BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 44, 3461—3462 (1971)

Formation Constants of Several Copper(II) Alkylthioacetates in a Dioxane-Water Solvent

Akira OUCHI, Toshio TAKEUCHI, and Yayoi OHASHI

Department of Chemistry, College of General Education, The University of Tokyo, Komaba, Meguro-ku, Tokyo

(Received January 14, 1971)

Recently the present authors synthesized and studied the alkylthioacetates of several metals in the solid state.[1-3] Concerning the stability of alkylthioacetato complexes, Irving[4] and Sandell[5] have published the formation constants of some ethylthioacetates of some metals, and Yamasaki[6] has reported on the phenylthioacetates of some metals. Recently Pettit[7] has studied the silver complexes of a series of alkylthioacetic acids and found a linear relation between their stabilities and the Taft σ^* values of their alkyl groups. However, the relation has not yet been examined with regard to the complexes of other metals. Consequently, it seems interesting to furnish the formation-constant data of the copper(II) complexes of a series of alkylthioacetic acids.

Experimental

Materials. *Alkylthioacetic acids*: Methyl-, ethyl-, *n*-propyl-, isopropyl-, *n*-butyl-, isobutyl-, *s*-butyl-, and benzylthioacetic acids were synthesized by the method described in the papers of Larsson[8] and Pettit.[7] They were used after the redistillation under reduced pressure.

1,4-Dioxane: G. R.-grade reagent of the Wako Chemical Co., Ltd. was used after being purified according to the directions of Riddich and Toops.[9]

All other reagents were G. R. reagents of the Wako Chemical Co., Ltd., and were used without any further purification.

General Procedure. The techniques employed were those of Calvin.[10] A Toa Denpa Co. model HM-5A pH meter, a saturated calomel electrode, and a glass electrode were used. All the measurements were made at 30.0±0.1°C. The pH meter was standardized against aqueous buffer solutions (6.86 and 4.00) of the Wako Chemical Co.

The Measurement of the Acid Dissociation Constants: 25 m*l* of dioxane, 5 mmol of potassium nitrate, and 1 mmol of alkylthioacetic acid were diluted to 50 m*l* with water. The sample was titrated with a 1.000N sodium hydroxide standard aqueous solution[11] to record the pH meter reading (B): the B value of the half-neutralization point on the titration curve was thus obtained. pK_D, where K_D is the acid dissociation constant, was obtained by $pK_D = B + (\log U_H^0 + \log 1/\gamma)$ where U_H^0 is a conversion factor independent of the ionic concentration and where the γ is the activity coefficient of the strong electrolytes in the solution; they were conveniently obtained by means of the diagram of Uitert.[12]

The Determination of the Formation Constants of the Complexes. 25 m*l* of dioxane, 4 mmol of potassium nitrate, 1 mmol of nitric acid, 0.1 mmol of metal nitrate, and 1 mmol of the ligand were mixed and diluted to 50.00 m*l* with water. The sample was thermostatted more than 4 hr to attain the equilibrium. However, to avoid the effect of decomposition, the sample was titrated within 6 hr after the dissolution. Each run was repeated 4 times, and the average readings were adopted. No precipitation was found during the process ($\bar{n}<2$). The calculation of the formation constants, including the correction for the effect of the dioxane solution, was made as has been described by Calvin,[10] Uitert,[12-14] and Goldberg.[15]

Results and Discussion

A typical run of the data and the results of the calculations are shown in Table 1. The acid dissociation constants obtained, as well as the formation constants of copper(II) complexes of alkylthioacetates are shown in Table 2.

The dissociation constants of these acids are almost all the same. This fact suggests that the inductive effect of the alkyl group does not seriously affect the carboxyl group, as they are separated by a $-S-CH_2-$ group. On the other hand, the coordination ability of sulfur atom should be affected by the alkyl group.

1) A. Ouchi, Y. Ohashi, T. Takeuchi, and Y. Yoshino, This Bulletin, **43**, 1088 (1970).
2) Y. Ohashi, T. Takeuchi, A. Ouchi, and Y. Yoshino, *ibid.*, **43**, 2845 (1970).
3) A. Ouchi, T. Takeuchi, and Y. Ohashi, *ibid.*, **44**, 731 (1971).
4) R. J. Irving and W. C. Fernelius, *J. Phys. Chem.*, **60**, 1427 (1956).
5) A. Sandell, *Acta Chem. Scand.*, **15**, 190 (1961), **24**, 1561, 1718 (1970).
6) K. Suzuki and K. Yamasaki, *J. Inorg. Nucl. Chem.*, **24**, 1093 (1962).
7) L. D. Pettit and C. Sherrington, *J. Chem. Soc., A*, **1968**, 3078.
8) E. Larsson, *Ber.*, **63**, 1347 (1930).
9) J. A. Riddich and E. E. Toops, Jr., "Organic Solvents," 2nd Ed., Interscience Publ. Ltd., London, 1955, p. 371.
10) M. Calvin and K. W. Wilson, *J. Amer. Chem. Soc.*, **67**, 2003 (1945).
11) As the sample was titrated with sodium hydroxide aqueous solution, the concentration of dioxane was not always 50% during the titration. Consequently, the conversion factors of each dioxane concentration were used for each of the calculations, assuming that the total volume was obtained by the addition of both volumes. In these regions the difference of $(U_H^0 + \log 1/\gamma)$ per 1% difference of dioxane concentration is about 0.02. Therefore the above correction is enough to keep the calculation error below 0.01, and the difference of pK_D and $\log K$ values in this dioxane concentration region is expected to be below 0.02. In Table 2, the concentration of dioxane was shown as 50%. It is only the approximate concentration where the data were obtained, even though the error from the value at 50% is expected to be below 0.02.
12) L. G. V. Uitert and W. C. Fernelius, *J. Amer. Chem. Soc.*, **76**, 5887 (1954).
13) L. G. V. Uitert and C. G. Haas, *ibid.*, **75**, 451 (1953).
14) L. G. V. Uitert, C. G. Haas, W. C. Fernelius, and B. E. Douglas, *ibid.*, **75**, 455 (1953).
15) D. E. Goldberg, *Chem. Educ.*, **40**, 341 (1963).

Table 1. Titration of 50% dioxane-water solution of copper nitrate (2.00×10^{-3}M), *n*-propylthioglycolic acid (2.00×10^{-2}M), potassium nitrate (8.00×10^{-2}M), and nitric acid (2.00×10^{-2}M) with standard aqueous solution of sodium hydroxide (1.000N)

NaOH (m*l*)	*B*	$\bar{n}$	p(Ch$^-$)
1.050	3.44	0.56	3.47
1.100	3.67	0.86	3.26
1.150	3.85	1.18	3.10
1.200	4.08	1.40	2.90
1.300	4.37	1.92	2.67

B: Readings of the pH meter standardized with aqueous buffer.
(Ch$^-$): Mole concentration of the monovalent chelate anion Ch$^-$.
$\bar{n}$: The number of coordinated ligand molecules per one metal ion.

Table 2. The dissociation constants and the formation constants of copper(II) complexes of alkylthioacetic acids in 50% dioxane[11] at 30°C

Metal Ligands (R=)	H^+ log K_1	Cu^{2+} log K_1	Cu^{2+} log K_2
$C_6H_5\cdot CH_2-$	-5.7_3	3.0	2.4
CH_3-	-5.5_6	3.4	2.7
C_2H_5-	-5.6_6	3.5	2.7
C_3H_7-	-5.6_8	3.5	2.9
$(CH_3)_2CH\cdot CH_2-$	-5.5_5	3.5	2.8
C_4H_9-	-5.6_6	3.6	2.9
$(CH_3)_2CH-$	-5.5_9	3.6	2.8
$(CH_3)(C_2H_5)CH-$	-5.6_6	3.6	2.8

Ligands are $RSCH_2COOH$ where R s are shown in the column above.

The relationship between the formation constants (in log *K*) of the copper complexes and the Taft σ* functions[16] of the substituent, R, for the $R\cdot S\cdot CH_2CO_2H$ ligand is shown in Fig. 1. As is shown in the figure, there is almost a linear relationship between them. This fact also seems to prove the existence of the sulfur-metal bond in the copper complexes, even in the solution.

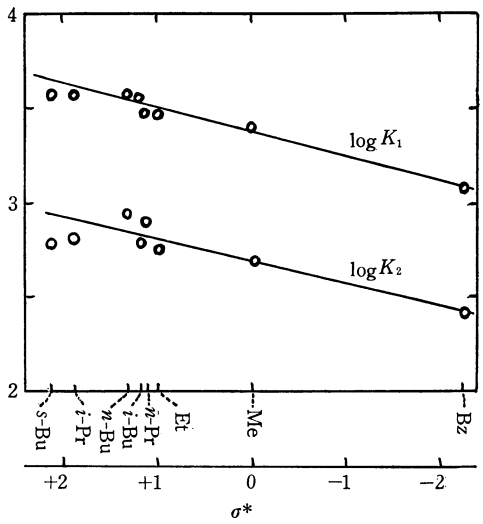

Fig. 1. The relationship between the formation constants of the copper(II) complex and the Taft σ* functions of the substituents R for the ligands $R\cdot S\cdot CH_2COOH$.
R of the ligansd are as follows: Bz : $C_6H_5CH_2$, Me : CH_3, Et : C_2H_5, *n*-Pr : C_3H_7, *i*-Pr : $(CH_3)_2CH$, *n*-Bu : C_4H_9, *i*-Bu : $(CH_3)_2CH\cdot CH_2$, *s*-Bu : $(C_2H_5)(CH_3)CH$

The points of isopropyl- and *s*-butyl-thioacetates, however, all a little lower than the line; this is probably due to the difficulty of the complex formation because of the steric effect of the ligand.

The authors wish to thank Professor Yukichi Yoshino and our colleagues of this laboratory for their helpful discussions.

16) R. W. Taft, Jr., *J. Amer. Chem. Soc.*, **75**, 4231 (1953).