1-Substituted Butane-1,3-diones: Acid Dissociation Constants and Stabilities of Manganese(II), Cobalt(II), and Copper(II) Chelate Complexes in Aqueous Dioxan (50% v/v)

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Values of the acid dissociation constants of seven 1-substituted butane-1,3-diones have been determined in 50% (v/v) aqueous dioxan at 25·0 °C. Stability constants of manganese(II), cobalt(II), nickel(II), and copper(II) complexes of 1-phenylbutane-1,3-dione, and nickel(II) complexes of 1-(4-methoxy-, 1-(4-methyl-, 1-(4-bromo-, and 1-(4-nitro-phenyl) derivatives of butane-1,3-dione have been obtained in the same solvent.

MANY metals form chelate complexes with β-diketones, (I). Stability constants are available [1a] for a wide range of metal complexes of the parent compound pentane-2,4-dione ($R^1 = R^2 = Me$), the complexes of some metals with 1-phenylbutane-1,3-dione [1b] ($R^1 = Me$, $R^2 = Ph$) and 1,2-diphenylpropane-1,3-dione [1c] ($R^1 = R^2 = Ph$), Ni^{II} chelates of dialkyl derivatives [2] (R^1, $R^2 =$ alkyl), and transition-metal bivalent cations with heptane-3,5-dione [3] ($R^1 = R^2 = Et$). Also, chelate complexes are known for β-ketoesters [1d] ($R^1 = Me$, $R^2 = OEt$) and β-ketoamides [4] ($R^1 = Me$, $R^2 = NHPh$). In this paper, we report the stabilities of complexes of

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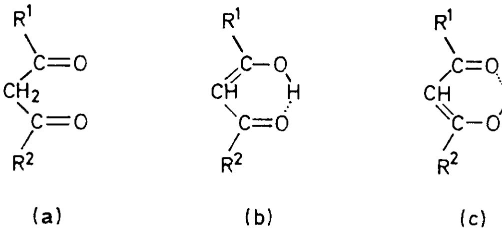
[1] 'Stability Constants of Metal–Ion Complexes,' The Chemical Society, Special Publ. No. 17 (1964), (*a*) pp. 443—446; (*b*) pp. 618—619; (*c*) p. 700; (*d*) p. 483; No. 25 (1971), (*a*) pp. 365—368; (*b*) pp. 601—603; (*c*) p. 737.

[2] I. Yoshida, H. Kobayashi, and K. Ueno, *Bull. Chem. Soc. Japan*, 1972, **45**, 1411, 2768.

[3] J. L. Ault, H. J. Harries, and J. Burgess, *J.C.S. Dalton*, 1973, 1095.

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

1-substituted butane-1,3-diones (R^1 = Me, R^2 = 4-XC_6H_4) with Ni^{2+} and of 1-phenylbutane-1,3-dione with Mn^{2+}, Co^{2+}, Ni^{2+}, and Cu^{2+}. We discuss the effects of the ligand substituents on the acid dissociation constants of the ligands and on the stability constants, and compare these substituent effects with those found in similar series of compounds.


(a) (b) (c)

(I)

EXPERIMENTAL

Materials.—1-Phenylbutane-1,3-dione (B.D.H.) was recrystallized from water. 1-(4-Methylphenyl)butane-1,3-dione (I; R^1 = Me, R^2 = 4-MeC_6H_4) was prepared by condensing 4-methylacetophenone with ethyl acetate in the presence of sodium ethoxide, and was purified by distillation.[5] 1-(4-Nitrophenyl)butane-1,3-dione (I; R^1 = Me, R^2 = 4-$NO_2C_6H_4$) was prepared *via* reaction of the copper(II) complex of pentane-2,4-dione with 4-nitrobenzoyl chloride in chloroform;[6] the ligand was released from the complex by the addition of dilute sulphuric acid, extracted with diethyl ether, and recrystallized from methanol. The other 1-substituted butane-1,3-diones were prepared by reacting the methyl ester of the appropriate 4-substituted benzoic acid with anhydrous acetone in 1,2-dimethoxyethane, in the presence of sodium hydride.[7] These ligands were purified by distillation (X = Me or F) or by recrystallization from light petroleum (b.p. 40—60 °C) or methanol (X = NO_2).

Metal salts used were AnalaR sulphates, their metal content being determined using ethylenediaminetetra-acetic acid. Dioxan was purified by the method of Weissberger and Proskauer;[8] water was freshly distilled, and was boiled and allowed to cool in a flask fitted with a soda-lime trap to exclude carbon dioxide.

Determination of pK_a *Values and Stability Constants*.—pK_a Values were determined potentiometrically. The experimental arrangements and method of calculation have been described elsewhere.[3] Standardization of the pH meter[9] involved the use of acetic acid–sodium acetate and anilinium chloride–aniline buffers made up in aqueous dioxan (50% v/v). Using pK_a data of Conway[10] and activities compiled by Harned and Owen,[11] calculated pH values for the above buffers (all components 0·1 mol dm^{-3}) were 6·29 and 4·24 respectively. Stability constants were obtained by the method previously described for heptane-3,5-dione complexes.[3]

RESULTS

Acid dissociation constants (pK_a) for the ligands and stability constants for manganese(II), cobalt(II), nickel(II), and copper(II) complexes of these ligands, all determined at 25·0 °C in aqueous dioxan (50% v/v), are listed in Table 1. The standard deviations of the pK_a values were ±0·02 or less; of the log K_1 and log K_2 values, ±0·03 or less. Also tabulated are Hammett substituent constants derived from acid dissociation constants of both substituted benzoic acids and phenols.

TABLE 1

Acid dissociation constants (pK_a) of phenyl-substituted 1-phenylbutane-1,3-diones, (I; R^1 = Me, R^2 = 4-XC_6H_4), and stability constants (K_1 and K_2) for their metal(II) chelate complexes, determined at 25 °C in aqueous dioxan (50% v/v)

		log K_1				log K_2				Hammett constants	
Substituent	pK_a	Mn^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Mn^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	σ^a	σ^b
(1) MeO	10·82			6·65				5·88		−0·27	−0·11
(2) Me	10·54			6·53				5·84		−0·17	−0·17
(3) H	10·38	4·95	6·09	6·51	8·55	4·40	5·56	5·76	8·35	0	0
(4) F	10·22									+0·06	+0·06
(5) Cl	9·98									+0·23	−0·23
(6) Br	9·96			6·32						+0·27	+0·27
(7) I	9·95									+0·30	+0·30
(8) O_2N	9·07			5·63						+0·78	+1·24

The Hammett σ constants (G. B. Barlin and D. D. Perrin, *Quart. Rev.*, 1966, **20**, 87) are values derived (*a*) for benzoic acids and (*b*) for phenols.

DISCUSSION

Ligand pK_a *Values*.—Figure 1 shows a linear correlation between ligand pK_a values and substituent constants derived from pK_a values of benzoic acids; the correlation is not linear for phenols. The substituent constants for the two series differ for the methoxy- and nitro-groups, both of which give a strong mesomeric interaction with the ring (+*M* for MeO, −*M* for O_2N). The carboxy-group in the benzoic acids and the CO·CH_2·CO·Me group in the ligands both have −*M* interactions with the aromatic ring while the hydroxy-group in phenols has a +*M* effect.

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[5] J. M. Sprague, L. J. Beckham, and H. Adkins, *J. Amer. Chem. Soc.*, 1934, **56**, 2665.

[6] W. J. Barry, *J. Chem. Soc.*, 1960, 670.

[7] K. R. Kopecky, D. Nonhebel, G. Morris, and G. S. Hammond, *J. Org. Chem.*, 1962, **27**, 1036.

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

[9] H. J. Harries, S. Savage, G. Wright, and N. Logan, *J. Inorg. Nuclear Chem.*, 1969, **31**, 2477.

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

[11] H. S. Harned and B. B. Owen, ' The Physical Chemistry of Electrolytic Solutions,' Reinhold, New York, 1950, p. 548.

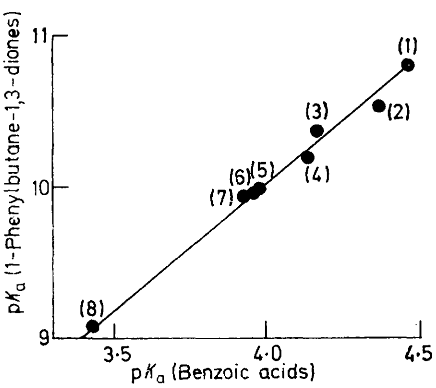

FIGURE 1 Relation between the acid dissociation constant (pK_a) of phenyl-substituted 1-phenylbutane-1,3-diones, (I; R^1 = Me, R^2 = $4\text{-}XC_6H_4$), and of analogous benzoic acids. Numbers refer to Table 1

Stability Constants; Ligand Variation.—Stabilities of the Ni^{II} chelate complexes ($\log K_1$, $\log K_2$) increased linearly with pK_a of the ligand (Figure 2). The absence of K_2 values for X = Br and O_2N is caused by precipitation of the chelate complex during potentiometric titration. Both plots have gradients less than unity. Irving and Rossotti [12] derived the relation below, where

$$\log K_{ML} = \log K_{HL} + \{[(G_M - G_H) + (G_{HL} - G_{ML})]/2{\cdot}303RT\}$$

$\log K_{ML}$ is identical with $\log K_1$ (defined above), $\log K_{HL} = pK_a$, HL and ML represent the protonated and metallated chelating anion, and G_Z represents the free energy of species Z. Since $(G_M - G_H)$ is constant for a given metal atom, there will be a linear relation between pK_a and $\log K$ provided that $(G_{HL} - G_{ML})$ is (*i*) negligible compared with $(G_M - G_H)$, (*ii*) constant, and (*iii*) a linear function of pK_a ($\log K_{HL}$). Conditions (*i*) and (*ii*) produce linear plots of gradient unity, while (*iii*) results in a gradient other than unity. The latter condition fits the data in Figure 2. A study of stabilities of chelate complexes of (I; R^1 = Me, R^2 = $4\text{-}XC_6H_4NH$) [13] showed this gradient to be unity for Be^{II} and less than unity for Cu^{II}.

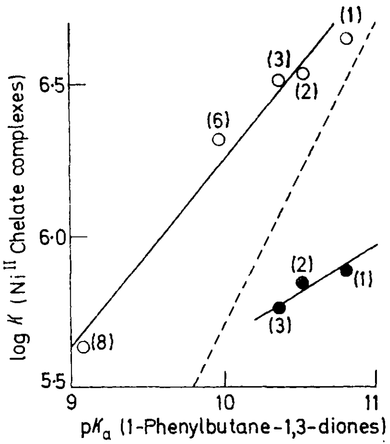

FIGURE 2 Plot of pK_a for phenyl-substituted 1-phenylbutane-1,3-diones (I; R^1 = Me, R^2 = $4\text{-}CX_6H_4$), against $\log K$ for their Ni^{II} chelate complexes: (○), $\log K_1$; (●), $\log K_2$; and (— - — —), line is of gradient unity. Numbers refer to Table 1

In Table 2 are collected equilibrium constants for chelating agents related to 1-phenylbutane-1,3-dione. The data were all obtained by the same techniques in this laboratory and are thus comparable. Results in Table 2 do not show a monotonic relation between $\log K$ and pK_a; this is interpreted as being due to change in the entropy term caused by structural changes in the group R. For the structurally similar series of butane-1,3-diones studied here, it is expected that ΔS will not vary greatly and thus will lead to a linear plot of $\log K$ against pK_a as already noted. The gradient of these plots (less than unity) may, in part, be due to metal–ligand π-bonding which is feasible for the d^8 ion Ni^{2+}.

TABLE 2

Acid dissociation constants of ligands $Me{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}R$ and stability constants of their metal chelate complexes, measured at 25·0 °C in aqueous dioxan (50% v/v)

R	pK_a	$\log K_1$ Ni^{2+}	$\log K_1$ Cu^{2+}	Ref.
Me	10·29	6·40	8·37	3
Ph	10·38	6·51	8·56	*a*
Et	10·79	6·53	8·69	*b*
PhNH	11·43	4·82	7·97	9

[a] This work. [b] J. L. Ault, H. J. Harries, and J. Burgess, unpublished work.

The relative ease of formation of complexes ML^+ and ML_2 is given by the ratio $K_1 : K_2$. Values of $\log (K_1/K_2)$, derived from Table 1, for metal chelate complexes of 1-phenylbutane-1,3-dione are as follows.

M^{II}	Mn	Co	Ni	Cu
$\log(K_1/K_2)$	0·55	0·53	0·75	0·20

Values for Ni^{II} chelate complexes of phenyl-substituted 1-phenylbutane-1,3-diones are:

X	4-MeO	4-Me	4-H
$\log(K_1/K_2)$	0·77	0·69	0·75

These values are in the normal range; the occurrence of unusually high values implies the intervention of a steric effect whereby the presence of the first chelate group retards the addition of subsequent groups. This latter effect is most likely for ligands which contain a bulky substituent near the donor atoms.[14] The small value for Cu^{II} is noteworthy and implies considerable

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[12] H. Irving and H. Rossotti, *Acta Chem. Scand.*, 1956, **10**, 72.

[13] H. J. Harries, R. K. Hughes, and T. Smith, *J. Inorg. Nuclear Chem.*, 1972, **34**, 1609.

[14] See, for example, F. J. C. Rossotti in 'Modern Co-ordination Chemistry,' eds. J. Lewis and R. J. Wilkins, Interscience, New York, 1960, p. 37.

overlap in the two stages of chelate formation. This type of behaviour has also been found by Ault[15] in Cu^{II} chelates of aliphatic diketones. Stabilities of the chelate complexes of 1-phenylbutane-1,3-dione (Table 1) are in agreement with the Irving–Williams sequence[16] which predicts the stability order $Mn^{II} < Fe^{II} < Co^{III} < Ni^{II} < Cu^{II} > Zn^{II}$ for a given ligand forming spin-free complexes.

[4/872 *Received, 2nd May,* 1974]

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[15] J. L. Ault, Ph.D. Thesis, University of Leicester, 1973; ref. 3.

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