

by another. These constants are tabulated in Table IV. This table shows the data in a form suitable for the comparison of relative structural effects. The dominating factor seems to be the larger entropy changes as the amines become larger. The free energy changes show the most

regular trends here reflecting the rough ordering according to base strengths mentioned earlier.

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[CONTRIBUTION FROM THE WILLIAM ALBERT NOYES LABORATORIES, DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ILLINOIS, URBANA, ILLINOIS]

Chelating Tendencies of Some *alpha*-Mercaptoacetamides with Bivalent-Metal Ions

BY DEAN F. MARTIN

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Acid dissociation constants of several α -mercaptoacetamides and formation constants of some bivalent-metal chelates have been determined. The effects of substitution are discussed.

Introduction

The efficacy of "thionalide,"^{1,2} 2-C₁₀H₇NHCO-CH₂SH, as an analytical precipitating agent has long been recognized.^{3,4} The use of "thionalide" in the volumetric analysis of various metals is discussed by Kolthoff and Belcher.⁵

In view of the usefulness of "thionalide," it would be of interest to study the properties of

pared by the method of Bersin.⁷ This consists in the reaction of an equimolar mixture of reactants (amine, NH₄SCN and α -chloroalkanoic acid), hydrolysis of the carbamate thus formed and acidification of the basic solution to obtain the mercaptoacetamide. The preparation of 2-mercapto-*N*-butyramide (VI) represents a typical preparation except that an α -bromo acid was used as a reactant.

CH₃CH₂CH(SH)CONHC₆H₅.—A mixture of aniline (18.6 g., 0.2 mole), α -bromobutyric acid (33.4 g., 0.2 mole) and NH₄SCN (14.2 g., 0.2 mole) in 50 ml. of 95% ethanol was

TABLE I
MERCAPTOACETAMIDES^a OF THE TYPE ArNHCOCH(SH)R

Compound No.	Ar	R	Yield, %	M.p., °C	Re-cryst. solvent ^a	Mol. wt.		Carbon, %		Hydrogen, %		Nitrogen, %	
						Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
I	C ₆ H ₅	H	167.23	170 ^d
II	4-CH ₃ C ₆ H ₄	H	61	126–128 ^e	A	181.26	180	59.63	59.38	6.12	5.83	7.73	7.72
III	2,5-(CH ₃ O) ₂ C ₆ H ₃	H	52	88–90	A	227.35	227	52.83	52.78	5.76	5.53	6.19	6.33
IV	2,6-(CH ₃) ₂ C ₆ H ₃	H	24	129–131 ^f	A	195.28	199	61.50	61.85	6.71	6.72	7.18	7.39
V	2,6-(C ₂ H ₅) ₂ C ₆ H ₃	H	8	118–120 ^e	B	223.34	225	64.54	64.82	7.67	7.47	6.28	6.38
VI	C ₆ H ₅	C ₂ H ₅	46	95.5–97 ^e	B	195.28	194	61.50	61.55	6.71	7.00	7.18	6.90

^a A, 50–75% ethanol; B, benzene-petroleum ether (b.p. 90–110°). ^b Purchased from Eastman Kodak Company. ^c Reported m.p. 110°, ref. 7. ^d Iodimetric titration, ref. 5. ^e Reported m.p. 126°, ref. 6. ^f Reported m.p. 129°, ref. 6. ^g Reported m.p. 95° [H. Beckurts and G. Frerichs, *J. prakt. Chem.*, [2] 66, 172 (1902)].

other mercaptoacetamides. A number of such compounds and their gold(I) derivatives have been prepared by Weiss,⁶ and the preparation of 2-mercaptoacetanilide (I) and its cobalt salts have been reported by Bersin.⁷ However, the dissociation constants of mercaptoacetamides and formation constants of the metal derivatives appear never to have been determined. In this communication, such data are reported.

Experimental⁸

Preparation of Mercaptoacetamides. (Table I).—The ligands, white solids, having a characteristic odor, were pre-

(1) 2-Mercapto-*N*-2-naphthylacetamide.

(2) The names and corresponding numbers of the compounds prepared for this study are: 2-mercapto-*N*-phenylacetamide, I; 2-mercapto-*N*-(4-methylphenyl)-acetamide, II; 2-mercapto-*N*-(2,5-dimethoxyphenyl)-acetamide, III; 2-mercapto-*N*-(2,6-dimethylphenyl)-acetamide, IV; 2-mercapto-*N*-(2,6-diethylphenyl)-acetamide, V; 2-mercapto-*N*-phenylbutyramide, VI.

(3) R. Berg and W. Roebing, *Z. angew. Chem.*, **48**, 430 (1935).

(4) For a summary of pertinent references see: J. H. Yoe and L. A. Sarver, "Organic Analytical Reagents," John Wiley and Sons, Inc., New York, N. Y., 1945, pp. 155, 258.

(5) I. M. Kolthoff and R. Belcher, "Volumetric Analysis," Vol. III, Interscience Publishers, Inc., New York, N. Y., 1957, pp. 391–393.

(6) U. Weiss, *THIS JOURNAL*, **69**, 2684 (1947).

warmed. The solution became yellow as a white solid precipitated and vigorous refluxing began. The mixture was quickly poured over ice, and a yellow-white solid crystallized.⁹ The carbamate was collected, air-dried (wt., 31 g.), then ground with about 50 ml. of concd. NH₄OH. The filtered hydroxide solution was acidified (1:2 HCl) at 0–10°. The resulting white solid was collected, dried (wt., 18.0 g.) and recrystallized.

Potentiometric Titrations.—Acid dissociation constants in dioxane-water mixtures were determined by the method of Van Uitert,¹⁰ using tetramethylammonium hydroxide. Potentiometric titrations were performed as previously described.¹¹ Formation constants were calculated using the method of Block and McIntyre.¹²

Discussion

Acid Dissociation Constants.—The pK_D values of the mercaptoacetamides were determined as a function of mole fraction of dioxane (N_2) at 30°. Mathematical expressions for the linear pK_D-N_2

(7) T. Bersin, *Z. anal. Chem.*, **85**, 428 (1931).

(8) Microanalyses were performed at the University of Illinois by Mrs. A. Bay, Miss J. Liu and Mr. J. Nemeth.

(9) Usually the carbamate crystallized at once, but the carbamate of V was obtained as an oil.

(10) (a) L. G. Van Uitert, *et al.*, *THIS JOURNAL*, **75**, 455 (1953);

(b) *ibid.*, **76**, 5887 (1954).

(11) L. G. Van Uitert, *et al.*, *ibid.*, **75**, 457 (1953).

(12) B. P. Block and G. H. McIntyre, Jr., *ibid.*, **75**, 5667 (1953).

relationship are listed in Table II. The pK_D values of β -diketones^{10a} and of β -ketoamines¹³ deviate from linearity at lower values of N_2 , presumably because of changes in tautomeric equilibria. However, such deviations were not noted in this study.

TABLE II

pK_D EQUATIONS ($pK_D = a + bN_2$)^a OF SOME MERCAPTO-ACETAMIDES

Compound	a	b
I	8.08	10.53
II	8.06	10.65
III	7.93	10.93
IV	8.35	10.38
V	8.08	11.12
VI	8.44	12.22

^a Reliable within ± 0.05 ; N_2 range 0.137-0.380.

The substitution of an ethyl group on the carbon atom adjacent to the mercapto group (VI) is accompanied by a marked increase in the pK_D value. This would be expected on the basis of an inductive effect. However, the replacement of an *N*-phenyl group by a 2,5-dimethoxyphenyl (III) or a 4-methylphenyl (II) has little or no effect on the pK_D value. A marked increase in pK_D is

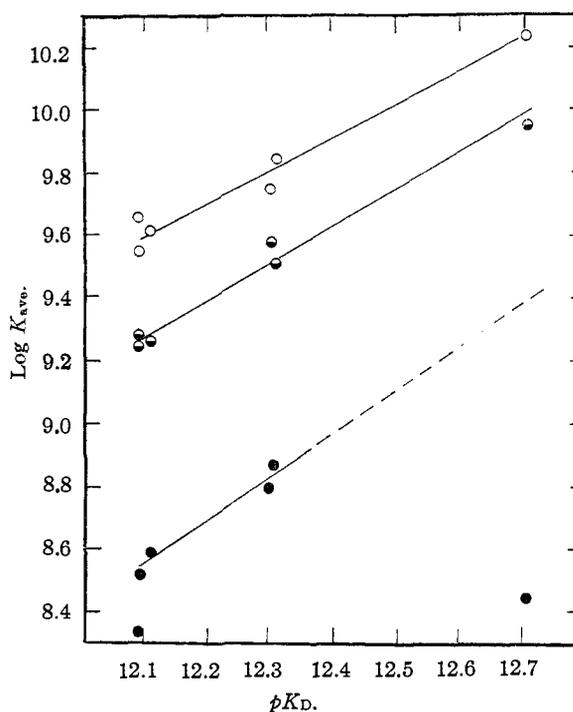


Fig. 1.—Variation of $\log K_{ave}$ of divalent-metal chelates as a function of pK_D for mercaptoacetamides: O, UO_2 ; ◐, Be; ●, Ni.

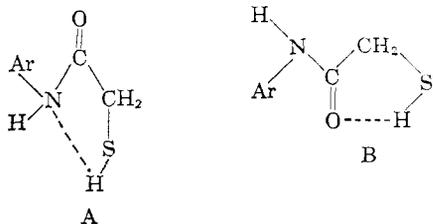
TABLE III

FORMATION CONSTANTS ($\log K_n$)^a OF BIVALENT-METAL CHELATES OF SOME MERCAPTOACETAMIDES IN 75 VOL. % DIOXANE ($N_2 = 0.380$) AT 30°

Compound	#	UO_2^b	Zn	Be ^b	Cu	Ni	Co	Mn
I	1	10.14 ± 0.01^a	10.38 ± 0.01	9.54 ± 0.03	Ppt.	8.83 ± 0.03	Ppt.	6.3^d
	2	$8.96 \pm .01$	$8.88 \pm .01$	$8.93 \pm .03$		$7.82 \pm .05$		Ppt.
II	1	$10.18 \pm .02$	$10.33 \pm .02$	$9.48 \pm .03$	Ppt.	$8.84 \pm .02$	Ppt.	6.4^d
	2	$9.03 \pm .02$	$9.16 \pm .01$	$9.02 \pm .04$		$8.34 \pm .01$		Ppt.
III	1	$10.21 \pm .02$	$10.04 \pm .01$	$9.59 \pm .01$		$8.79 \pm .02$	Ppt.	6.4^d
	2	$9.10 \pm .01$	$8.66 \pm .02$	$8.96 \pm .02$		$8.25 \pm .03$		Ppt.
IV	1	$10.30 \pm .02$	$10.28 \pm .03$	$9.84 \pm .02$	Ppt.	$9.06 \pm .02$	Ppt.	Ppt.
	2	$9.17 \pm .01$	$9.30 \pm .03$	$9.30 \pm .03$		$8.52 \pm .02$		
V	1	$10.42 \pm .02$	$10.18 \pm .02$	$9.81 \pm .02$		$9.18 \pm .02$		
	2	$9.26 \pm .01$	$9.07 \pm .01$	$9.20 \pm .03$		$8.57 \pm .02$		
VI	1	$10.78 \pm .01$	$10.56 \pm .01$	$10.21 \pm .02$	Ppt.	$8.74 \pm .03$	Ppt.	Ppt.
	2	$9.68 \pm .01$	$9.09 \pm .02$	$9.68 \pm .02$		$8.14 \pm .02$		

^a $\log K_1$ and $\log K_2$ for the equilibria $M^{++} + Ch^- \rightleftharpoons MCh^+$ and $MCh^+ + Ch^- \rightleftharpoons MCh^2$ respectively. ^b These values were obtained using nitrate rather than perchlorate salts. ^c 95% confidence limits. ^d Approximate values calculated by method of Van Uitert and Haas [L. G. Van Uitert and C. G. Haas, THIS JOURNAL, 75, 451 (1953)].

noted with alkyl groups in the 2,6 positions (compounds IV and V).



(13) D. F. Martin, G. A. Janusonis and B. B. Martin, *J. Am. Chem. Soc.*, 83, 73 (1961).

These observations suggest that structure A is of little importance because the substituents present in II and III would surely increase the electron density about the nitrogen atom. The fact that 2,6- but not 2,5-disubstitution causes an increase in the pK_D may be rationalized in terms of structure B: It is suggested that the presence of substituents in the 2,6 positions introduces steric restrictions and forces the carbonyl oxygen toward the mercapto group. This is reflected in an increased pK_D value.

Formation Constants.—The formation constants, obtained in 75 volume % dioxane ($N_2 = 0.380$) at 30°, are recorded in Table III. Clearly, the chelates of beryllium, uranyl and zinc are very stable,

those of nickel are much less so. The order of relative stabilities appears to be: $\text{UO}_2 > \text{Be} > \text{Ni} > \text{Mn}$. The position of zinc in this series depends upon the ligand. Unfortunately, data are not available for the copper chelates because of their general insolubility. However, titration data indicate that the copper chelate of III is more stable than the uranyl derivative.¹⁴

In general, there is a good correlation between $\log K_{\text{ave}}$, $1/2(\log K_1 + \log K_2)$, for a given metal and the pK_D of the mercaptoacetamides (Fig. 1). A similar relationship is observed using $\log K_1$ or $\log K_2$ instead of $\log K_{\text{ave}}$. This observation has been made for other ligands including β -diketones,¹¹ tropolones¹⁵ and salicylaldehydes.¹⁶

The relationship depicted in Fig. 1 indicates that steric effects are of minor importance in determin-

(14) The value of $\log K^2$ for the copper chelate is estimated to be about 12. Presumably, $\log K_1$ is greater.

(15) B. E. Bryant and W. C. Fernelius, *THIS JOURNAL*, **76**, 1696 (1954).

(16) M. Calvin and K. W. Wilson, *ibid.*, **67**, 2003 (1945).

ing the stabilities of the uranyl, beryllium and (generally) nickel chelates. A steric effect may be involved with the nickel derivative of VI. This chelate is markedly less stable than would be predicted from the $\log K-pK_D$ relationship. The deviation is genuine since the value in question is reproducible. The effect is reminiscent of the reduced stability which results when β -diketones are substituted in the methylene position^{16,17} and may well stem from a common cause. Steric factors may be responsible for the poor $\log K-pK_D$ correlation of zinc chelates. This view is supported by the lessened stability of the 2,6-diethylphenyl derivative (V) relative to that of the unsubstituted compound (I).

Acknowledgments.—This investigation was conducted during the tenure of a Summer Faculty Fellowship for which the author expresses his gratitude to the University of Illinois Research Board. The author is indebted to the Ethyl Corporation for supplying the 2,6-diethylaniline used in the preparation of V.

[CONTRIBUTION FROM SCHOOL OF CHEMISTRY, UNIVERSITY OF MINNESOTA, MINNEAPOLIS, MINNESOTA]

The Exchange of Iron between the Aquo Ferrous and Ferric Versenate Ions

BY W. L. REYNOLDS, NORA LIU AND J. MICKUS

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Electron transfer in the ferrous Versenate–ferric Versenate exchange reaction occurs chiefly between the Versenate complexes of Fe(II) and Fe(III) and not between any dissociation products of these complexes at pH 2. The electron transfer between the undissociated Versenate complexes of Fe(II) and Fe(III) probably occurs by tunnelling. The exchange of ⁵⁹Fe between $\text{Fe}^{+2}(\text{aq})$ and FeY^- was found to be slow, and this exchange was compared with other electron-transfer reactions involving $\text{Fe}^{+2}(\text{aq})$ and ionic oxidants on the basis of Marcus' theory of electron-transfer reactions.

The rate of the electron-transfer reaction between ferrous Versenate and ferric Versenate complexes, or their protonated forms, has been reported¹ to be immeasurably rapid under the experimental conditions employed. At pH 2, the acidity employed by Adamson and Vorres,¹ one must consider the presence of the protonated species HFeY^- and HFeY ,² as well as FeY^{-2} and FeY^- . Here Y^{-4} represents the ethylenediaminetetraacetic acid anion. Three general mechanisms have to be considered for this exchange. The first is the direct electron-transfer reaction 1 between FeY^{-2} and FeY^- or an analogous reaction involving one or more protonated species

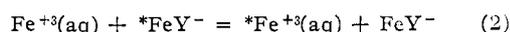


The second mechanism involves the dissociation of the Versenate complexes, an electron-transfer reaction between the aquo ions and reformation of the complexes. This mechanism can be immediately discounted for the following two reasons. First, the formation constants of these complexes are sufficiently large² so that the equilibrium concentrations of $\text{Fe}^{+2}(\text{aq})$ and $\text{Fe}^{+3}(\text{aq})$, and hence

(1) A. W. Adamson and K. S. Vorres, *J. Inorg. Nuclear Chem.*, **3**, 206 (1956).

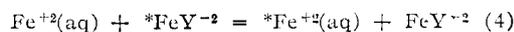
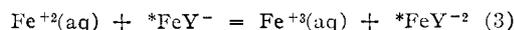
(2) G. Schwarzenbach and J. Heller, *Helv. Chim. Acta*, **34**, 576 (1951).

the rate of exchange between these ions, would be too small to account for the rapid rate of the exchange observed between the Versenate complexes of Fe(II) and Fe(III). Second, Jones and Long³ have measured the rate of the exchange in (2) as



a function of pH. The fact that the exchange is slow means that the dissociation of FeY^- is at least as slow under the same conditions. Hence the dissociation of FeY^- is too slow to be part of the mechanism by which exchange of iron occurs between the Versenate complexes.

The third mechanism to be considered is



This mechanism involves an electron-transfer reaction in (3) and an exchange without electron transfer in (4). Jones and Long³ found that the exchange in (4) was too rapid to measure in the pH range from 1.50 to 4.74. Adamson and Vorres¹ used an excess of Fe^{+2} over Y^{-4} so that aquo Fe^{+2} was present. Hence if the rate constant of the forward reaction in (3) was not too small, re-

(3) S. S. Jones and F. A. Long, *J. Phys. Chem.*, **56**, 25 (1952)