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Stability of Some Bivalent Metal Complexes of Benzoyl-thiobenzoylmethane in Aqueous Dioxane

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Concentration equilibrium constants of benzoyl-thiobenzoylmethane (SdbmH) complexes of bivalent magnesium, cobalt, nickel, copper and zinc have been measured in 75% (v/v) aqueous dioxane containing 0.05 M sodium perchlorate. The values for the transition metal ions are greater than those of dibenzoylmethane (dbmH) complexes measured under the same conditions, although the p*K* value of SdbmH is smaller than that of dbmH. Contribution of d_π–d_π interaction seems to be responsible for such an unusual relationship.

Although the first example of thio homologues of β-diketones was presented by Mitra in 1933,[1] nothing had been known of their metal complexes until Chaston *et al.* prepared several monothio-β-diketones and their metal chelates.[2] Since then further varieties of mono- and di-thio-β-diketones and their transition metal chelates have been prepared and their properties described.[3-5] However, no information is available concerning the stability of their metal complexes in solution. Such studies seem very useful in discussing the characteristics of sulfur as donor atom and the a and b character of metal ions.[6]

We have attempted to measure the stabilities of metal chelates of some monothio-β-diketones in aqueous solution and found that they are soluble only in solutions containing a large amount of organic solvent such as dioxane. Monothio-β-diketones are liable to undergo hydrolysis in such media. Especially thiothenoyl-trifluoroacetone, sulfur derivative of thenoyltrifluoroacetone, is converted into thenoyltrifluoroacetone and hydrogen sulfide in 75% (v/v) aqueous dioxane (molar fraction, 0.380) within a few hours. Its absorption spectrum approaches to that of thenoyltrifluoroacetone, and an isosbestic point is observed at 307 mμ. Such a rapid change seems to be associated with its low p*K* value. Other monothio-β-diketones decompose more or less similarly, and the weakest acid benzoyl-monothiobenzoylmethane is expected to stand against such a hydrolysis best.

We have found that this compound is stable in the given conditions, and measured its dissociation constant and the stability constants of some of its metal chelates by an alkalimetric titration. The results have been compared with those of dibenzoylmethane (dbmH) under the identical condition.

Experimental

Materials. Thioacetylacetone, thiothenoyltrifluoroacetone, benzoylthioacetone, and benzoylthiobenzoylmethane (SdbmH) were prepared by Chaston *et al.*'s method from their oxo homologues, and identified by melting point, UV and IR spectra and the chemical analysis of carbon and hydrogen of their appropriate metal chelates.

Perchlorates of sodium, copper(II), cobalt(II), zinc, nickel and magnesium were recrystallized from aqueous solutions and dissolved in redistilled and decarbonized water. Their concentrations were determined by EDTA titration with appropriate indicators. Guaranteed grade dioxane was refluxed with concentrated hydrochloric acid and water in a current of nitrogen, shaked with solid potassium hydroxide, the aqueous layer discarded, refluxed with sodium, distilled and preserved in nitrogen atmosphere. Concentrated sodium hydroxide solution free from carbonate was diluted with water and dioxane and mixed with sodium perchlorate to produce 0.02 M sodium hydroxide solution in 0.03 M sodium perchlorate in 75% aqueous dioxane.

Measurement. Hitachi-Horiba Model P pH meter was used for the pH measurement. Horiba's Glass Electrode Type 1026-05T with a double junction mantle was used with 3.33 M potassium chloride in water and 0.05 M sodium perchlorate in 75% aqueous dioxane as bridging solution.

Metal perchlorate (1.5 to 2.0×10^{-3} M), SdbmH (5.0×10^{-3} M), perchloric acid (0.003 M) and sodium perchlorate (0.05 M) were dissolved in 75% aqueous

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2) S. H. H. Chaston, S. E. Livingstone, T. N. Lockyer and V. A. Pickles, *Aust. J. Chem.*, **18**, 673 (1965).

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5) A. Furuhashi, K. Watanuki and A. Ouchi, *ibid.*, **41**, 110 (1968).

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dioxane in a current of nitrogen. A 20 m*l* portion was placed in a beaker shielded with copper plates in a thermostat (25.0±0.1°C) and titrated with the alkali solution. The solution was agitated by a current of pure nitrogen saturated with the vapor of 75% aqueous dioxane. The titration was initiated *ca.* 2 hr after the electrodes were inserted into the solution. The time taken to obtain a constant reading of the meter during the course of titration was ordinarily less than 20 min, but sometimes 30 to 60 min, when the pH change between two reading points was large.

Results

In order to know the concentration of hydrogen ions in 75% aqueous dioxane, a potentiometric titration method modified by Ohtaki(7) was used. The pH_C values are interrelated with the reading of the pH meter by Eq. (1).

$$pH_C = pH_R + \Delta pH \tag{1}$$

where pH_R is the reading of the pH meter, and ΔpH is dependent on the concentration of dioxane, the ionic strength, *etc.* The ΔpH value obtained from Gran's plot(8) was $+0.355 \pm 0.003$ on addition of up to 2.5 m*l* of the sodium hydroxide solution. Hence the apparatus is useful for obtaining concentration equilibrium constants. The results were calculated by the curve fitting method.(9)

The $\log(h-H-K_w h^{-1})$ *vs.* $\log h$ diagrams for dbmH and SdbmH are shown in Fig. 1, where h and H denote the hydrogen ion concentration in equilibrium obtained from Eq. (1), and analysed excessive hydrogen ion concentration, respectively. The H values are known from the following formula,

$$H = [ClO_4^-] - [Na^+] - 2B \tag{2}$$

where B is the total concentration of the metal ion. K_w is the ion product of water under the given experimental conditions. (3.45×10^{-19}) A normalization function $y = -\log(1+x)$ is drawn and the coordinates are chosen to get the best fit with Fig. 1. The pK values are known from $\log x - \log h$. The results are given in Table 1.

Figure 2 illustrates Z *vs.* $\log a$ diagrams of bivalent metal chelates of SdbmH, where Z is the average number of the ligand bound per metal ion and a the concentration of deprotonated free ligand. The molar ratio of the formed complex is 1 to 2 and the Z is related to the overall formation constants β_1 and β_2 as follows:

$$Z = \frac{\beta_1 a + 2\beta_2 a^2}{1 + \beta_1 a + \beta_2 a^2} \tag{3}$$

This formula is simplified to

$$y = \frac{p_2 v + 2v^2}{1 + p_2 v + v^2} \tag{4}$$

where the notations are as follow: $y = Z$, $x = \log a$, $p_1 = \frac{1}{2}\log\beta_2$, $x + p_1 = \log v$ ($v = a\beta_2^{1/2}$) and $p_2 = \beta_1 \cdot \beta_2^{-1/2}$. A variety of y *vs.* $\log v$ diagrams are drawn for differing p_2 values, and one of them is chosen to get the best fit with those in Fig. 2. The $\log\beta_2$ values are then known from the reading of $\log a$ at $\log v = 0$.

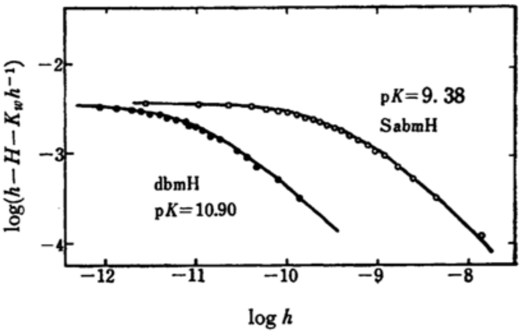

Fig. 1. Determination of pK values of dibenzoylmethane and benzoyl-thiobenzoylmethane by the curve fitting method. (25°C, in 75% aqueous dioxane containing 0.05 M $NaClO_4$)
● dbmH ○ SdbmH

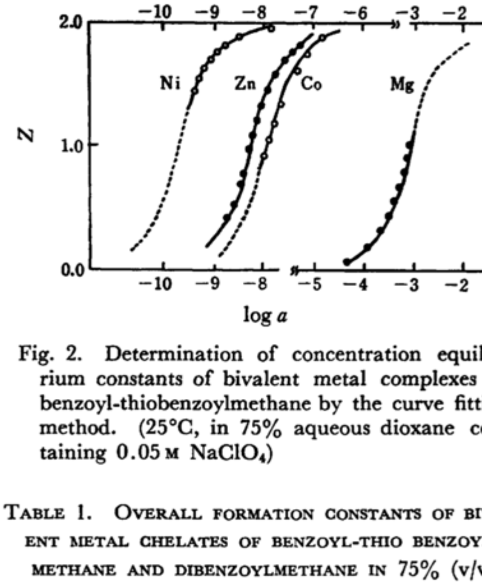

Fig. 2. Determination of concentration equilibrium constants of bivalent metal complexes of benzoyl-thiobenzoylmethane by the curve fitting method. (25°C, in 75% aqueous dioxane containing 0.05 M $NaClO_4$)

TABLE 1. OVERALL FORMATION CONSTANTS OF BIVALENT METAL CHELATES OF BENZOYL-THIO BENZOYLMETHANE AND DIBENZOYLMETHANE IN 75% (v/v) AQUEOUS DIOXANE SOLUTION AT 25°C, μ, 0.05 (Concentration equilibrium constants, $\log\beta_2$)

Complex	Mg^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}	H^+ (pK)
$M(dbm)_2$	9.9	14.4	14.7	20	13.6	10.90
$M(Sdbm)_2$	6.1	16.0	19.5	>23*	16.6	9.38
(Error)			±0.2			±0.02

* The complex formation is almost complete at the start of titration under the given condition.

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From similar diagrams for dibenzoylmethane complexes their β_2 values are also known. All these results are summerized in Table 1. These are all concentration equilibrium constants.

Discussion

van Uitert and his colaborators measured the p*K* values and the stability constants of several β-diketones and their bivalent metal chelates in 75% aqueous dioxane and discussed the conversion of concentration stability constants into thermodynamic data.[10] On evaluating the activity coefficients of the chemical species concerned, they gave several assumptions. In case of thio derivatives, however, fundamental information is missing. Dibenzoylmethane is claimed to have the biggest interaction with sodium ions among common β-diketones, and its monothio homologue is expected to have a similar trend. Neither is known its keto-enol tautometric equilibrium under the given conditions. Hence we had to give up to convert our data into thermodynamic parameters. The data in Table 1, however, were obtained under an identical condition, and we can compare them with one another. Although our experimental condition was not equal to van Uitert *et al.*'s, our data of p*K* and log β_2 values of dbmH and its chelates are parallel with and smaller than their thermodynamic equilibrium constants by more than 4. Such a difference is quite reasonable as they stated.[10]

The results in Table 1 are in accord with Irving-Williams series.[11] On the other hand, the log β_2 values of the thio homologue for the transition elements are greater than those of dbmH, regardless of the fact that the p*K* value of dbmH is greater than that of SdbmH. Hence the parallel relationship between p*K* and log β[12] is not seen for the transition metal ions. Only magnesium obeys this empirical law qualitatively. Such a discrepancy could be accounted for by considering the contribution of π-bonding between the transition metal ions and sulfur. Sulfur has vacant 3d orbitals, and can accept d_π electrons of transition metal ions to reinforce ordinary σ-bonding. Magnesium has no delectrons which can be donated to sulfur and gives a lower log β_2 value with SdbmH. A similar trend could have been observed with other thio homologues of β-diketones, if the experimental difficulty had been overcome. Details of the structure of monothio-β-diketone complexes are still unknown. The nickel complexes are diamagnetic and expected to have square planar structures,[2] but their geometrical isomerism is not known. Similar ambiguity remains for the copper complexes. Hence the skeletal structues of dbmH and SdbmH complexes of the semetals ions are different. Nevertheless, the difference between log β_2 values of dbmH and SdbmH complexes of various metal ions could provide an approximate measure indicating the difference in affinity of the metals towards sulfur and oxygen.

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