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Stability Constants of Some Bivalent Metal Chelates of 3-Aryl-2,4-pentanedione in 75% v/v 1,4-Dioxane–Water Medium

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A new ligand, 3-(1-naphthyl)-2,4-pentanedione, was prepared. Concentration proton-dissociation constants of 3-aryl-2,4-pentanedione (aryl group; phenyl, 2,4-dinitrophenyl, and 1-naphthyl) and concentration stability constants of some bivalent metal chelates of 3-aryl-2,4-pentanedione were determined in a 75% v/v 1,4-dioxane–water medium containing 0.05 mol dm^{-3} sodium perchlorate by a pH-titrimetric method. The dissociation constant (pK_a) of 3-(2,4-dinitrophenyl)-2,4-pentanedione, 2,4-pentanedione, 3-phenyl-2,4-pentanedione, and 3-(1-naphthyl)-2,4-pentanedione were found to be 8.87, 10.93, 11.50, and 11.71, respectively. The order of acidity in 2,4-pentanedione was explained by the field effect of the aryl group. The stability constants of the bivalent metal chelates of these ligands were in accord with the Irving-Williams series. The stepwise stability constant of the chelate increased with an increasing pK_a value of 3-aryl-2,4-pentanedione. This result cannot be explained by the steric and solvation effect of an aryl substituent.

There have been a large number of articles describing the preparation of 2,4-pentanedione derivatives, their proton-dissociation[1,2] and partition[3,4] equilibrium constants, stability and partition equilibrium[5] constants of their metal chelates, and solvent extraction[6] of metal ions with 2,4-pentanedione derivatives. The investigations involving metal chelates of 3-substituted 2,4-pentanedione seem to be rare compared to those involving metal chelates of 1-substituted 2,4-pentanedione.

The effect of alkyl substituents at the 1-position of 2,4-pentanedione on the stability constant of a metal chelate has been studied.[1,2] An alkyl substituent lowers the acidity, and the stability constants of copper(II) chelates are generally smaller than expected on the basis of a pK_a–log β (overall stability constant) relationship.

Martin and Martin[7] studied the steric and solvation effect of an alkyl substituent at the 3-position of 2,4-pentanedione on the chelating tendency and found that there was no linear pK_a–log β relationship for bivalent metal chelates of 3-alkyl-2,4-pentanedione. They assert that the effect of an alkyl substituent at the 3-position on the chelating tendency is complicated, and that the solvation effect may be more important than the steric effect.[7]

When methylene-hydrogen of 2,4-pentanedione was substituted with an aryl group, the aromatic ring of an aryl group should adopt a conformation perpendicular to the 2,4-pentanedione ring, and all mesomeric effects of the aromatic ring shold be excluded. The authors' interest lies in clarifying the effect of the aryl group on the proton-dissociation constant and the stability constant of bivalent metal chelates of 3-aryl-2,4-pentanedione.

Experimental

Synthesis of 3-(1-Naphthyl)-2,4-pentanedione. A mixture of 1-naphthylacetonitrile (100 g, 0.60 mol) and ethyl acetate (60 cm^3) was added to a 1-butanol solution of butoxide (sodium metal 7.1 g +1-butanol 100 cm^3) while being stirred. After the reaction mixture was warmed to 80 °C, it was allowed to cool to room temperature while being stirred. The whole mixture became a gray cake. It was dissolved in water and acidified. The oily layer was extracted with ether and the ether was evaporated. A mixture of acetic acid, water, and sulfuric acid (520 cm^3 each) was added to the crude product. The resulting mixture was refluxed for 6 h. Black oil was extracted with ether and crude 1-naphthylacetone was obtained after the usual work-up. 40.5 g (32.4%), bp 115—120 °C/0.1 mm Hg. The 1-naphthylacetone was treated with a mixture of acetic anhydride (55.1 cm^3, 0.59 mol) and a BF_3–acetic acid complex (264 g) at 50 °C for 20 h. To the reaction mixture was added 1100 cm^3 of a sodium acetate solution (about 8%) and the resulting mixture was refluxed for 2 h. A crude product was extracted with ether, transferred to an aqueous sodium hydroxide solution (5%) and then the resultant alkaline solution was acidified with 5 mol dm^{-3} hydrochloric acid. Crude 3-(1-naphthyl)-2,4-pentanedione precipitated was recrystallized from ethanol: Yield 20.0 g (14.7%). It was further chromatographed (Wako gel C-200). mp 105.0—106.5 °C, IR (KBr): 3020, 2930, 1600 cm^{-1}; ^{1}H-NMR ($CDCl_3$, δ): 17.02 (s, 1H), 8.0—7.3 (m, 7H), 1.75 (s, 6H); MS: m/z 226 (parent), 211, 183, 165 (base), 43. Anal ($C_{15}H_{14}O_2$) C,H.

Since the ^{1}H-NMR spectrum showed intramolecular hydrogen-bonded OH proton equivalent to about one proton in $CDCl_3$, 3-(1-naphthyl)-2,4-pentanedione should adopt the enol form. The fact that two methyl ring are magnetically equivalent, suggests that an aromatic ring of substituent is perpendicular to the 2,4-pentanedionate ring and 2,4-pentanedione is in equilibrium between the tautomeric isomers at a more rapid rate than NMR time scale.

Materials. 3-(2,4-dinitrophenyl)-2,4-pentanedione was prepared by a method described in the reference,[8] and identified by its melting point, ^{1}H-NMR and IR spectra, and a chemical analysis of carbon, nitrogen, and hydrogen, Reagent-grade 3-phenyl-2,4-pentanedione (Tokyo Kasei Co., Ltd.) was used without purification. Reagent-grade 2,4-pentanedione (Wako Co., Ltd.) was distilled before use. Reagent-grade 1,4-dioxane (Kanto Co., Ltd.) was shaken with solid potassium hydroxide, refluxed with sodium metal for 10 h, and distilled. The distilled 1,4-dioxane was preserved in a nitrogen atmosphere. Sodium perchlorate was recrystallized from an aqueous solution and dissolved in redistilled and decarbonized water. The concentration of the sodium perchlorate solution was determined by the titration of the hydrogen ion concentration after an aliquot of the perchlorate solution was passed through a column of cation-exchange resin in the hydrogen from. The solutions of metal perchlorate were prepared by converting the metal powder (Mitsuwa Co., Ltd.) to metal perchlorate. Their concentrations were determined by EDTA titration using appropriate indicators. The concentration of the perchloric acid in a metal perchlorate solution was determined by the method similar to that used for the determination of sodium perchlorate.

pH Measurement. The pH measurement was conducted using a Hitachi-Horiba model F-7 type pH meter. A Horiba glass-electrode type 1026-05T was used. A Horiba 2535A-06T type reference electrode, with a double-junction mantle with 3.33 mol dm^{-3} potassium chloride in water and 0.05 mol dm^{-3} sodium perchlorate in 75% v/v 1,4-dioxane-water as an internal solution, was used. The pH meter was standardized using buffer solutions (pH 4.01, 6.86, 10.02 at 25 °C). A fifty-cm^3 portion of 75% v/v 1,4-dioxane-water containing (1.5—2.0)$\times 10^{-3}$ mol dm^{-3} metal ion, (5.0—6.5)$\times 10^{-3}$ mol dm^{-3} ligand, 0.003 mol dm^{-3} perchloric acid, and 0.05 mol dm^{-3} sodium perchlorate was placed in a 100-cm^3 tall beaker shielded with copper plates and thermostated at 25±0.1 °C. The solution was titrated with 0.02 mol dm^{-3} sodium hydroxide solution containing 0.03 mol dm^{-3} sodium perchlorate. The solution was agitated continuously by passing pure nitrogen. The titration was started 2 h after the electrodes were thermostated in the solution. The response of the electrode was very slow in the 75% v/v 1,4-dioxane-water medium. It took less than 20 min to get a constant reading after each addition of titrant.

Calculation of the Results. A. personal computer (PC 8001 mk II (NEC Co., Ltd.)) was used for the calculatation of the results. N$_{80}$-basic was used as the language.

Results and Discussion

Determination of pK$_a$ of 3-Aryl-2,4-pentanedione. The concentration of hydrogen ions (pH$_c$) in 1,4-dioxane-water could not be directly determined from the reading of the pH meter. A potentionmetric titration method modified by Ohtaki[9] was used to find the hydrogen ion concentration in a 75% v/v 1,4-dioxane-water medium. When the concentration of the bulk electrolyte was larger than that of the hydrogen ion concentration, the activity coefficient of the hydrogen ion became constant. The pH$_c$ value can be calculated using the analytical hydrogen ion concentration. The pH$_c$ values are related to the reading of the pH meter, pH$_R$, by

$$\mathrm{pH_c} = \mathrm{pH_R} + \Delta\mathrm{pH}, \tag{1}$$

ΔpH depending on the concentration of 1,4-dioxane, the ionic strength, *etc.* The ΔpH value obtained using Gran's plot[10] was +0.13±0.04. The electrode worked well enough to obtain the proton-dissociation and stability constants. The concentration of deprotonated 3-aryl-2,4-pentanedione can be given by $a=h-[\mathrm{ClO_4^-}]+[\mathrm{Na^+}]-K_\mathrm{w}h^{-1}$ where h and K_w are the hydrogen ion concentration and the ion product of water in 75% v/v 1,4-dioxane-water medium (3.45×10^{-19})[11] and the proton-dissociation constant can be represented by $K_\mathrm{a}=ah/[\mathrm{HL}]$. The ratio of $[\mathrm{HL}]:[\mathrm{HL}]_\mathrm{T}$ can be represented as follows:

$$Z = \frac{(C_\mathrm{L}-a)}{C_\mathrm{L}},$$

where C_L represents the total concentration of 3-aryl-2,4-pentanedione. This ratio was calculated by the hydrogen ion concentration and the proton-dissociation constant as follows:

$$Z = \frac{10^{x+p}}{1+10^{x+p}},$$

where $x=\log h$, $p=\log K_\mathrm{a}$ ($\equiv -\mathrm{p}K_\mathrm{a}$). Normalized curve Z is obtained as follows:

$$Z = \frac{10^x}{1+10^x}. \tag{3}$$

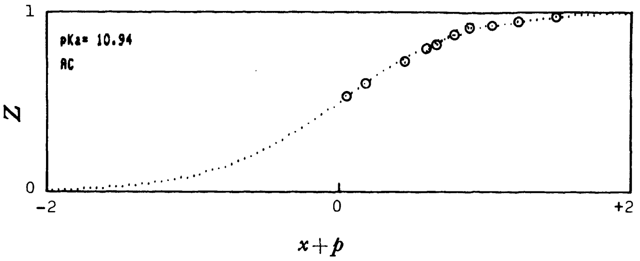

Fig. 1. Determination of pK_a value of 2,4-pentanedione by curve-fitting method (in 75% v/v 1,4-dioxane–water medium containing 0.05 mol dm^{-3} NaClO$_4$, 25 °C). (……): Normalized curve, (⊙⊙): Experimental data.

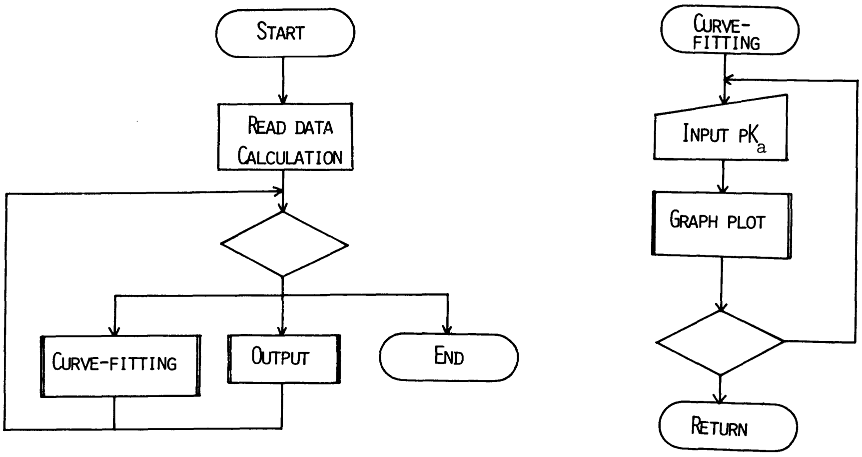

Fig. 2. Block flow chart of program used for dtermination of proton-dissociation constant of 3-aryl-2,4-pentanedione.

A plot of the experimental data Z $(=10^{x+p}/1+10^{x+p})$ was adjusted to coincide with a normalized curve Z until a best fit was obtained. Then, the x value coinciding with $X=0$, $p=-x$ was read. In this work, we attempted to determine the proton-dissociation constant using a program for curve-fitting.[12] The procedure for obtaining the best fit was performed on the display unit of a microcomputer. Fugure 1 shows plots of Z *vs.* $(x+p)$ and a normalized curve of $Z=10X/1+10X$. Thus, the pK_a value of 2,4-pentanedione was obtained to be 10.93 ± 0.08 which is in good agreement with that obtained graphically. Figure 2 represents the block flow chart of the program used for the determination of the proton-dissociation constant of 3-aryl-2,4-pentanedione. The values of pK_a of 3-aryl-2,4-pentanedione are listed in Table 1.

Determination of the Stability Constant. The reaction of the chelate formation of bivalent metal ions with 3-aryl-2,4-pentanedione can be represented by Eqs. 4 and 5:

$$\mathrm{M} + \mathrm{L} \overset{K_1}{\rightleftharpoons} \mathrm{ML}, \tag{4}$$

$$\mathrm{ML} + \mathrm{L} \overset{K_2}{\rightleftharpoons} \mathrm{ML_2}, \tag{5}$$

where K_1 and K_2 represent the stepwise stability constants of 1:1 and 1:2 metal chelates. The average number of 3-aryl-2,4-pentanedione bound per metal ion, Z, is related with K_1 and K_2:

$$Z=\frac{K_1a+2K_2a^2}{1+K_1a+K_2a}. \tag{6}$$

This formula is derived to

$$Z=\frac{p_2 10^{x+p_1}+2(10^{x+p_1})^2}{1+p_2 10^{x+p_1}+(10^{x+p_1})^2}, \tag{7}$$

where notations are: $x=\log a$, $p_1=1/2\log K_2$, $p_2=K_1\cdot K_2^{-1/2}$. The normalized curve Z is represented as

$$Z=\frac{p_2 10^X+2(10^X)^2}{1+p_2 10^X+(10^X)^2}. \tag{8}$$

In order to find the required parameters, experimental data Z should be moved along the X axis until the best fit is found. The log K_2 values are then determined by reading log a at $X=0$. Again the curve-fitting

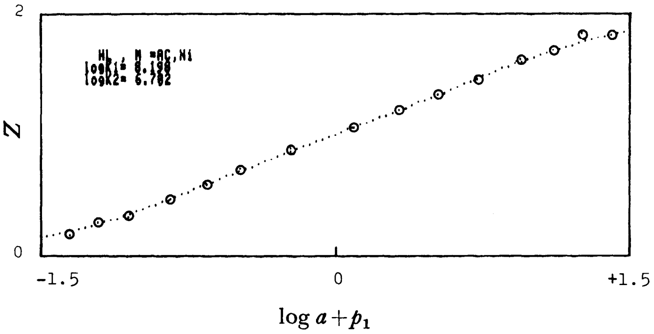

Fig. 3. Determination of concentration stability constant of nickel(II) chelate of 2,4-pentanedione by curve-fitting method (in 75% v/v 1,4-dioxane–water medium containing 0.05 mol dm^{-3} NaClO$_4$, 25 °C). (······): Normarized curve, (⊙⊙): Experimental data.

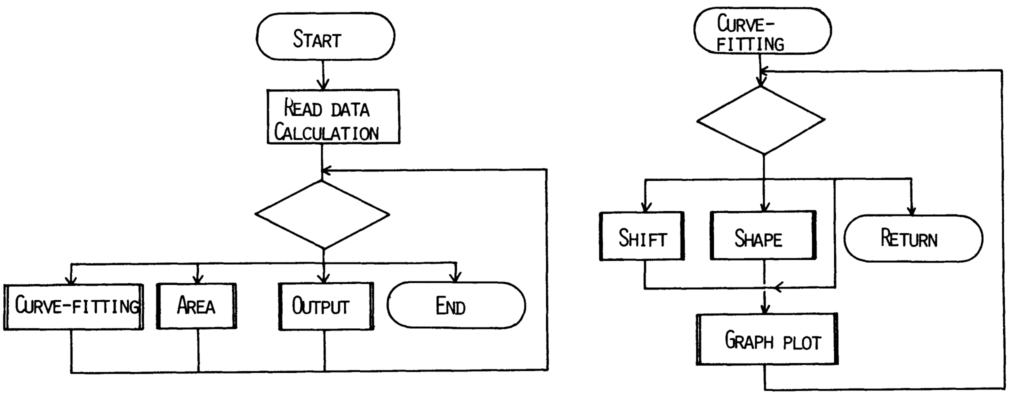

Fig. 4. Block flow chart of program used for determination of stability constant of bivalent metal chelates of 3-aryl-2,4-pentanedione.

TABLE 1. CONCENTRATION PROTON-DISSOCIATION CONSTANTS AND STABILITY CONSTANTS OF SOME BIVALENT METAL CHELATES OF 3-ARYL-2,4-PENTANEDIONE (IN 75% v/v 1,4-DIOXANE-WATER MEDIUM, 25 °C)

3-aryl-2,4-pentanedione	pK_a	Co(II)		Ni(II)		Cu(II)		Zn(II)	
		log K_1	log K_2	log K_1	log K_2	log K_1	log K_2	log K_1	log K_2
2,4-pentanedione	10.93	7.8	6.6	8.2	6.7	10.5	9.1	7.6	7.0
3-(3,4-dinitrophenyl)-2,4-pentanedione	8.87	5.9	5.4	6.6	5.9	8.6	7.6	5.8	5.0
3-phenyl-2,4-pentanedione	11.50	7.4	6.8	8.1	7.0	10.5	9.4	7.2	6.7
3-(1-naphthyl)-2,4-pentanedione	11.71	7.7	7.1	8.7	7.8	10.9	9.7	7.5	6.7
(Error)	±0.08	±0.2						±0.4	

was performed on the display unit of a microcomputer. The plot of Z *vs.* $\log a+p_1$ is shown in Fig. 3. The obtained values of K_1 and K_2 agreed with those obtained graphically. A block flow chart of the program for the determination of the stepwise stability constants, K_1 and K_2, is shown in Fig. 4.

The thermodynamic proton-dissociation constant (pK_a) of 2,4-pentanedione and stability constant of bivalent metal chelates of 2,4-pentanedione in 75% v/v 1,4-dioxane-water medium, which were obtained by van Uitert and his colaborators,[13] were larger than those obtained in this study. The difference in the results may be ascribed to a difference in experimental conditions. Since the keto-enol tautometric equilibrium of these 3-aryl-2,4-pentanedione in 75% v/v 1,4-dioxane–water is not known, the thermodynamic proton-dissociation and stability constants could not be determined. Manome and Saito[11] found that the pK_a value and the stability constant of the 1:1 bivalent metal chelates of 1,3-diphenyl-1,3-propanedione obtained under almost the same experimental conditions as ours were smaller than thermodynamic data obtained by van Uitert.[13]

The pK_a value of 3-aryl-2,4-pentanedione obtained in the present study increased in the following order: 3-(2,4-dinitrophenyl)-2,4-pentanedione<2,4-pentanedione<3-phenyl-2,4-pentanedione≦3-(1-naphthyl)-2,4-pentanedione. Since the aromatic ring of the substituent should adopt a conformation perpendicular to the 2,4-pentanedione ring, all the mesomeric effect of aryl group may be excluded for these 3-aryl-2,4-pentanedione.

The pK_a values of acetic acid, cyclohexyl acetic acid, and phenyl acetic acid were 4.75, 4.80, and 4.31, respectively.[14] Acidity of these acetic acid derivatives was explained in terms of the inductive effect or the field effect, that is, the interaction between the dipole of the substituent and dissociatable hydrogen through an intervening medium.[14] As mentioned above, there should be no mesomeric effect of 3-aryl group for 3-aryl-2,4-pentanedione. The pK_a value of 3-aryl-2,4-pentanedione and 2,4-pentanedione indicates the order opposit to the case of acetic acid derivatives. Consequently, the order of the acidity of 2,4-pentanedione and 3-aryl-2,4-pentanedione cannot be explained by the inductive effect of an aryl group. For 3-phenyl-2,4-pentanedione and 3-(1-naphthyl)-2,4-pentanedione, the field effect may be an important factor controlling the acidity rather than the inductive effect. Thus, phenyl and naphthyl groups which are rich in π-electrons would be considered to destabilize the conjugate base and decrease the acidity. In the case of 3-(2,4-dinitrophenyl)-2,4-pentanedione having π-electron-withdrawing nitro groups, benzene moiety of 2,4-dinitrophenyl ring may become electron defficient. The positively polarized benzene ring would interact with 2,4-pentanedione moiety. The interaction stabilizes the conjugate base to make the acidity greater than 2,4-pentanedione.

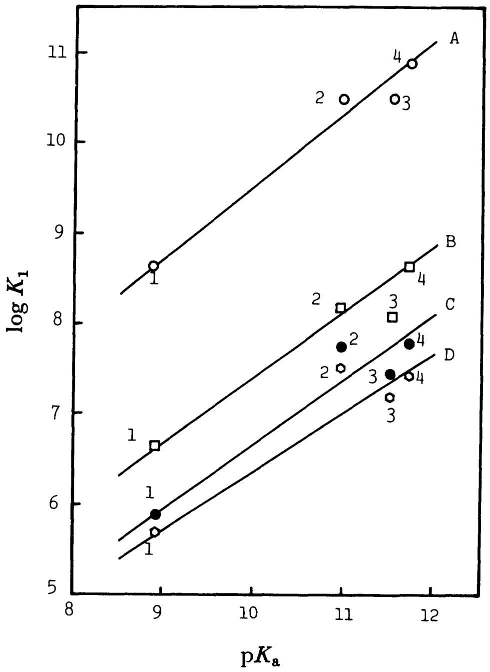

Fig. 5. Variation of $\log K_1$ of bivalent metal chelates as a function of pK_a for 3-aryl-2,4-pentanedione. Metal ion: A, copper(II); B, nickel(II); C, cobalt(II); D, Zinc(II). 3-aryl-2,4-pentanedione: 1) 3-(2,4-dinitrophenyl)-2,4-pentanedione; 2) 2,4-pentanedione; 3) 3-phenyl-2,4-pentanedione; 4) 3-(1-naphthyl)-2,4-pentanedione.

The stepwise stability constants of the 1:1 and 1:2 bivalent metal chelates are in accord with the Irving-Williams series.[15] The relationship between pK_a and $\log K_1$ for 3-aryl-2,4-pentanedione is shown in Fig. 5, indicating that there is no linear relationship between pK_a and the stability constant, $\log K_1$. However, the stability constant increased with increasing pK_a value of 3-aryl-2,4-pentanedione. Also, a similar result was obtained for the 1:2 metal chelates. The linear relationship between pK_a and the overall stability constant, $\log \beta$, has been observed for the copper(II) chelates of 2,4-pentanedione derivatives (1,1,1-trifluro-2,4-pentanedione, 2,4-pentanedione, 1-phenyl-1,3-butanedione, and 3-methyl-2,4-pentanedione).[16]

Though the pK_a value of 3-phenyl-2,4-pentanedione was larger than that of 2,4-pentanedione by 0.6, the stability constants of these metal chelates of 3-phenyl-2,4-pentanedione were found to be smaller than those of 2,4-pentanedione or to be of the same magnitude.

The linear pK_a–$\log \beta$ relationship was not observed for copper(II) and other bivalent metal chelates of 3-alkyl-2,4-pentanedione,[3] as mentioned above. The hydrophobic character of the ligand was proposed as one reason for the above results. However, it may be very difficult to clearly explain the effect of a substituent at the 3-position of 2,4-pentanedione on the stability constant at the present stage.

3-(2,4-dinitrophenyl)-2,4-pentanedione can be a useful extractant for metal ions because of the complex formation of metal chelates in an acidic medium and the large hydrophobic character.

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