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Equilibrium Studies of Mn(II), Mg(II), Ca(II), Sr(II) and Ba(II) with *p*-Fluoro-, *p*-Chloro-, *p*-Bromo-, *p*-Methyl-Benzoylacetones and 1-(4-Fluorophenyl)-1,3-Pentanedione

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The raw *pH*-data, obtained from the potentiometric titrations of the titled ligands with NaOH in 75% (*v*/*v*) dioxane-water mixture performed at 20, 30 and 40 °C at constant ionic strength ($\mu = 0.1$ *M*-$NaClO_4$), have been adequately corrected for dilution and solvent effects in order to evaluate thermodynamic dissociation constants. Variance of the latter as a function of temperature has also been accounted for. The differing magnitudes of thermodynamic dissociation constants of the titled ligands have been explained on the basis of the non coplanar orientation of the phenyl ring in the ligands and a comparison has been made with those of unsubstituted benzoylacetone, dibenzoylmethane and acetylacetone.

Following similar technique, thermodynamic stepwise and overall formation constants of the titled metal-ligand systems have been obtained and the results correlated with ligand basicity, inverse metal crystal radii and second potentials of metals. Decrease in the free enthalpy ($-\Delta G$) of complexation reaction has also been evaluated.

(Keywords: Equilibrium constants of complexes; Stability constants of complexes; Thermodynamic data)

Untersuchung der Gleichgewichte von Mn(II), Mg(II), Ca(II), Sr(II) *und* Ba(II) *mit p-Fluor-, p-Chlor-, p-Brom-, p-Methyl-benzoylaceton und 1-(4-Fluorphenyl)-1,3-pentanedion*

Aus der potentiometrischen Titration der Titelverbindungen mit NaOH in 75 (*v*/*v*) Dioxan—Wasser bei 20, 30 und 40 °C bei konstanter Ionenstärke ($\mu = 0{,}1$ *M*-$NaClO_4$) wurden die thermodynamischen Dissoziationskonstanten ermittelt. Verdünnungs-, Lösungsmittel- und Temperatureffekte wurden berücksichtigt. Die unterschiedlichen Dissoziationskonstanten werden mit der Nichtplanarität des Phenylrings in den Liganden erklärt. Außerdem wurden die Komplexbildungskonstanten bestimmt; sie sind in die Diskussion miteinbezogen.

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Introduction

In continuation with our earlier studies[1–5] we describe herein the results of seventy five equilibrium studies, twenty five for each temperature, of Mn(II), Mg(II), Ca(II), Sr(II) and Ba(II) with *p*-fluoro-, *p*-chloro-, *p*-bromo-, *p*-methyl benzoylacetones (4-*p*-substituted 1-phenyl-1,3-butanediones) and 1-(4-fluorophenyl)-1,3-pentanedione in dioxane-water mixture (75% *v*/*v*) at 20, 30 and 40 °C at constant ionic strength ($\mu = 0.1\ M\text{-NaClO}_4$).

Experimental

The ligands have been prepared by standard procedures[6–8]. Dioxane was dried and purified by the literature method[9]. Metal perchlorates were obtained by decomposing their carbonates with requisite amounts of perchloric acid and the solution standardized[10]. Dioxane-water mixture (75% *v*/*v*) was prepared by adding 250 ml of deionised water to 750 ml of freshly distilled dioxane. The same mixture was used for preparing master solutions of metal salts, ligands and sodium perchlorate. The ionic strength (μ) of the equilibrium mixture was maintained constant (0.1 *M*) throughout the experiment by adding an appropriate amount of master solution of sodium perchlorate.

Procedure

Potentiometric titrations were carried out with an expand *pH* Meter PH 821 equipped with a glass electrode and a saturated calomel electrode (SCF) in a titration cell kept in a water-bath maintained at 20, 30 and 40 ± 0.1 °C. The solutions of ligand, and ligand plus metal ions were titrated with 0.5 and 0.1 *M*-NaOH, respectively, in oxygen-free nitrogen atmosphere. The changes in *pH* were recorded as a function of hydroxyl ion concentration.

Prior to affecting correction pertaining to the solvent effect, corrections for the dilution have been made in each of the *pH* meter reading of the potentiometric titration. From the corrected *pH* meter readings the values of $\bar{n}$ were evaluated. Only those readings were chosen where no noticeable precipitation of the metal complex occured.

Calibration of Glass Electrode

Using the cell similar to the one employed by *Van Uitert* and *Haas*[11]

(—) Glass Electrode	HCl in aq. dioxane [mole fraction of dioxane n_2, ionic strength ($\mu = 0.1\ M\text{-NaClO}_4$)]	Saturated solution of KCl	Calomel Electrode (+)

in conjunction with the *pH*-meter appropriately calibrated with buffers of *pH* 4.02 and 9.00, respectively, to furnish the *pH* of the aqueous dioxane-water mixture, the corrected *pH* of the same mixture in aqueous solution is given by:

$$pH_{\text{corr.}} = B + \log U_H \tag{1}$$

where B is the *pH* meter reading and the correction factor, $\log U_H$, for a given composition of the medium and temperature can be obtained at any ionic strength by the following expression:

$$\log U_H = \log U_H^\circ - \log (1/\gamma_\pm) \tag{2}$$

where U_H° is the correction appropriate to zero ionic strength ($\mu = 0$) and $\gamma \pm$ refers to the mean activity coefficient of both cations and anions. But the value of log $U^\circ{}_H$ is reported to be independent of the ionic strength, thus remains a function of both temperature and dioxane-water composition.

The value of log U_H° was calculated by using the least-squares equation given by *Rao* and *Mathur*[12]. The latter had shown the temperature dependence of log U_H° in dioxane-water mixture (75% v/v)

$$\log U_H^\circ = (0.007406)t + 0.828 \qquad (3)$$

where t is the temperature in °C. The values of log U_H° evaluated at 20, 30 and 40 °C are collected in Table 1.

Table 1. *Parameters*, $\log U_H^\circ$, $\log(1/\gamma_\pm)$ *and* $\log U_H$ *evaluated for different temperatures*

Temp., °C	$\log U_H^\circ$	$\log(1/\gamma_\pm)$	$\log U_H$
20	0.98	0.90	0.08
30	1.05	0.92	0.13
40	1.12	0.92	0.17

The value of log $(1/\gamma_\pm)$ calculated at 30 °C agrees well with the one obtained by the following polynominal given by *Irving* and *Mahnot*[13]:

$$\log(1/\gamma_\pm)_{30\,°\mathrm{C}} = 0.0933 + 1.0351\,n_2 + 0.3142\,n_2^2 + 6.6350\,n_2^3 \qquad (4)$$

where n_2 is the mole fraction of dioxane.

On substituting the value of $\log U_H^\circ$ and log $(1/\gamma_\pm)$ in equation (2), the correction factors, $\log U_H$, were evaluated at 20, 30 and 40 °C (Table 1). The values of $\log U_H$ were added to each pH-meter readings (B), already corrected for the dilution effect, in each set of experiments performed at 20, 30 and 40 °C, respectively.

Calculation of Thermodynamic Dissociation Constant (pk_D)

The stoichiometric dissociation constants (pq_D) of titled ligands were determined by potentiometric titration of the ligand solution (0.01 M) in dioxane-water mixture (75% v/v) with carbonate-free sodium hydroxide (0.5 M) in sodium perchlorate ($\mu = 0.1\,M$). In the expression for the evaluation of pq_D the correction factors have been included. The thermodynamic dissociation constant, pk_D, was calculated by using the equation[12]:

$$pk_D = pq_D + 2\log(1/\gamma_\pm) \qquad (5)$$

The data of stoichiometric and thermodynamic dissociation constants are listed in Table 2.

Calculation of Thermodynamic Stepwise Formation Constants

For a system, having $N = 2$, the following equations were used to express the formation of bis-β-diketonato-metal complexes:

$$M^{2+} + L^- \rightleftharpoons ML^+;\ q_1 = \frac{[ML]}{[M^{2+}]\,[L^-]}$$

$$ML^+ + L^- \rightleftharpoons ML_2\ ;\ q_2 = \frac{[ML_2]}{[ML^+]\,[L^-]} \qquad (6)$$

Table 2. *Data of stoichiometric* (pq_D) *and thermodynamic* (pk_D) *dissociation constants for 1,3-diones* $R'COCH_2COR$

R'	R	Temp., °C	pq_D	pk_D
p-FC_6H_4-	-CH_3	20	10.65 ± 0.07	12.45 ± 0.07
		30	10.25 ± 0.06	12.09 ± 0.06
		40	10.10 ± 0.06	12.00 ± 0.06
p-ClC_6H_4-	-CH_3	20	10.43 ± 0.08	12.23 ± 0.08
		30	10.10 ± 0.05	11.94 ± 0.05
		40	9.97 ± 0.05	11.87 ± 0.05
p-BrC_6H_4-	-CH_3	20	10.40 ± 0.08	12.20 ± 0.08
		30	10.08 ± 0.05	11.92 ± 0.05
		40	9.93 ± 0.04	11.83 ± 0.04
p-$CH_3C_6H_4$-	-CH_3	20	11.16 ± 0.04	12.96 ± 0.04
		30	10.78 ± 0.04	12.62 ± 0.04
		40	10.60 ± 0.02	12.50 ± 0.02
p-FC_6H_4-	-C_2H_5	20	10.91 ± 0.07	12.71 ± 0.07
		30	10.57 ± 0.07	12.46 ± 0.07
		40	10.36 ± 0.07	12.41 ± 0.07
CH_3-	-CH_3	30		12.70[14]
C_6H_5-	-CH_3	30		12.85[15]
C_6H_5-	-C_6H_5	30		13.75[16]

The values of log q_1 and log q_2, stoichiometric formation constants, for Mn(II), Mg(II), Ca(II), Sr(II) and Ba(II) p-substituted β-diketone systems were computed from the data, $\bar{n}$ and (L^-) by using the *Irving-Rossotti* equation[14].

$$\bar{n} = \left\{[L_0] - [L^-]\left(\frac{[H^+]}{q_D} + 1\right)\right\} \frac{1}{M_0} \qquad (7)$$

$$\frac{\bar{n}}{(\bar{n}-1)\,(L^-)} = \frac{(2-\bar{n})\,[L^-]}{(\bar{n}-1)}\,q_1 q_2 - q_1 \qquad (8)$$

where $\bar{n}$, (L_0) and (M_0) refer to the formation number, total ligand and metal concentrations.

The thermodynamic stepwise formation constants were then evaluated by adding respectively, $4 \log (1/\gamma_\pm)$ and $2 \log (1/\gamma_\pm)$ to q_1 and q_2:

$$\log k_1 = \log q_1 + 4 \log (1/\gamma_\pm) \qquad (9)$$

$$\log k_2 = \log q_2 + 2 \log (1/\gamma_\pm) \qquad (10)$$

The values of $\log k_1$, $\log k_2$ and $\log \beta_2$ are listed in Table 3. The most probable error in each set has been worked out by using least-squares method.

Table 3. *Thermodynamic stepwise and overall formation constants, and the change in free enthalpy* ($-\Delta G$), *of* Mn(II), Mg(II), Ca(II), Sr(II) *and* Ba(II) *with 1,3-diones; solvent dioxane-water mixture (75% v/v);* $\mu = 0.1\,M$ ($NaClO_4$)

Metal ion	Temp., °C	$\log k_1$	$\log k_2$	$\log \beta_2$	$-\Delta G$ (kcal/mol)
p-Fluoro-benzoylacetone					
Mn(II)	20	9.68 ± 0.01	7.06 ± 0.03	16.74 ± 0.02	22.46
	30	9.75 ± 0.01	6.95 ± 0.03	16.70 ± 0.02	23.17
	40	9.67 ± 0.01	6.89 ± 0.03	16.56 ± 0.02	23.73
Mg(II)	20	9.12 ± 0.03	6.28 ± 0.05	15.40 ± 0.02	20.66
	30	9.17 ± 0.01	6.20 ± 0.04	15.37 ± 0.03	21.32
	40	9.17 ± 0.02	6.14 ± 0.05	15.31 ± 0.03	21.94
Ca(II)	20	8.20 ± 0.05	5.21 ± 0.08	13.41 ± 0.03	17.99
	30	8.15 ± 0.03	4.95 ± 0.05	13.10 ± 0.02	18.18
	40	8.20 ± 0.03	4.88 ± 0.06	13.08 ± 0.03	18.75
Sr(II)	20	7.36 ± 0.04	4.93 ± 0.08	12.29 ± 0.04	16.49
	30	7.26 ± 0.06	4.45 ± 0.09	11.71 ± 0.03	16.25
	40	7.29 ± 0.02	4.27 ± 0.04	11.56 ± 0.02	16.57
Ba(II)	20	6.99 ± 0.06	4.58 ± 0.10	11.57 ± 0.04	15.52
	30	6.97 ± 0.05	3.97 ± 0.11	10.94 ± 0.06	15.18
	40	6.95 ± 0.02	3.17 ± 0.12	10.12 ± 0.12	14.50
p-Chloro-benzoylacetone					
Mn(II)	20	9.89 ± 0.03	6.84 ± 0.06	16.73 ± 0.03	22.45
	30	9.73 ± 0.01	6.73 ± 0.04	16.46 ± 0.03	22.84
	40	9.76 ± 0.01	6.65 ± 0.02	16.41 ± 0.01	23.52
Mg(II)	20	9.12 ± 0.02	6.10 ± 0.04	15.22 ± 0.02	20.42
	30	8.95 ± 0.02	5.89 ± 0.06	14.84 ± 0.04	20.59
	40	9.08 ± 0.01	5.86 ± 0.03	14.94 ± 0.02	21.41
Ca(II)	20	7.95 ± 0.04	5.10 ± 0.09	13.05 ± 0.05	17.51
	30	7.75 ± 0.04	4.82 ± 0.08	12.57 ± 0.04	17.44
	40	7.89 ± 0.03	4.75 ± 0.06	12.64 ± 0.03	18.12
Sr(II)	20	6.99 ± 0.10	5.08 ± 0.15	12.07 ± 0.05	16.19
	30	6.95 ± 0.04	4.67 ± 0.07	11.62 ± 0.03	16.12
	40	7.02 ± 0.04	4.52 ± 0.07	11.54 ± 0.03	16.54
Ba(II)	20	6.70 ± 0.10	4.83 ± 0.17	11.53 ± 0.07	15.47
	30	6.65 ± 0.04	4.31 ± 0.09	10.96 ± 0.05	15.21
	40	6.67 ± 0.05	4.01 ± 0.12	10.68 ± 0.07	15.31
p-Bromo-benzoylacetone					
Mn(II)	20	9.76 ± 0.02	6.89 ± 0.03	16.65 ± 0.01	22.34
	30	9.70 ± 0.02	6.74 ± 0.06	16.44 ± 0.04	22.81
	40	9.72 ± 0.01	6.66 ± 0.02	16.38 ± 0.01	23.48
Mg(II)	20	9.13 ± 0.03	6.12 ± 0.05	15.25 ± 0.02	20.46
	30	8.96 ± 0.08	5.93 ± 0.10	14.89 ± 0.02	20.66
	40	9.05 ± 0.01	5.88 ± 0.04	14.93 ± 0.03	21.40

Table 3 (continued)

Metal ion	Temp., °C	$\log k_1$	$\log k_2$	$\log \beta_2$	$-\Delta G$ (kcal/mol)
Ca(II)	20	7.93 ± 0.04	5.16 ± 0.09	13.09 ± 0.05	17.56
	30	7.84 ± 0.05	4.89 ± 0.09	12.73 ± 0.04	17.66
	40	7.88 ± 0.04	4.72 ± 0.06	12.60 ± 0.02	18.06
Sr(II)	20	6.79 ± 0.15	5.21 ± 0.21	12.00 ± 0.06	16.10
	30	6.92 ± 0.05	4.75 ± 0.08	11.67 ± 0.03	16.19
	40	7.01 ± 0.04	4.56 ± 0.06	11.57 ± 0.02	16.58
Ba(II)	20	6.59 ± 0.09	5.02 ± 0.14	11.61 ± 0.05	15.58
	30	6.61 ± 0.06	4.58 ± 0.10	11.91 ± 0.04	15.53
	40	6.53 ± 0.07	4.38 ± 0.12	10.91 ± 0.05	15.64
p-Methyl-benzoylacetone					
Mn(II)	20	10.24 ± 0.01	7.23 ± 0.03	17.47 ± 0.02	23.44
	30	10.04 ± 0.01	7.00 ± 0.02	17.04 ± 0.01	23.64
	40	10.05 ± 0.01	6.89 ± 0.04	16.94 ± 0.03	24.28
Mg(II)	20	9.50 ± 0.01	6.41 ± 0.03	15.91 ± 0.02	21.35
	30	9.29 ± 0.02	6.14 ± 0.04	15.43 ± 0.02	21.41
	40	9.39 ± 0.01	6.08 ± 0.04	15.45 ± 0.03	22.14
Ca(II)	20	8.32 ± 0.03	5.31 ± 0.07	13.63 ± 0.04	18.29
	30	8.13 ± 0.03	5.02 ± 0.06	13.15 ± 0.03	18.24
	40	8.20 ± 0.03	4.93 ± 0.06	13.13 ± 0.03	18.82
Sr(II)	20	7.43 ± 0.08	5.05 ± 0.13	12.48 ± 0.05	16.74
	30	7.31 ± 0.05	4.70 ± 0.08	12.01 ± 0.03	16.66
	40	7.36 ± 0.04	4.53 ± 0.07	11.89 ± 0.03	17.04
Ba(II)	20	7.06 ± 0.11	4.97 ± 0.16	12.03 ± 0.05	16.14
	30	6.86 ± 0.03	4.53 ± 0.05	11.39 ± 0.02	15.80
	40	6.95 ± 0.05	4.13 ± 0.10	11.08 ± 0.05	15.88
1-(4-Fluorophenyl)-1,3-pentanedione					
Mn(II)	20	9.96 ± 0.01	7.37 ± 0.02	17.33 ± 0.01	23.25
	30	9.89 ± 0.01	7.16 ± 0.03	17.05 ± 0.02	23.65
	40	9.89 ± 0.02	7.07 ± 0.05	16.96 ± 0.03	24.31
Mg(II)	20	9.28 ± 0.01	6.53 ± 0.03	15.81 ± 0.02	21.21
	30	9.21 ± 0.01	6.32 ± 0.02	15.53 ± 0.01	21.55
	40	9.28 ± 0.01	6.27 ± 0.02	15.55 ± 0.01	22.29
Ca(II)	20	8.49 ± 0.07	5.31 ± 0.14	13.80 ± 0.07	18.51
	30	8.17 ± 0.04	5.14 ± 0.07	13.31 ± 0.03	18.47
	40	8.24 ± 0.03	5.05 ± 0.06	13.29 ± 0.03	19.05
Sr(II)	20	7.54 ± 0.07	5.00 ± 0.11	12.54 ± 0.04	16.82
	30	7.36 ± 0.04	4.73 ± 0.07	12.09 ± 0.03	16.77
	40	7.44 ± 0.04	4.47 ± 0.05	11.91 ± 0.01	17.07
Ba(II)	20	7.22 ± 0.09	4.78 ± 0.14	12.00 ± 0.05	16.10
	30	7.00 ± 0.06	4.39 ± 0.09	11.39 ± 0.03	15.80
	40	7.14 ± 0.05	3.72 ± 0.14	10.86 ± 0.09	15.56

Results and Discussion

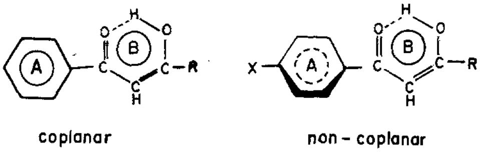
Several views concerning the orientation of the phenyl ring or rings in benzoylacetone, *p*-substituted benzoylacetone and dibenzoylmethane have been expressed in the literature. *Gould*[15] and *Brown*[16] have reported independently both the electron donor and electron acceptor properties of the phenyl ring in organic compounds. The electron donor effect becomes evident when the phenyl ring is co-planar with the enolic ring. *Brudett* and *Rogers*[17] have shown on the basis of nmr studies that phenyl ring and enolic ring are non-coplanar with respect to each other in *p*-substituted benzoylacetones and the net effect of phenyl ring is, therefore, electron withdrawl through induction alone. On the other hand *Lintvedt* and *Holtzclaw*[18] have suggested from nmr studies the donating influence of the phenyl ring in benzoylacetone. Likewise *Rao* and *Mathur*[19], from the thermochemical measurements on the heat of ionisation of substituted β-diketones, have concluded the electron donating effect of the phenyl ring.

The marked difference in pk_D value of dibenzoylmethane and benzoylacetone can be explained on the basis of the fact that the presence of two phenyl rings co-planar with the enolic ring accumulates electron density on the carbonyl and hydroxyl oxygens. The former in turn holds the proton of the latter through strong intramolecular hydrogen bonding. Consequently its ionisation is checked in comparison with benzoylacetone. In the latter there is only one co-planar phenyl ring which raises the electron density over only one carbonyl oxygen and not on the hydroxyl oxygen. Therefore, the proton of the —OH group is less firmly bound and it ionises more readily than dibenzoylmethane.

Further the substitution of a F-, Cl-, or Br-group at the *para* position of the phenyl ring (*p*-halobenzoylacetone) results in the marked decrease in pk_D as compared to benzoylacetone.

The decrease in pk_D values cannot be justifiably explained on the basis of inductive effect of the *p*-substituent. Because of the remoteness of the *p*-substituent from the hydroxyl group, inductive effect could fade away rapidly without producing any change in the electronic environment around the enolic group. The only major contributing factor controlling pk_D's of the *p*-substituted ligand is the non-coplanar orientation of the phenyl ring with the enolic ring. In the absence of conjugation *p*-substituted phenyl ring gets lop-sided with respect to the enolic ring as the barrier to internal rotation is much less. In this way the non-coplanar *p*-substituted phenyl ring acts as an electron acceptor. However, the order of pk_D in the *p*-halo series can be explained on the basis of mesomeric effect. This is larger in *p*-fluoro- than in *p*-chloro- and *p*-bromo-derivatives.

Hence the sequence of pK_D follows the order: (p-F) > (p-Cl) $\simeq$ (p-Br)



To prove it further that it is the non-coplanarity of the phenyl ring which is the chief governing factor as far as pk_D of the substituted ligands is concerned, we have measured the dissociation constant of p-methyl benzoylacetone. Methyl group has an electron donating effect (+ I) hence an increase in pk_D would be expected if the inductive effect and coplanarity of the phenyl ring are assumed. But the situation is entirely different, i.e., the effect of methyl group is completely masked by the non-coplanar phenyl ring, causing thereby the lowering of pk_D by 0.23 log units in comparison to benzoylacetone.

Further the substitution, at the side chain, of ethyl in place of methyl in p-fluorobenzoylacetone raises the pk_D from 12.09 to 12.41. This can be explained on the basis of inductive effect of the substituent.

The thermodynamic dissociation constant of the titled ligands measured at 20, 30 and 40 °C is a hyperbolic function of temperatures (Fig. 1). This has been explained by considering both the temperature and solvent effects.

Normally the ionisation of an electrolyte increases by 2% per degree rise in temperature, provided the dielectric constant of the medium remains constant throughout the temperature range studied.

But this is partially offset by the decrease in the dielectric constant of dioxane-water mixture (75% v/v) with the rise in temperature (14.10, 13.30 and 12.50 at 20, 30 and 40 °C, respectively); these values have been obtained by interpolation of the data given by *Harned* and *Owen*[20]. Decrease in the dielectric constant facilitates recombination reaction occuring at high temperature leading to the small concentration of the ionic species at equilibrium. The effect being a non-linear increase in the ionisation with temperature. From the thermodynamic data for the titled metal-ligand equilibria the following order has been found:

$$\mathrm{Mn(II)} > \mathrm{Mg(II)} > \mathrm{Ca(II)} > \mathrm{Sr(II)} > \mathrm{Ba(II)}$$

The order is consistent with those of *Irving-William*[21,22] and *Van Uitert*[23]. The variation of $\log k_1$, $\log k_2$ and hence $\log \beta_2$ with temperature can be explained as above.

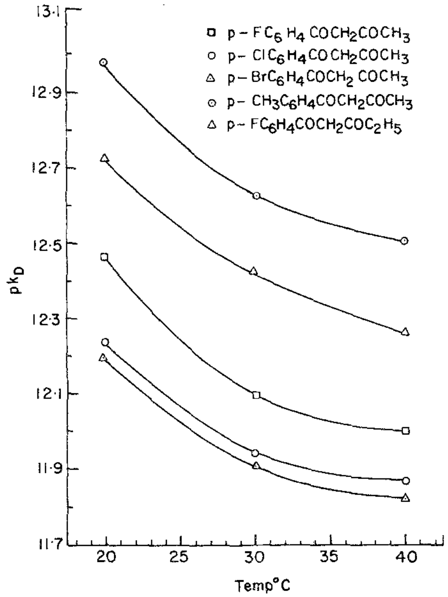


Fig. 1. Thermodynamic dissociation constants of *p*-substituted β-diketones

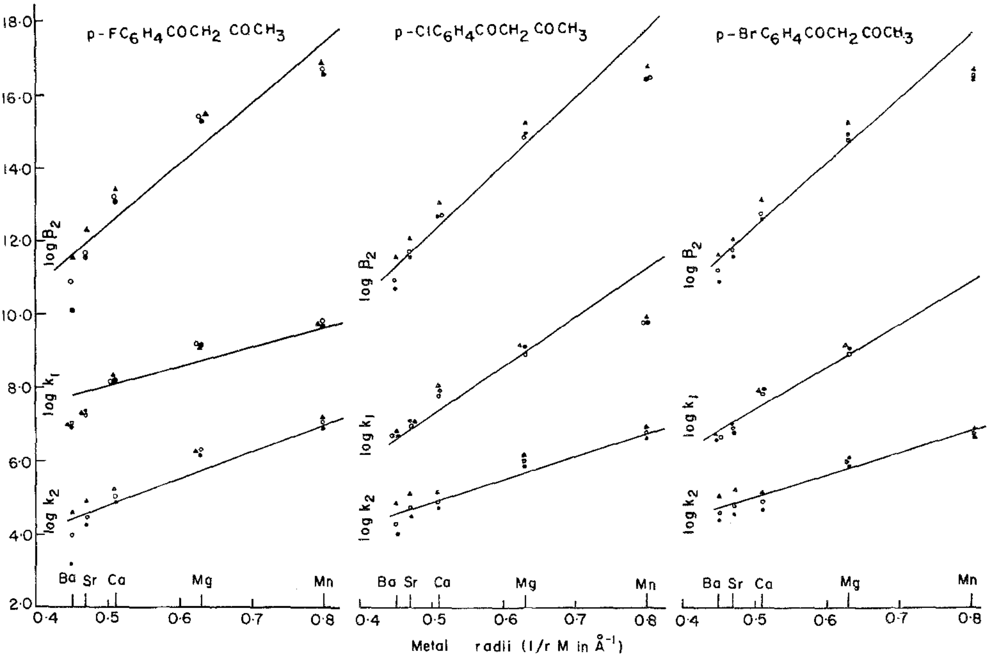


Fig. 2. Correlation between thermodynamic stepwise and overall formation constants and inverse of metal radii (1/*r* in Å^{-1}) at (△) 20°, (○) 30° and (●) 40 °C

Conjugated bases of strong acids are known to form weak complexes with metal ions and vice-versa. For basic ligands the greater the proton affinity constant of a base more stable its complexes[24–29].

In the present work the pk_D of *p*-fluoro-, *p*-chloro-, *p*-bromo-, *p*-methyl-benzoylacetones and 1-(4-fluorophenyl)-1,3-pentanedione have been plotted against thermodynamic stepwise and overall formations constants ($\log k_1$, $\log k_2$, and $\log \beta_2$) of the metal-ligand complexes formed with Mn(II), Mg(II), Ca(II), Sr(II), and Ba(II). In each case straight lines of different slopes have been obtained.

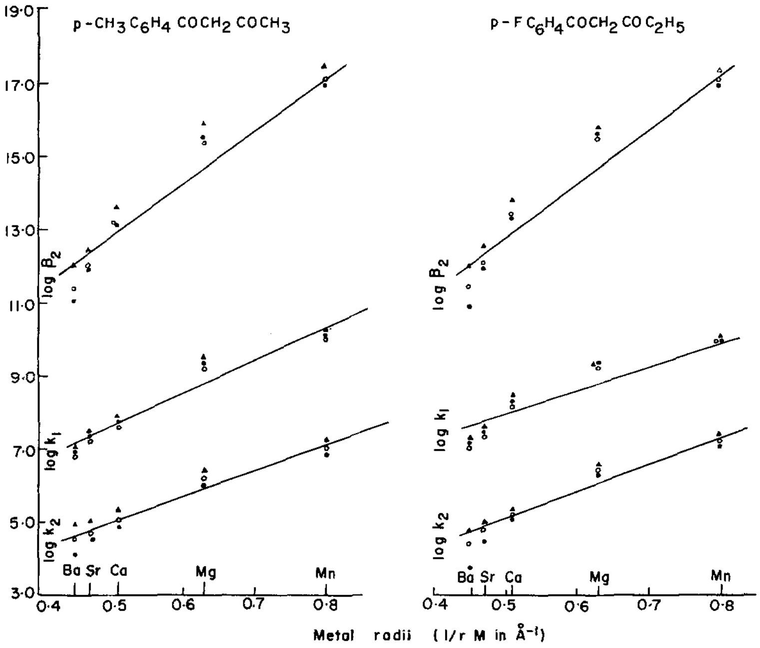


Fig. 3. Correlation between thermodynamic stepwise and overall formation constants and inverse of metal radii ($1/r$ in Å^{-1}) at (Δ) 20°, (○) 30° and (●) 40 °C

Further wide ranges of complexation capabilities of oxygen and nitrogen donor ligands, hard bases in *Pearson*'s terminology, have been correlated with the metal-ion radius, and linear plots have been obtained. For the fixed charge on the metal-ion, the smaller the metal-ion radius the stronger the complex formed with hard bases, while the stability order decreases in descending the group[30–34].

However, in lanthanides the reverse sequence has been obtained[35]. If the metal-ions are of the same size then the stability constants increases with the charge on the metal cations[36]. Other correlations, for instance, $\log k_1$ versus standard entropies of the metal cations or $\log k_1$ versus the reciprocal of the radius of the hydrated metal cations[37, 38] instead of crystal radii, have been made.

In the present work the logarithms of successive stability ($\log k_1$, $\log k_2$) and overall formation constants ($\log \beta_2$) evaluated at 20, 30 and 40 °C, respectively, have been plotted as ordinate and the reciprocal of the metal (crystal) radii ($1/r_M$ in $Å^{-1}$) as abcissa, to give straight lines of different slopes. (In Figs. 2 and 3 overall formation constants, $\log \beta_2$, have been plotted against the inverse of metal crystal radii.)

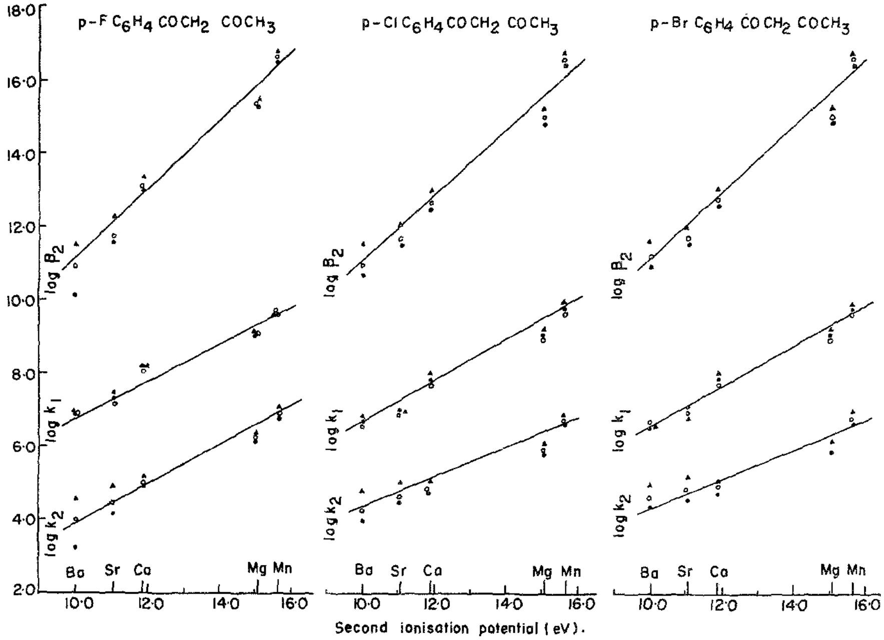


Fig. 4. Correlation between thermodynamic stepwise and overall formation constants and second ionisation potential of metal-ions at (Δ) 20°, (○) 30° and (●) 40 °C

Finally several attempts have been made to correlate formation constants for a series of complexes with a common ligand with the second ionisation potential[39], and linear correlations, for bivalent metal-ions have been given by several workers[21, 22, 30, 33, 40–43].

In the present work linear correlations have been found between the thermodynamic stepwise ($\log k_1$, $\log k_2$) as well as formation constant ($\log \beta_2$), evaluated at 20, 30 and 40 °C, and the second ionisation potential of Mn(II), Mg(II), Ca(II), Sr(II), and Ba(II) (Fig. 4).

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