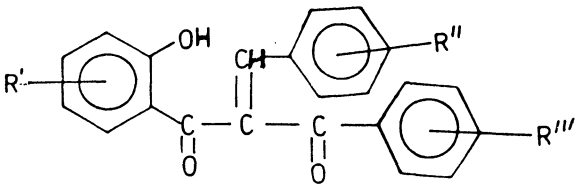
Group B: Those which are derived from 5-chloro-2-hydroxyacetophenone. *e.g.*,

(R_4) = 1-(2′-hydroxy-5-chlorophenyl)-2-(4′-nitrobenzoyl)-3-(phenyl)-2-propene-1-ones,

(R_5) = 1-(2′-hydroxy-5-chlorophenyl)-2-(4′-methyl- benzoyl)-3-(phenyl)-2-propene-1-ones,

(R_6) = 1-(2′-hydroxy-5-chlorophenyl)- 2-(4′-methylbenzoyl)-3-(4′-methoxyphenyl)-2-propene-1-ones.

IR spectra of the chalcones show two carbonyl bands at 1700–1695 cm^{-1} and 1670–1650 cm^{-1}. The band at lower frequency is assigned to the carbonyl group which is *ortho* to —OH group. The band at higher frequency is assigned to the carbonyl group which is relatively away from the hydroxyphenyl radical. The absorption due to hydroxyl group is observed near 3077 cm^{-1}. The peak due to ethylene group is observed at 1600–1580 cm^{-1} in all of the chalcones. (Fig 1).



R′ = H (Group A), R″ = CH_3, NO_2, R‴ = H, OCH_3 R′ = Cl (Group B)

Fig. 1

The proton-ligand and metal-ligand stability constants

The acid + ligand curve deviates from acid curve from pH 9.5 indicating the deprotonation of phenolic —OH group in this pH range. From these curves values of $\bar{n}_A$ for various pH were calculated and they are found to be in the range 0.2 to 0.8 indicating the presence of only one pK for each chalcone. The pK values were calculated by pointwise calculation and half integral methods and were found to be in good agreement.

The displacement of metal titration curve with respect to ligand titration curve along volume axis indicate the formation of complex species and lies in the pH region where hydrolysis is not expected. The probability of formation of polynuclear complexes was ruled out as the metal concentrations were very dilute.

The values of pL were calculated and plotted against $\bar{n}$ to get the formation curve. The metal-ligand stability constant (log K) was obtained by pointwise calculation, half integral and least squares methods. The pK and log K values are listed in Table-1.

TABLE-1
pK AND log K VALUES IN 60% (v/v) ETHANOL-WATER MEDIUM
TEMP = 25 ± 0.1°C; μ = 0.1 M ($NaClO_4$)

Ligand pK		R_1 10.829	R_2 11.210	R_3 11.400	R_4 10.320	R_5 10.500	R_6 10.670
V(II)	log K_1	8.778	10.648	10.618	10.280	9.738	9.970
	log K_2	7.665	9.812	10.039	8.725	8.900	9.034
	log K_3	6.554	8.774	9.071	7.664	7.901	8.169
	log β	22.997	29.205	29.729	26.670	26.539	27.173
Cr(II)	log K_1	9.504	10.429	10.608	10.454	9.524	10.020
	log K_2	8.214	9.886	10.004	9.042	8.900	9.020
	log K_3	7.005	8.759	9.091	7.839	8.293	8.179
	log β	24.723	29.074	29.074	27.336	26.717	27.219
Mn (II)	log K_1	10.331	10.648	10.620	10.480	9.891	10.039
	log K_2	9.566	9.986	10.140	9.761	9.420	9.071
	log K_3	8.454	8.922	9.166	8.554	8.000	8.269
	log β	28.371	29.557	29.927	28.795	27.311	27.379
Fe(II)	log K_1	11.382	11.452	11.600	10.860	10.945	10.309
	log K_2	10.596	10.350	10.524	10.126	9.983	9.548
	log K_3	10.167	9.259	9.421	9.743	9.401	8.604
	log β	32.146	31.061	31.547	30.730	30.330	28.462

The hydroxy chalcones and their substituted derivatives may be considered as monobasic acids having only one dissociable proton from —OH group and hence only one pK value. This is confirmed by $\bar{n}_A$ which were less than one for each ligand.

The pK Values of the parent *ortho*-hydroxy and 5-chloro-2-hydroxy acetophenones were also determined for the purpose of comparison with the pK values of chalcones prepared from them. It is revealed that the pK values of chalcone are lower than the corresponding acetophenones. The overall decrease in the pK values of chalcone is attributed o the presence of phenyl ring at 2 and 3 positions which act as electron withdrawing groups and reduce the strength of intramolecular hydrogen bonding due to which the ligands become more acidic. It is observed from Table-1 that the pK values of the ligands R_1 and R_4 in the respective groups A and B are relatively lower than the other ligands. This may be due to the combined negative inductive effect (–I) of phenyl and *para*-nitro phenyl groups, which act as electron sink.

The larger pK values of R_2 and R_5 in their respecive groups are due to the

presence of electron releasing —CH_3 group preset at *para* position. The introduction of methyl group in the *para* position increases the charge density on phenyl ring by positive inductive (+I) effect and opposes the charge transfer from —OH group which causes the bonding of proton to oxygen atom. The ligands R_3 and R_6 having highest values in their respective groups because they contained —CH_3 and —OCH_3 groups at *para* positions of two phenyl rings which enhance the above effect thereby increases the pK values of these ligands. Thus the order of pK values is $R_3 > R_2 > R_1 > R_6 > R_5 > R_4$. The interaction of the chalcones with metal ions like V(II), Cr(II), Mn(II) and Fe(II) was studied in 60% (v/v) ethanol-water medium at an ionic strength 0.1 M and the log K values are set out in Table-1.

The effects of the factors such as ligand basicity and metal ions on the stability have been examined.

Effect of ligand basicity

The relation $\log K = a\,pK + b$ was tested. Since these ligands form a close series, they have identical binding sites and hence a plot of log K *vs.* pK is expected to be linear. The validity of linear relationship has been observed by plotting pK *vs.* log β (overall stability constant) since the differences between $\log K_1$, $\log K_2$ and $\log K_3$ are very small. The linear relationship indicated identical binding sites in the ligands. The magnitude of the slopes of such correlation plots also depends upon a number of factors such as ionisation potential of the metal ion, nuclear repulsion between metal ion and donor atoms, tendency of metal ions to form bonds, etc.

According to Earnst and Meenashi[10], the effect of substituent in ligand on stability of metal ligand complexes as compared to that of proton-ligand complexes will be:

(a) to the same extent if slope = 1
(b) a lesser extent if slope < 1 and
(c) to a greater extent if slope > 1.

The values of slopes obtained are as follows:

V(II) = 0.83 Cr(II) = 0.86

Mn(II) = 0.99 Fe (II) = 1.00

The slopes of the correlated plots are nearly one in case of Mn(II) and Fe(II) suggesting that the effect of substituent in the ligands on the stability of metal-ligand complexes as compared to that of proton-ligand stability constant is same. This is in agreement with the suggestions of Narwade *et al.*[11] The complexes of V(II) and Cr(II) have slopes less than one. This is similar to the observations of Jones *et al.*[12] who suggested that the deviation of slope from unity is due to the σ bonding in chelate formation.

In view of the bulky size of the ligands, one would expect a large difference between $\log K_1$ or $\log K_2$ and $\log K_3$ values because of the possible steric hindrance to the linking of second and third ligand to the metal ion. The smaller difference suggests the *trans* structures. The ratio $\log K_1/\log K_2$ is smaller in all cases. Separation factors between first-second and second-third formation

constants are well within the expected range and absence of high values implies that there is little or no steric hindrance to the addition of second and third ligand in *trans* structure.

Effect of metal ion

The stability constants of bivalent metal complexes derived from similar type of ligands generally follow Irving-Williams order. The order could be explained on the basis of ligand field stabilization energy (LFSE).

The present complexes follow the order of stability as

$$Fe(II) > Mn(II) > V(II) > Cr(II).$$

The Fe(II) complexes are found to be most stable which may be attributed to the fact that the Fe(II) ion gains LFSE more than the other metal ions and shows a greater affinity for the ligands.

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