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Acid Dissociation Constants of Dialkyldithiocarbamic Acids and *O,O'*-Dialkyl *S*-Hydrogen Dithiophosphates and Formation Constants of Their Complexes with Cadmium(II), Zinc(II), and Lead(II) in 1 : 1 v/v Water-DMF Medium

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Synopsis. The log values of β_3, the formation constants of metal complexes with dialkyldithiocarbamates and *O,O'*-dialkyl dithiophosphates, were determined by polarography. The pK_a values, the acid-dissociation constants of these ligands, were also determined kinetically. A linear relationship exists between these two variables for each metal and straight parallel lines were obtained.

Dithio-acids such as alkylxanthic acids (*O*-alkyl hydrogen dithiocarbonates, HRxan), dialkyldithiocarbamic acids (HR$_2$dtc), and *O,O'*-dialkyl *S*-hydrogen dithiophosphates (HR$_2$dtp) are chelating reagents which coordinate to metal ions through two sulfur atoms and have been used for the solvent extraction of metal ions.[1-3]

The present authors have been studying the thermodynamical stability of metal dithioato complexes using a solvent-extraction method.[4,5] Furthermore, in a preceding paper[6] the formation constants of metal-Rxan complexes in a 1:1 v/v water–*N,N*-dimethylformamide (DMF) medium were determined by polarography.

Following the previous research, the formation constants of metal–R$_2$dtc and –R$_2$dtp complexes in a water–DMF medium were determined. The stabilities of these complexes are discussed on the basis of the basicity of the ligands.

Experimental

Reagents. KR$_2$dtp and NaR$_2$dtc were synthesized and purified according to methods described in the literature.[7,8] Aqueous solutions of KR$_2$dtp were freshly prepared and those of NaR$_2$dtc were prepared immediately before use due to the instability of their solutions.

Stock solutions of cadmium(II), zinc(II), and lead(II) were prepared by dissolving each nitrate salt in 0.1 mol dm^{-3} of nitric acid, respectively. These solutions were volumetrically standardized with EDTA.

Apparatus and Procedures. The decomposition rate of R$_2$dtc$^-$ was spectrophotometrically measured at 285 nm according to a previously described procedure.[6]

Direct-current polarographic waves were recorded with the same apparatus and under the same conditions as previously described.[6]

Results and Discussion

Acid Dissociation Constant of HR$_2$dtc. The decomposition rate of R$_2$dtc$^-$ depended on the pH of the test solution. Hence, the decomposition rate (k_3) and the acid-dissociation (K_a) constants of HR$_2$dtc were determined using similar equations to those of the preceding paper:[6]

$$-\frac{\mathrm{d}\ln([\mathrm{R_2dtc^-}]+[\mathrm{HR_2dtc}])}{\mathrm{d}t} = \frac{k_3}{1+K_a[\mathrm{H^+}]} \equiv \kappa$$

$$\log\frac{\mathrm{Abs_1}}{\mathrm{Abs_2}} = \frac{\kappa}{2.303}(t_2-t_1)$$

where Abs$_1$ and Abs$_2$ denote the absorbances at time t_1 and t_2, respectively. The obtained constants are given in Table 1.

On the other hand, HR$_2$dtp were too stable for determining the constants by a method based on the decomposition rate.

Figure 1 shows plots of the pK_a value in an aqueous medium vs. that in a water–DMF medium. The data used in Fig. 1, except that determined in this paper, are quoted from the preceding paper[6] and others.[9-11] Obviously, a linear relationship exists between the

Table 1. Acid Dissociation (K_a) and Decomposition Rate (k_3) Constants of HR$_2$dtc

	R			
	Methyl	Ethyl	Propyl	Butyl
pK_a	4.25	4.62	4.72	4.80
k_3/min^{-1}	11.2	21.4	15.6	15.9

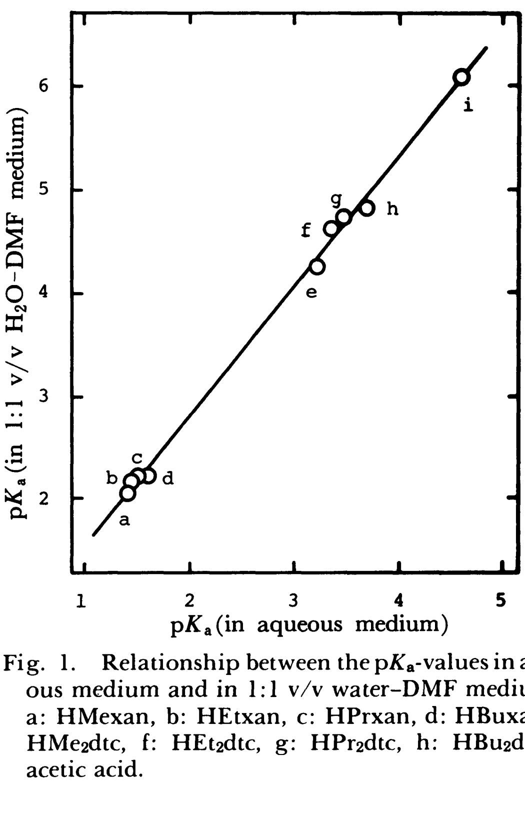

Fig. 1. Relationship between the pK_a-values in aqueous medium and in 1:1 v/v water–DMF medium. a: HMexan, b: HEtxan, c: HPrxan, d: HBuxan, e: HMe$_2$dtc, f: HEt$_2$dtc, g: HPr$_2$dtc, h: HBu$_2$dtc, i: acetic acid.

two variables. Therefore, the unknown pK_a values of HEt_2dtp and HBu_2dtp in the water–DMF medium can be estimated from the values for the aqueous medium[12] by means of a straight-line relationship. Thus, their values were obtained as 0.18 and 0.58, respectively.

Formation Constants of Metal–R_2dtc and –R_2dtp Complexes. The direct-current polarographic waves, which were all cathodic and quasi-reversible waves for the two-electrons reduction of metal ions, were analyzed in the same manner as described previously[6]

Table 2. Formation constants (β_j) of Metal-R_2dtc and -R_2dtp Complexes

			R			
			Methyl	Ethyl	Propyl	Butyl
R_2dtc	Cd	log β_3	19.12	19.83	20.03	20.30
R_2dtp	Cd	log β_2	4.70	5.96	5.92	—
		log β_3	6.33	7.82	7.82	8.83
		log β_4	7.01	8.76	8.76	9.95
	Zn	log β_3	—	2.47	2.57	—
	Pb	log β_2	5.85	7.38	—	—
		log β_3	8.02	9.64	9.71	10.66
		log β_4	8.76	10.44	10.86	11.84

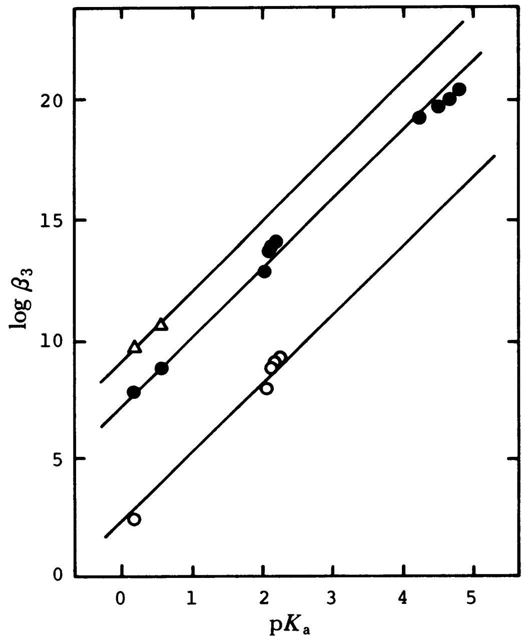

Fig. 2. Plots of log β_3 for metal complex vs. pK_a for ligand.
△: lead(II) complex, ●: cadmium(II) complex, ○: zinc(II) complex.

and the overall formation constants, β_j, of the complexes were obtained (Table 2).

It was observed that the β_j value for each metal increased upon increasing the pK_a value, i.e., the basicity of the ligand. This tendency was confirmed for β_3, including the results for metal–Rxan complexes[6] (Fig. 2). The individually observed points for each metal lie well along straight parallel lines. This is one instance of a "linear free-energy relationship",[13] indicating that R_2dtc^-, R_2dtp^-, and $Rxan^-$ have similar charactaristics regarding the formation of a metal complex. The difference in the complex-forming abilities of these ligands might be due to a difference in the electron density on the sulfur atoms in the ligand molecules.[14]

The β_3 values of the lead- and zinc-R_2dtc complexes could not be determined because of the difficulty in finding the pH region in which neither the hydrolysis of the metal ion nor the acid decomposition of the ligand occurred. However, these values can be estimated, respectively, by reading off a point on the line in Fig. 2.

References

1) E. M. Donaldson, *Talanta,* **23**, 417 (1976).

2) J. Stary, "The Solvent Extraction of Metal Chelates," Pergamon Press, London (1964), pp. 155—168.

3) H. Bode and W. Arnswald, *Fresenius' Z. Anal. Chem.,* **185**, 13 (1962).

4) Y. Sasaki, *Bunseki Kagaku,* **31**, E107 (1982).

5) K. Hayashi, Y. Sasaki, S. Tagashira, and M. Nakashima, *Anal. Sci.,* **1**, 51 (1985).

6) K. Hayashi, Y. Sasaki, S. Inomata, and T. Yanagidani, *Bull. Chem. Soc. Jpn.,* **57**, 3074 (1984).

7) K. Hayashi, Y. Sasaki, S. Tagashira, S. Inomata, J. Rikitake, Y. Hisatomi, and M. Suzuki, *Bunseki Kagaku,* **33**, 247 (1984).

8) D. Oktavec, J. Štefanec, B. Sîleš, V. Konečný, and J. Garaj, *Collect. Czech. Chem. Commun.,* **44**, 2487 (1979).

9) K. I. Aspila, C. L. Chakrabarti, and V. S. Sastri, *Anal. Chem.,* **45**, 363 (1973).

10) H. Majima, *Sci. Rep. Res. Inst. Tohoku Univ., Ser. A,* **13**, 183 (1962).

11) The values for acetic acid were obtained by the analysis of the acid-base titration curve of acetic acid with sodium hydroxide solution in each medium by using the same pH meter.

12) R. H. Zucal, J. A. Dean, and T. H. Handley, *Anal. Chem.,* **35**, 988 (1963).

13) P. R. Wells, *Chem. Rev.,* **63**, 171 (1963).

14) R. Eisenberg, "Progress in Inorganic Chemistry," ed by S. J. Lippard, J. Wiley and Sons Inc., New York (1970), Vol. 12, p. 330.