Complex Formation with Heptane-3,5-dione. Stabilities of Some Bivalent Metal Chelate Complexes in Aqueous Dioxan (50%)

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The acid dissociation constant of heptane-3,5-dione, together with the stability constants of its chelate complex with cobalt(II), have been determined in aqueous dioxan (50% v/v) over the temperature range 5—45 °C. From these results, values of the enthalpy and entropy of protonation and chelation have been calculated. Stability constants of heptane-3,5-dione chelate complexes of copper(II), nickel(II), manganese(II), and magnesium(II) have been measured at 25 °C.

THE formation of metal chelate complexes by the β-diketone pentane-2,4-dione (acetylacetone) has been extensively studied. Stability constants of many metal chelate complexes have been reported [1] and Izatt and his co-workers [2] have measured the enthalpy and entropy of protonation of the pentane-2,4-dionato-anion in water. Heptane-3,5-dione (dipropionylmethane) is the next symmetrical aliphatic β-diketone related to pentane-2,4-dione and little work on its metal chelate complexes has been reported. In this paper, the stability constants, obtained by potentiometric titration, of chelate complexes of heptane-3,5-dione with several bivalent metal ions are reported. From a study of the acid dissociation constant (pK_a) of the ligand and the stability constants of the Co^{II} chelate complexes ($\log K_1$ and $\log K_2$) over a range of temperature, values for the enthalpy (ΔH) and entropy (ΔS) of the protonation and chelation processes were obtained.

EXPERIMENTAL

Dioxan was purified as recommended by Weissberger and Proskauer.[3] Heptane-3,5-dione (dipropionylmethane) was prepared from ethyl propionate and methyl ethyl ketone as described by Swamer and Hauser.[4] The product was purified by preparation of its copper(II) chelate complex, washing with water, hydrolysis with dilute H_2SO_4, and extraction into ether. After removal of ether, the residue was distilled under reduced pressure and the fraction boiling between 77 and 79 °C at 28 mmHg collected (lit.,[4] b.p., 78—80 °C at 30 mmHg). G.l.c. of the product, on a column (2 m) of Apiezon L/Diatomite C (10%), showed it to

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[1] ' Stability Constants of Metal-ion Complexes,' *Chem. Soc. Special Publ.*, no. 17, 1964, pp. 444—446.

[2] R. M. Izatt, W. C. Fernelius, and B. P. Block, *J. Phys. Chem.*, 1955, **59**, 80, 235.

[3] A. Weissberger and E. S. Proskauer, ' Technique of Organic Chemistry,' Interscience, New York, 1955, vol. 7, p. 371.

[4] F. W. Swamer and C. R. Hauser, *J. Amer. Chem. Soc.*, 1950, **72**, 1352.

be pure. AnalaR hydrated sulphate complexes of copper(II), nickel(II), zinc(II), manganese(II), and magnesium(II), and cobalt(II) chloride hexahydrate were used in the stability-constant measurements, the metal-ion content of stock solutions being determined using EDTA titration.

Buffer solution was prepared from AnalaR sodium acetate trihydrate and acetic acid. Solutions (0·2M) of each were prepared, at the temperature of the experiment, in aqueous dioxan (50% v/v). At 25 °C, 50·0 cm^3 of this medium contained 25·0 cm^3 of dioxan and 26·3 cm^3 of boiled-out distilled water. The pH of a 1 : 1 mixture of the above solutions was calculated from the pK_a values of Conway [5] and activities compiled by Harned and Owen [6] (Table 1). pH-Measurements were made using an EIL Vibron pH-meter 39A which was standardized using the acetate buffer. EIL–GHS–33B glass and EIL–RJ–23 calomel electrodes containing dioxan (50%) saturated with KCl were used.

TABLE 1

Acid dissociation constants (pK_a) of heptane-3,5-dione and stability constants (log K_1 and log K_2) of Co^{II} chelate complexes in aqueous dioxan (50%) *

Temp./°C	5	15	25	35	45
pK_a	11·40	11·33	11·21	11·20	11·12
log K_1	7·34	7·29	7·31	7·24	7·24
log K_2	5·85	5·81	5·81	5·71	5·70
log (K_1/K_2)	1·49	1·48	1·50	1·53	1·54
pH of Standardization	6·289	6·289	6·292	6·291	6·287

* The standard deviation of pK_a, log K_1, and log K_2 values is 0·02 units or less.

Determination of the pK_a *of Heptane-*3,5-*dione in Dioxan.*—Stock and titration solutions were prepared and stored in a water-bath maintained within ±0·1 °C. Heptane-3,5-dione (0·01M, 50·0 cm^3) was titrated with 0·1M-KOH [5·00 cm^3; made in dioxan (50%)] added in ten equal portions, the pH being measured after each addition. During titration, mixing and exclusion of CO$_2$ was achieved by bubbling with nitrogen gas which had been passed through Fieser's solution [7] and then dioxan (50%) at the water-bath temperature; the latter solution removed alkaline spray and saturated the nitrogen with the reaction medium.

pK_a Values were calculated from each measurement using equation (1),[7] where HL and L$^-$ represent the neutral chelating agent and its anion. Activity corrections, a, were obtained from data of Harned and Owen.[6] Allowance was made for the temperature variation of the ionic product of water in dioxan (50%) [6] in calculating [OH$^-$]. The success of this method of calculating pK_a is dependent on accurate knowledge of the initial concentration of the ligand. Even small errors produced significant drift in the pK_a values during a titration. More consistent results were obtained from a graphical method which does not require the ligand concentration to be known accurately. This method is based on expression (2) for the acid dissociation constant which may be rewritten in the form (3), where [HL]$_T$ = [HL] + [L$^-$].

$$\mathrm{p}K_a = \mathrm{pH} + \log_{10}\frac{[\mathrm{HL}] + [\mathrm{OH}^-]}{[\mathrm{L}^-] - [\mathrm{OH}^-]} + a \qquad (1)$$

$$K_a = a_{\mathrm{H}^+}[\mathrm{L}^-]\gamma_{\mathrm{L}}/[\mathrm{HL}] \text{ (assuming } \gamma_{\mathrm{HL}} = 1) \qquad (2)$$

$$(K_a[\mathrm{HL}]_{\mathrm{T}}/[\mathrm{L}^-]) - K_a = a_{\mathrm{H}^+}\gamma_{\mathrm{L}} \qquad (3)$$

A plot of 1/[L$^-$] (due to the low degree of hydrolysis, [L$^-$] ≈ [K$^+$]) against $a_{\mathrm{H}^+}\gamma_{\mathrm{L}}$ gave a straight line of gradient K_a[HL]$_T$ and intercept $-K_a$. After obtaining [HL]$_T$, pK_a values at each stage in the titration were recalculated to give consistency. The final set of values included activity corrections and are thus thermodynamic constants.

*Stability Constants of Heptane-*3,5-*dione Chelate Complexes.*—The initial solution contained 0·01M-ligand (25·0 cm^3) and 0·005M-metal ion (10·0 cm^3), both in dioxan (50%), and dioxan (50%, 15·0 cm^3), giving a metal : ligand ratio of 1 : 5. 0·1M-KOH [1·00 cm^3 in dioxan (50%)] was then added in aliquot portions (0·04 cm^3), the pH being measured after each addition. The procedure was repeated using 0·01M-ligand (15·0 cm^3), 0·005M-metal solution (10·0 cm^3), and dioxan (50%, 25·0 cm^3) giving a metal : ligand ratio of 1 : 3.

The stability constants K_1 and K_2, which refer to the equilibria $\mathrm{M}^{2+} + \mathrm{L}^- \rightleftharpoons \mathrm{ML}^+$ and $\mathrm{ML}^+ + \mathrm{L}^- \rightleftharpoons \mathrm{ML}_2$ respectively, were obtained as follows. From the titrimetric results, values of [L$^-$] and $\bar{n}$ at each point in the titration were calculated [8] {$\bar{n}$, the degree of complex formation, is defined by ([ML$^+$] + 2[ML$_2$])/c_{M}, where c_{M} is total metal concentration}. By use of equation (4),[9] a plot of $\bar{n}/(\bar{n} - 1)[\mathrm{L}^-]$ against $(2 - \bar{n})[\mathrm{L}^-]/(\bar{n} - 1)$ gave K_1K_2 as gradient and $-K_1$ as intercept. Because of the uncertainty in obtaining reliable activity coefficients for M^{2+} and ML$^+$ in this solvent, no activity corrections were made and K_1 and K_2 are presented as concentration quotients, as distinct from thermodynamic equilibrium constants.

$$\frac{\bar{n}}{(\bar{n} - 1)[\mathrm{L}^-]} = \frac{(2 - \bar{n})[\mathrm{L}^-]}{(\bar{n} - 1)} \cdot K_1K_2 - K_1 \qquad (4)$$

Calculation of the Enthalpy and Entropy of Protonation and Chelation.—ΔH Values were obtained from gradients of plots of pK_a (or log K_1 or log K_2) against $1/T$. Acid dissociation constants used in the calculation of log K_1 and log K_2 were taken from the best straight line through the experimental points of the pK_a against $1/T$ plot. ΔS Values were obtained from gradients of $T \log K_{1,2}$ against T plots as described previously.[10]

Determination of the pK_a *of Heptane-*3,5-*dione in Water.*—*Spectrophotometrically.* The absorption spectra of heptane-3,5-dione and its anion in water were obtained from measurements, using a Unicam SP 800 spectrometer, on dilute solutions of the ligand in 0·05M-HCl and 0·05M-NaOH. The analytical wavelength chosen was 294 nm. A series of ligand solutions (5 × 10^{-5}M) was prepared in borate buffers in the pH range 9—10. For each solution, the pH (using an EIL-39A pH-meter standardized with 0·05M-borax buffer, pH 9·185 at 25 °C) and absorbance were measured (Unicam SP 500 spectrometer) in a thermostatted cell at 25 °C at 294 nm, using borate buffers of the appropriate pH values as optical blanks. If A is the absorbance measured for a given buffer solution and A_{I} and A_{M} represent the absorbances of equimolar solutions con-

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[5] B. E. Conway, 'Electrochemical Data,' Elsevier, New York, 1952, p. 196.

[6] H. S. Harned and B. B. Owen, 'The Physical Chemistry of Electrolytic Solutions,' Reinhold, New York, 1955, pp. 548, 581.

[7] A. Albert and E. P. Serjeant, 'Ionization Constants of Acids and Bases,' Methuen, London, 1962, p. 20.

[8] H. J. Harries, *J. Inorg. Nuclear Chem.*, 1963, **25**, 519.

[9] F. J. C. Rossotti and H. Rossotti, 'The Determination of Stability Constants,' McGraw-Hill, New York, 1961, p. 91.

[10] H. J. Harries and G. Wright, *J. Inorg. Nuclear Chem.*, 1969, **31**, 3149.

taining ligand anion (in NaOH) and neutral ligand (in HCl) respectively, the pK_a of heptane-3,5-dione was calculated from equation (5).[7]

$$\mathrm{p}K_a = \mathrm{pH} + \log_{10}\frac{A_{\mathrm{I}} - A}{A - A_{\mathrm{M}}} \qquad (5)$$

Potentiometrically. A solution (0·01M) of the ligand was neutralized stepwise by ten equal portions of 0·100M-KOH and the pH measured on each addition, the EIL 39A pH-meter being standardized with aqueous 0·05M-borax and checked using a phosphate buffer of pH 7·413 (both solutions at 25 °C).

RESULTS

Equilibrium constants over the temperature range 5—45 °C are shown in Table 1, and the ΔH and ΔS values derived from them are included in the Discussion section. Table 2 presents stability constants for all the metal ions studied at 25 °C. pK_a Values for the heptane-3,5-dione ligand in water and in aqueous dioxan determined in this laboratory are compared with results in the literature for the ligand and other β-diketones in Table 3.

TABLE 2

Stability constants (log K_1 and log K_2) of metal-ion chelate complexes of heptane-3,5-dione in aqueous dioxan (50%) at 25 °C *

	Cu^{II}	Ni^{II}	Co^{II}	Mn^{II}	Zn^{II}	Mg^{II}
log K_1 (*a*)	9·02	6·67	7·31	5·06	ppt.	4·52
(*b*)	9·20	6·69	7·33	5·01	ppt.	4·52
log K_2 (*a*)	8·85	5·86	5·81	4·46	ppt.	3·83
(*b*)	8·94	5·83	5·87	4·45	ppt.	3·77
log (K_1/K_2) (*a*)	0·17	0·81	1·50	0·60		0·69
(*b*)	0·26	0·86	1·46	0·56		0·75

* (*a*) and (*b*) Represent results for 5 : 1 and 3 : 1 ligand : metal ratios.

TABLE 3

Acid dissociation constants (pK_a) of β-diketones $RCOCH_2COR'$

			pK_a *					
			In water			In dioxan (50%)		In dioxan (75%)
Compd.	R	R′	(i)	(ii)	lit.	(ii)	lit.	lit.
(I)	Me	Me	8·88	8·96	8·98 [2]	10·29	9·70 [a]	12·70 [b]
(II)	Ph	Me				10·43	9·80 [c]	12·85 [d]
(III)	Ph	Ph				11·25		13·75 [b]
(IV)	Et	Et	9·65	9·78		11·21		

* (i) and (ii) Refer to potentiometric and spectrophotometric measurements made in this laboratory.

[a] Ref. 12. [b] L. G. van Uitert, W. C. Fernelius, and B. E. Douglas, *J. Amer. Chem. Soc.*, 1953, **75**, 457, 2736, 2739. [c] Ref. 13. [d] E. H. Holst, Doctoral dissertation, Pennsylvania State University, 1955.

DISCUSSION

The value of pK_a for the ligand is in accord with values obtained for other β-diketones. In particular, the increase in pK_a obtained on replacing Me by Et [compounds (I) and (IV) in Table 3] is in parallel with the greater electron-releasing effect ($+I$) of the Et group.[11] Data for dioxan (50%) show a small increase in pK_a on replacing the first Me group in acetylacetone by Ph (0·14 and 0·15 units in 50 and 75% dioxan), while replacement of the second Me group by Ph produces a much larger increment (0·82 and 0·90 units in 50 and 75% dioxan). This effect cannot be rationalized in terms of Hammett σ constants.

pK_a Values in dioxan (50%) obtained in this laboratory are approximately 0·6 units higher than those obtained in the literature.[12,13] This may be attributable to different pH-standardization procedures used in other laboratories; if aqueous buffer standardization is followed by measurements in aqueous dioxan (50%), this introduces a liquid-junction potential error which, in this laboratory, has been measured as approximately 30 mV. The change of solvent from water to dioxan (50%) produces similar pK_a increments [1·33 and 1·43 for compounds (I) and (IV) in Table 3], while a different but almost constant increment accompanies the change 50 to 75% dioxan [2·41, 2·42, and 2·50 for compounds (I), (II), and (III)]. Solvent change here would thus appear to be purely a solvent effect rather than to involve any differential change in solvent–solute interaction due to the different substituent groups. However, more enthalpy data would be required to apportion the almost constant free-energy solvent effect to enthalpy and entropy factors.

Stability Constants.—Table 2 shows good agreement between constants determined at 3 : 1 and 5 : 1 ligand : metal ratios. This agreement, and the fact that both results give linear plots of $\bar{n}/(\bar{n} - 1)[L^-]$ against $(2 - \bar{n})[L^-]/(\bar{n} - 1)$, indicates the validity of the mathematical model for these equilibria; hydroxo-complexes and polymeric species are thus unlikely. The normal Irving–Williams series[14] is followed with the exception that $Co^{II} > Ni^{II}$ for these complexes. Log (K_1/K_2) values are rather low but within the normal range; the exception, Cu^{II}, shows a very low value. These findings differ from literature values for pentane-2,4-dione chelate complexes in dioxan (50%) which show normal log (K_1/K_2) values and $Co^{II} < Ni^{II}$ as in the Irving–Williams series (Table 4). This difference in behaviour between the two ligands will not be discussed

TABLE 4

Stability constants of Co^{II}, Ni^{II}, and Cu^{II} chelate complexes of pentane-2,4-dione and heptane-3,5-dione in dioxan (50%) at 25 °C

		Co^{II} [a]	Ni^{II} [b]	Cu^{II} [b]
Pentane-2,4-dione	log K_1	6·30	6·91	9·55
	log K_2	4·88	5·17	8·13
	log (K_1/K_2)	1·42	1·74	1·42
Heptane-3,5-dione [c]	log K_1	7·32	6·68	9·11
	log K_2	5·84	5·84	8·89
	log (K_1/K_2)	1·48	0·84	0·22

[a] Ref. 12. [b] B. E. Bryant, *J. Phys. Chem.*, 1954, **58**, 573. [c] From Table 2 (average values).

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[11] L. P. Hammett, ' Physical Organic Chemistry,' McGraw-Hill, New York, 1940.

[12] L. E. Maley and D. P. Mellor, *Austral. J. Sci. Res.*, 1949, **2A**, 92.

[13] M. Calvin and K. W. Wilson, *J. Amer. Chem. Soc.*, 1945, **67**, 2003.

[14] H. Irving and R. J. P. Williams, *J. Chem. Soc.*, 1953, 3192.

further here since work in this laboratory on chelate complexes of pentane-2,4-dione and analogous compounds shows behaviour similar to that reported here and will be published later.

Enthalpy and Entropy Values.—Values for the protonation reaction obtained in this work are comparable to those obtained for pentane-2,4-dione by other workers.

Reagent (solvent)	ΔH kJ mol^{-1}	ΔS J K^{-1} mol^{-1}	Ref. (Method)
Pentane-2,4-dione (water)	−11·7	134	2 (Indirect)
Pentane-2,4-dione (water)	−14·8	117	15 (Calorimetry)
Pentane-2,4-dione [dioxan (50%)]	−12·3	159	15 (Calorimetry)
Heptane-3,5-dione [dioxan (50%)]	−11·7	175	This work

These results do not indicate large changes in the enthalpies and entropies of reaction with substituent and solvent change, other than the possibility of larger entropies of reaction in the mixed solvent, but there are insufficient data available (obtained under the same conditions) at present to be more definite.

Enthalpies and entropies of chelation of the Co^{II} complexes may be compared with corresponding data[2,16] obtained for Co^{II}–pentane-2,4-dione chelate complexes in water.

Co^{II}–Heptane-3,5-dionate chelate complexes in dioxan (50%) (this work)

$\Delta H_1 = -4{\cdot}2$ kJ mol^{-1} $\Delta S_1 = 127$ J K^{-1} mol^{-1}

$\Delta H_2 = -6{\cdot}7$ kJ mol^{-1} $\Delta S_2 = 90$ J K^{-1} mol^{-1}

Co^{II}–Pentane-2,4-dionate chelate complexes in water[2,16]

$\Delta H_1 = -5{\cdot}0$ kJ mol^{-1} $\Delta S_1 = 87{\cdot}8$ J K^{-1} mol^{-1}

$\Delta H_2 = -20{\cdot}9$ kJ mol^{-1} $\Delta S_2 = 10{\cdot}0$ J K^{-1} mol^{-1}

While ΔH and ΔS values are comparable for formation of the first chelate group, ΔH and ΔS values for formation of the second chelate group increase and decrease significantly for the pentane-2,4-dione–water system. Further discussion awaits the publication of additional thermodynamic data.

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[15] J. O. Hill and R. J. Irving, *J. Chem. Soc.* (*A*), 1969, 2759.

[16] R. M. Izatt, C. G. Haas, jun., B. P. Block, and W. C. Fernelius, *J. Phys. Chem.*, 1954, **58**, 1133.