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Substituted β-diketones and Their Complexes: Substituent Effects on Ligand Stabilities and Anion Effects on Complex Stability Constants

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Acid dissociation constants are reported for variously 1-, 3-, and 5- substituted pentane-2,4-diones in aqueous solution, and in 50% v/v dioxan. The instability of 3-substituted compounds in solution is described. The 1- and 5- substituted compounds are stable in solution; stability constants for their cobalt-(II) complexes in 50% v/v dioxan are reported. The dependence of apparent stability constant on the nature of the anion present is described; values obtained in perchlorate or trifluoromethylsulphonate media are presumed to be true stability constants.

Introduction

The properties of metal chelate complexes formed by β-diketones, $R^1COCHR^2COR^3$, have been much investigated, though attention has been focussed on the parent ligand, pentane-2,4-dione ($R^1 = R^3 = CH_3$, R_2 = H). There is considerable information available on ligand basicities (pK_a) and stability constants ($\log K_n$, $\log\beta_n$) of metal complexes [1]. These are often determined in aqueous dioxan rather than water, due to solubility limitations in the latter medium. In the present paper we deal with two complications in this area of chemistry – the instability of some derivatives of pentane-2,4-dione and the possibility of ternary complex formation when working in aqueous dioxan.

Pentane-2,4-dione is stable for very long periods in aqueous and in mixed aqueous solutions over a wide range of pH. Some substituted compounds are much less stable, indeed some are too unstable to permit the determination of stability constants for their metal complexes by conventional techniques. We, and others, have found that alkyl and aryl (but not perfluoroalkyl [2]) substituents at the 1- or 5- carbon atoms of pentane-2,4-dione have little or not effect on ligand stability. However, the introduction of a variety of groups into the 3-position has a marked effect, generally making the resulting β-diketones considerably less stable than pentane-2,4-dione itself. We describe qualitatively the stability of a range of potential ligands of this type below.

Although the use of aqueous dioxan media avoids solubility difficulties attendant on determining stability constants of β-diketones in water, it can lead to other complications. In the frequently-used 50% and 75% dioxan mixtures the likelihood of significant ion-pairing or complex formation between a metal ion and its accompanying gegenion (*e.g.* sulphate or chloride), or of ternary complex formation between metal β-diketonate and the inorganic anion present, is real. This has been recognised for some time [3], at least for chlorides and nitrates in 75% dioxan. We report anion effect for several β-diketonate complexes of cobalt(II) in 50% dioxan.

Experimental

Preparations

The methods used to prepare the ligands are listed in Table I which also includes abbreviations used henceforth in the text. Ligands were characterized by their boiling points (Table I) and gas–liquid chromatography [4]. Bis- and tris-ligand complexes were prepared by standard procedures [5–8] and characterized by C, H, N (Analytical Services Department, National Physical Laboratory) and metal analysis.

Ligand Decomposition

Half lives for decomposition of substituted β-diketones in acid, neutral and alkaline solution were estimated spectrophotometrically by use of the Unicam SP.800 and SP.500 containing thermostatted cell holder. These were also used for investigation of the decomposition kinetics of 3-methylpentane-2,4-dione.

TABLE I. Ligands $R^1COCHR^2COR^3$ Used in This Investigation, with Abbreviations Used, Methods of Preparation, and Boiling Points.

	R_1	R_2	R_3	Abbreviation	Ref. to Preparation	B. pt/°C (lit value/°C)	
Parent	Me	H	Me	acacH	–	140–141.5(139)	*a*
1,5-Series							
	Et	H	Me	pracH	*b*	158–160 (155–158)	*a*
	Et	H	Et	prprH	*c*	77–80/28mm(78–80/30mm)	*c*
	Ph	H	Me	bzacH	–	m.pt.59.5–60(60)	*d*
	Ph	H	Ph	bzbzH	–	m.pt.80–80.5(81)	*d*
3-Series							
	Me	Me	Me	3-MeacacH	*e*	169–171 (170–172)	*e*
	Mc	Et	Me	3-EtacacH	*f*	74–75/18mm(80–81/20mm)	*g*
	Me	*n*Pr	Me	3-*n*PracacH	*f*	83–86/15mm(75–77/12mm)	*h*
	Me	*i*Pr	Me	3-*i*PracacH	*f*	183–187 (183–185)	*g*
	Me	$-CH_2CH{=}CH_2$	Me	3-AlacacH	*j*	72–73/10mm(82/16mm)	*j*
	Me	$=CHCH_2CH_2CH_3$	Me	3-ButacacH	*k*	75–78/4mm(83–84/8mm)	*k*
	Me	–COOEt	Me	3-EtOacacH	*l*	93–94/15mm(95–98/12mm)	*h*
	Me	$-COCH_3$	Me	3-AcacacH	*m*	94–95/15mm(89–89.5/10mm)	*m*
	Me	Cl	Me	3-ClacacH	*h*	151–154 (154–156)	*h*
	Me	Br	Me	3-BracacH	*n*	Prepared as the copper chelate	
	Me	NO_2	Me	3-NO_2acacH	*p*		
1,3,5-Series							
	Et	Me	Me	3-MepracH	*c*	186–188(181–184)	*c*
	Et	Me	Et	4-MeprprH	*q*	85–86/15mm(90.5–92.5/16mm)	*q*

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Results

Ligand pK_a Values

Acid dissociation constants, determined by potentiometric and spectrophotometric techniques in water and in 50% v/v dioxan are reported in Table II. There is good agreement between pK_a values obtained by the two methods.

Ligand Stabilities

The stabilities of several 3-substituted pentane-2,4-diones in acid, neutral and alkaline solution are qualitatively indicated in Table II A*, which gives half-lives for decomposition.

The decomposition of 3-methylpentane-2,4-dione was investigated. GLC retention times showed the products of alkaline decomposition to be butan-2-one and acetate. Quantitative estimation of the acetate (acetic acid) potentiometrically showed that 1 mol of 3-methylpentane-2,4-dione decomposed to give 1.08 mol of acetic acid and 0.99 mol of butan-2-one (determined spectrophotometrically at 267nm):

$$CH_3COCH(CH_3)COCH_3 + OH^- \rightarrow CH_3COO^- + CH_3CH_2COCH_3$$

There is no discernible hydrolysis in acidic or neutral solution, but as pH rises above 10 decomposition occurs at measurable rates. The hydrolysis is first order in diketone over the range studied; the dependence of the rate constant is shown in the Figure. This pattern is very similar to that described for alkaline hydrolysis (at higher temperatures) of pentane-2,4-dione in the presence of barium hydroxide [9].

Stability Constants

The variation of measured stability constants with the nature of the metal, the β-diketone and of the anion present is shown in Tables III and IV.

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*Copies of Table II A available from the authors.

TABLE II. Potentiometric and Spectrophotometric pK_a Values Determined in Water and in Aqueous Dioxan (50% by Volume) at 25 °C for β-diketones $R^1COCHR^2COR^3$ (R^1, R^2, R^3 and respective abbreviations given in Table I).

Compound	pK_a at 25 °C		
	Water Spec[a]	Pot[b]	50% Dioxan Pot[b]
acacH	8.90	8.96	10.28
pracH	9.26	9.30	10.79
prprH	9.66	9.78	11.21
bzacH	–	–	10.43
bzbzH	–	–	11.26
3MeacacH	10.66	10.77	11.94
3MepracH	–	11.15	12.24
3MeprprH	–	12.43	13.37
3AcacacH	6.05	5.95	–
3EtacacH	–	11.12	–
3Pr^{n}acacH	–	11.20	–
3Pr^{i}acacH	–	11.30	–
3EtOacacH	–	6.54	–
3ClacacH	–	6.25	–
3AllylacacH	–	10.43	–

[a] Spec = by UV spectrophotometry. [b] Pot = by potentiometric method.

Discussion

Ligand pK$_a$ Values

Substitution at the 3-position of pentane-2,4-dione has a considerably greater effect than substitution at the 1- or 5- position (*cf.* 3-MeacacH and pracH respectively with acacH, Table II). Acid dissociation constants for 3-substituted pentane-2, 4-diones in water follow the normal trends expected from the variation of inductive and mesomeric effects of the substituents. A plot of pK_a values against Taft σ^* values for aliphatic systems [10] is linear, with the exception of the point for 3EtOacacH.

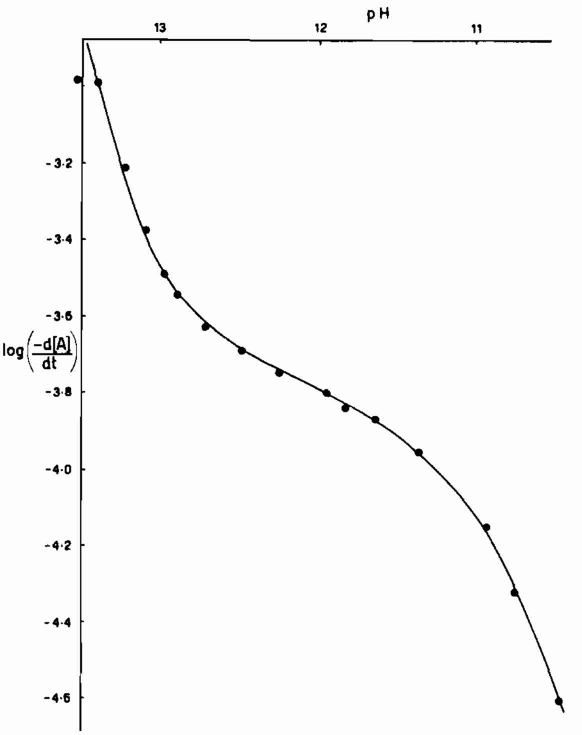

Figure. Variation of initial decomposition rate of 3-methylpentane-2,4-dione (=A) with pH.

Ligand Stabilities

The 3-substituted pentane-2,4-diones are stable enough for pK_a values to be determined satisfactorily, but not long enough for equilibration and accurate measurement of metal complex formation. The relative stabilities of the ligands are indicated by their half-lives listed in Table II A, unfortunately there seems to be no simple pattern. The 1- and 5-alkyl or aryl substituted compounds are much more stable; accurate pK_a and metal complex stability constants can be obtained. However, perfluoroalkyl groups in these positions, as in 1,1,1-trifluoro- and 1,1,1,5,5,5-hexafluoropentane-2,4-dione, lead to lowered stabili-

TABLE III. Stability Constants[a] of Metal(II) Chelates of β-Diketones Measured in Aqueous Dioxan (50% v/v) at 25 °C.

Metal	acacH logK_1	logK_2	pracH logK_1	logK_2	bzacH logK_1	logK_2	bzbzH logK_1	logK_2
Magnesium(II)	4.31_5	3.39_5	4.38_5	3.55	4.45_5	3.83	Too insoluble	
Manganese(II)	4.82_5	4.06_5	4.85	4.08	4.96	4.30_5	Too insoluble	
Cobalt(II)	5.77_5	4.78	5.98	4.99_5	6.06	5.29	6.96_5	–
Nickel(II)	6.39_5	5.48	6.53_5	5.64_5	6.61_5	5.89	Too insoluble	
Copper(II)	8.36_5	8.26	8.69	8.61	8.55_5	8.39	Too insoluble	
Zinc(II)	5.70	5.14	5.91	5.26	5.84	–	Too insoluble	

[a] logK values are means of values obtained for 5:1 and 3:1 ligand: metal ratios. Units of K_1 and K_2 are mol^{-1} dm^3.

TABLE IV. Variation of Stability Constant[a] With Anion for the Cobalt(II) Chelates of β-Diketones, Measured in Aqueous Dioxan (50% v/v) at 25 °C.

Anion	acacH $\log K_1$	$\log K_2$	pracH $\log K_1$	$\log K_2$	prprH $\log K_1$	$\log K_2$	bzacH $\log K_1$	$\log K_2$	bzbzH $\log K_1$	$\log K_2$
Perchlorate	7.09_5	5.32_5	7.23	5.51_5	7.33_5	6.07_5	7.30_5	5.79_5	8.13	7.04
Chloride	7.01	5.32	7.19	5.57	7.31	5.83_5	7.18	5.74	7.99	6.94_5
Nitrate	6.94	5.25	7.07_5	5.44	7.25_5	5.79_5	7.20	5.75	8.00	–
Sulphate	5.77_5	4.78	5.98	4.99_5	6.28	5.44	6.06_5	5.29	6.96_5	–

[a] logK values are means of values obtained for 5:1 and 3:1 ligand: metal ratios. Units of K_1 and K_2 are $\mathrm{mol^{-1}\ dm^3}$.

TABLE V. A Comparison between Anion Effects on Stability Constants ($\log K_1$) for Metal(II) Complexes of β-Diketones in Aqueous Dioxan Comprising 50% and 75% by Volume Dioxan.

Complex % Dioxan		$\mathrm{Co^{II}}$/acac 50	75	$\mathrm{Co^{II}}$/bzbz 50	75	$\mathrm{Cd^{II}}$/acac 75
Temp		25 °C	30 °C	25 °C	30 °C	30 °C
	$\mathrm{ClO_4^-}$	7.10	9.68	8.13	10.74	–
Medium	$\mathrm{NO_3^-}$	6.94	9.22	8.00	10.35	7.64
	$\mathrm{Cl^-}$	7.01	8.88	7.99	9.97	6.42

ty [2]. However, for the latter compounds stability constants have been reported [1] and the solvent extraction characteristics of the trifluoro-derivative investigated [11].

Anion Effects

These are shown in Table IV, for a series of anions varying from perchlorate and trifluoromethylsulphonate to sulphate. In 50% v/v dioxan, apparent stability constants are identical within experimental uncertainty for $\mathrm{ClO_4^-}$ and $\mathrm{CF_3SO_3^-}$ media, and change very little on changing to chloride media. However, $\log K_1$ values are 0.10 to 0.15 lower in nitrate media and up to 1.3 lower in sulphate media. The last cited difference in $\log K_1$ corresponds to a difference of 20 times in the apparent K_1 value. All differences are smaller for $\log K_2$ values. Anion effects in 50% v/v and 75% v/v dioxan are compared in Table V; such effects are considerably larger in the latter solvent mixture.

The results contained in Tables IV and V can be explained in terms of ion-pairing or complex formation between the metal ion and its accompanying gegenion, or of ternary complex formation:

e.g.

$$\mathrm{M^{2+} + X^- \rightleftharpoons MX^+}$$

$$\mathrm{M^{2+} + dik^- \rightleftharpoons M(dik)^+}$$

$$\mathrm{MX^+ + dik^- \rightleftharpoons M(dik)X}$$

$$\mathrm{M(dik)^+ + X^- \rightleftharpoons M(dik)X}$$

($\mathrm{dik^-}$ = β-diketonate anion)

Such interactions involving $\mathrm{X^-}$ are obviously on electrostatic grounds more important in the formation of the mono-diketonato complex:

$$\mathrm{M^{2+} + dik^- \rightleftharpoons M(dik)^+}$$

than in the formation of the bis-diketonato complex:

$$\mathrm{M(dik)^+ + dik^-n \rightleftharpoons M(dik)_2}$$

The greater magnitude of these effects in 75% dioxan than in 50% dioxan is as expected from the dielectric constants of these solvent mixtures. The ordering of anions ($\mathrm{CF_3SO_3^-} \sim \mathrm{ClO_4^-} > \mathrm{Cl^-} > \mathrm{NO_3^-} \gg \mathrm{SO_4^{2-}}$) is also as expected; the close similarity of values for $\mathrm{CF_3SO_3^-}$ and $\mathrm{ClO_4^-}$ media is consistent with the expected and hoped-for insignificance of added anion effects with these anions present. Unfortunately it is not possible to allow for M + X complex formation and thence recalculate stability constants for $\mathrm{M(dik)^+}$ and $\mathrm{M(dik)_2}$ since the nearest appropriate stability data were determined in aqueous media [1]. We are able to propose that values determined in the presence of these anions ($\mathrm{CF_3SO_3^-}$ and $\mathrm{ClO_4^-}$) are, at least in 50% dioxan, true stability constants for binary metal(II)–diketonate complex formation with some confidence.

Anion effects might be expected to be greater for 'soft' cations, such as $\mathrm{Cd^{2+}}$ or $\mathrm{Pb^{2+}}$, than for 'harder' cations, such as first row transition metal(II) cations. This is confirmed by the results reported earlier [3] for 75% dioxan (see Table V).

It has been stated recently [12] that side reactions, such as exist here, will hardly affect the statistical contribution to K_2/K_1. As our ratios of K_2/K_1 do vary with anion, it is apparent that other factors are important here.

Enthalpies and Entropies of Complex Formation

These have been estimated for the cobalt(II) complexes of acacH, pracH, bzacH and bzbzH (and prprH [4]) in 50% dioxan from the temperature variation of stability constants over the range 278 to 318 K. For monoligand complexes of the aliphatic ligands acac, prac and prpr, $\Delta H_1^{\ominus}$ values lie between 3 and 6 kJ mol^{-1} (standard errors 1 to 2 kJ mol^{-1}). For the other ligands, $\Delta H_1^{\ominus}$ values are more meaningful at −7 (±0.5) kJ mol^{-1} for bzac and −9 (±0.3) kJ mol^{-1} for bzbz. $\Delta S_1^{\ominus}$ values in the range +110 to +130 JK^{-1} mol^{-1}. The pattern is similar for the bis-ligand complexes with $\Delta H_2^{\ominus}$ values varying from about −5 kJ mol^{-1} for aliphatic ligands to −14 kJ mol^{-1} for bzbz, and $\Delta S_2^{\ominus}$ between +75 and +95 JK^{-1} mol^{-1}.

Spectra of the Complexes

The infrared and ultraviolet/visible spectra of the complexes are very similar to those of the parent β-diketone complexes. Substitution in the 1-, 3-, or 5-positions of pentane-2,4-dione makes only a small difference to infrared stretching frequencies. Thus, the metal–oxygen stretching frequency, 466 cm^{-1} in Co(acac)$_2$, is reduced to 455 cm^{-1} in Co(prac)$_2$ and to 450 cm^{-1} in Co(bzbz)$_2$; a similar range is observed for the analogous metal(III) series, Cr(dik)$_3$. Similarly, diffuse reflectance spectra of the series of Ni(dik)$_2$ complexes with dik = acac, prac, prpr, bzac or bzbz are very similar, with the λ_{max} value for the $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ transition lying between 625 and 650 nm. Such a range is too small for the establishment of a Dq series for these ligands, in view of the uncertainty in diffuse reflectance spectra maxima.

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