distribution of the nitrogen is such that errors may be introduced into both the "basic" nitrogen and the "non-basic nitrogen" fractions of a Van Slyke determination.

ST. PAUL, MINN.

[COMMUNICATION FROM THE CHEMICAL LABORATORY OF JOHNS HOPKINS UNIVERSITY.]

A SULFIDE ACID OR THE BUTYL ETHER OF THIOGLYCOLIC ACID.

BY YOSHISUKE UYEDA AND E. EMMET REID.

Received August 30, 1920.

Introduction.

Sulfur, when present in an organic compound in the sulfide condition, $= CH—S—CH =$, may have comparatively slight influence on the chemical and physical properties of the compound while in some cases it gives rise to peculiar properties, as in β,β′-dichloro-ethyl sulfide. In this remarkable compound the presence of the sulfur atom renders the chlorine atoms very reactive.

It seemed of interest to prepare other compounds containing a sulfide grouping along with some other group with a distinctive function. The present investigation is a study of the acid, $CH_3CH_2CH_2CH_2 — S — CH_2$-COOH, and some of its derivatives. Thiophene has nearly the same boiling point as benzene but a considerably higher density and the same may be said of ethyl sulfide as compared with hexane. In physical properties the above acid and its esters should resemble caprylic acid, $C_8H_{16}O_2$, and its esters to which they are nearest in molecular weight. This has been found to be true in a general way, though the acid boils at 282.2°, which is 45° higher than caprylic.

The sulfide acid forms salts readily, the sodium salt being very soluble in water while the barium and calcium salts are only moderately so. When mineral acids are added to water soltuions of its salts the acid separates readily as a heavy oil which would easily be mistaken for one of the fatty acids of about its molecular weight, even to the odor. It is very slightly soluble in water and distils without decomposition. The odors of its esters are somewhat like those of the higher aliphatic esters.

The acid is readily prepared by the action of sodium chloro-acetate on the sodium salt of butyl mercaptan in water solution. Its esters and many of its salts are easily obtained by the usual methods. The esters give good results on quantitative saponification as the acid is accurately titrated with phenolphthalein.

The remarkable fact about β,β′-dichloro-ethyl sulfide is that the influence of the sulfur renders the chlorine atoms quite movable.[1] This

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[1] Marshall, *J. Am. Med. Assoc.*, 73, 684 (1919); *C. A.*, 13, 2929 (1919).

same influence appears in the instability of the corresponding acetate as recently brought out by Helfrich and Reid.[1] It appears here that the amide of this new acid decomposes readily and its anilide and toluidide were found too unstable to prepare for analysis.

Historical.

Letts and Collie[2] prepared the methyl ether of thioglycolic acid by the action of methyl sulfide on ethyl iodoacetate and made the sodium and barium salts of the corresponding acid.

Claesson[3] obtained the corresponding ethyl derivative by the action of the ethyl chloro-acetate on sodium ethyl mercaptide in alcohol solution and the saponification of the ethyl ester with a solution of barium hydroxide in a sealed tube. They prepared a number of its salts and the amide (m. p. 44°). The amyl ether was made in the same way but was not studied. His method is cumbersome and round about.

Experimental.

To 600 cc. of water are added 120 g. of sodium hydroxide and 360 g. of crude butyl mercaptan (containing 75% BuSH) and into this solution, while it is stirred and cooled, is poured a concentrated solution of 285 g. of chloro-acetic acid previously neutralized with sodium carbonate. Much heat is evolved in the reaction and efficient cooling is required. After some hours, the mixture is heated and then steam distilled to drive off volatile impurities derived from the crude mercaptan. On addition of dil. sulfuric acid to the filtered solution, the free acid forms as an oily layer, which is separated, dried, and distilled under diminished pressure. From the above amounts, 395 g. of crude acid or 87% of that calculated, was obtained. The fraction, 245 g., boiling 140–4° at 10–15 mm., was collected.

Properties.—It is a slightly yellowish oil, still liquid at —14°; it boils with only slight decomposition. It is almost insoluble in water but mixes with alcohol and ether.

Identification Derivative.—The *p*-nitrobenzyl ester[4] was found to be an oil but the *p*-bromophenacyl ester[5] was readily obtained, m. p. 95°.

Salts.—The barium and calcium salts were made by adding the respective carbonates to the acid suspended in hot water, after which the solutions were filtered and cooled. The barium salt separates as transparent tablets with the peculiar property of being quite flexible. It is readily soluble in hot water and only sparingly so in cold water. The calcium salt separates as an aggregate of white leaflets, readily soluble in water. The

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[1] Helfrich and Reid, THIS JOURNAL, **42**, 1208 (1920).

[2] Letts and Collie, *Jahresb.*, **1878**, p. 685.

[3] Claesson, *Bull. soc. chim.* [2] **23**, 444 (1875).

[4] THIS JOURNAL, **39**, 124 (1917).

[5] *Ibid.*, **42**, 1043 (1920).

strontium salt was made from solutions of the sodium salt by precipitation with strontium chloride. It is obtained as transparent tablets, rather soluble in water. The nickel and cobalt salts were prepared from solutions of the barium salt and of the sulfates of these metals. The nickel salt is obtained as minute faintly green crystals, sparingly soluble in water.

The zinc salt was prepared from the carbonate and a suspension of the acid in hot water. It separates as fine silky needles rather soluble in water.

The cadmium and manganese salts were prepared by double decomposition from the sodium salt and sulfates of these metals. The cadmium salt forms minute colorless crystals sparingly soluble in water. The manganese salt separates as faintly pink flakes, rather soluble in water.

The copper salt was prepared from the barium salt and copper sulfate and came down as minute blue crystals, fairly soluble in water. The silver salt was obtained from the barium salt with silver nitrate solution, as minute gray crystals only sparingly soluble in water. It is anhydrous and melts at 137.5°.

By passing dry ammonia into an ether solution of the acid according to McMaster's method[1] the ammonium salt separated as a crystalline mass but it is unstable and analysis showed partial decomposition.

The magnesium and lead salts could not be obtained in crystalline form. The sodium salt is left as a syrupy very soluble mass when its water solution is evaporated but could not be obtained in condition for analysis.

For the corresponding ethyl acid, Claesson found the calcium and barium salts to be anhydrous. His zinc, cadmium, cobalt, nickel and copper salts agree with ours, while his silver salt contained one molecule of water of crystallization.

COMPOSITION AND ANALYSES OF SALTS.

	Water.		Metal.	
R = $C_6H_{11}O_2S$.	Calc. %.	Found. %.	Calc. %.	Found. %.
Ba $R_2 \cdot 0.5H_2O$	2.04	2.18	31.13	31.55
Ca $R_2 \cdot 0.5H_2O$	2.62	2.71	11.66	11.71
Sr $R_2 \cdot 1.5H_2O$	6.61	6.61	21.32	21.57
Ni $R_2 \cdot 2H_2O$	9.25	9.20	15.16	14.98
Co $R_2 \cdot 2H_2O$	9.25	9.25	15.16	15.32
Zn $R_2 \cdot 2H_2O$	9.13	9.65	16.45	15.72
Cd $R_2 \cdot H_2O$	4.24	4.08	26.41	26.16
Mn $R_2 \cdot H_2O$	4.90	5.14	14.98	15.45
Cu $R_2 \cdot 2H_2O$	9.16	9.09	16.03	16.43
Ag R	....	....	42.36	42.96

Acid Chloride, $C_4H_9SCH_2COCl$.—A mixture of 150 g. of the acid and 70 g. of phosphorus trichloride (calc. 45 g. for $^1/_3$ mol.) was heated for 2

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[1] McMaster, *Am. Chem. J.*, **49**, 84 (1913).

hours at 100°, then cooled to 0° and the acid chloride decanted.[1] The product was fractionated and the portion which boiled from 89–91° at 8 to 9 mm. was collected as the pure substance. Yield, 155 g. or 93%. The chloride is a colorless liquid with a peculiar odor; it fumes only slightly in the air. It boils at 218° (corr.) at 758 mm. with considerable decomposition. It has d_{25}^{25} 1.0956 and n_D 1.4810. Analysis gave 21.20% Cl, calculated 21.32.

Amide.—The amide is readily obtained by pouring the chloride into strong cold ammonium hydroxide. It melts at 65° and is not stable in contact with moist air.

Calc.: S, 21.76; N, 9.52. Found: S, 21.20; N, 9.30, 9.46.

Attempts were made to prepare the anilide and *p*-toluidide, but they could not be obtained pure.

Esters.—The esters were made from the acid chloride and the alcohols. The products were washed with water and sodium carbonate solution, dried and fractionated at reduced pressures. Weighed samples were saponified with standard sodium butylate in butyl alcohol according to method of Pardee and Reid.[2] The sulfur was determined by the Carius method. The properties and analyses are given in the table.

Analyses of Acids and its Esters.

	Mol. wt.				Sulfur.	
	Calc.	Found.	Subs. G.	$BaSO_4$. G.	Calc. %.	Found. %.
Acid	148	149	0.1707	0.2635	21.62	21.14
Methyl ester	162	160	0.1730	0.2480	19.75	19.65
Ethyl ester	176	179	0.1795	0.2347	18.18	17.93
Propyl ester	190	189	0.1750	0.2100	16.84	16.45
Butyl ester	204	202	0.2130	0.2365	15.68	15.25

Properties of Acid and its Esters.

	B. p. pressure. Mm.	B. p. cor. pressure. Mm.	d_0^0.	d_{25}^{25}.	Mol. vol. 0°.	$[n]_D^{25°}$.
Acid	$140°^{10}$	282.2^{764}	1.0771	1.0631	137.6	1.4780
Me ester	$85°^{10}$	224.0^{758}	1.0299	1.0125	157.5	1.4590
Et ester	$89–90°^{10}$	235.5^{758}	1.0044	0.9881	175.5	1.4560
Pr ester	$93–4°^{6}$	250.2^{758}	0.9892	0.9723	192.3	1.4555
Bu ester	$105–6°^{6}$	263.8^{758}	0.9794	0.9630	210.2	1.4555

Comparing the boiling points of our acid and its esters with those of *n*-hexoic acid and its esters, we find the following differences: acid, 77°; Me ester, 74°; Et, 67°; Pr, 65°; Bu, 59°. These differences are about as we would expect, when we consider that dibutyl sulfide (b. p. 182°) boils 57° higher than *n*-octane (b. p. 125°).

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[1] Aschan, *Ber.*, **31**, 2346 (1898).

[2] Pardee and Reid, *J. Ind. Eng. Chem.*, **12**, 129 (1920).

Summary.

The *n*-butyl ether of thioglycolic acid, $C_4H_9SCH_2COOH$, and some of its salts and derivatives have been studied. The following new compounds have been prepared. In each case R indicates the radical $C_4H_9SCH_2$.

$RCOOH$
$RCOCl$
$RCONH_2$
RCO_2CH_3
$RCO_2C_2H_5$
$RCO_2C_4H_9$
$(RCO_2)_2Ba.0.5H_2O$
$(RCO_2)_2Ca.0.5H_2O$
$(RCO_2)_2Sr.1.5H_2O$
$(RCO_2)_2Ni.2H_2O$
$(RCO_2)_2CO.2H_2O$
$(RCO_2)_2Zn.2H_2O$
$(RCO_2)_2Cd.H_2O$
$(RCO_2)_2Mn.H_2O$
$(RCO_2)_2Cu.2H_2O$
RCO_2Ag

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[FORTY-FOURTH CONTRIBUTION FROM THE COLOR LABORATORY, U. S. BUREAU OF CHEMISTRY.]

ISOCYANINE DYES FROM LEPIDINE AND ITS HOMOLOGS.

BY ELLIOT Q. ADAMS AND HERBERT L. HALLER.

Received Sept. 7, 1920.

The mixed alkyl halides[1] of quinoline[2] and lepidine[3] give with alcoholic alkalies blue dyes known as "cyanines;"[4] when quinaldine[5] replaces lepidine, pink "isocyanines"[6] are formed. In both cases the quinoline may be replaced by quinaldine so that the mixed alkyl halides of quinaldine and lepidine give with alcoholic alkalies a blue;[7] and alkyl halides of quinaldine only, a pink color.

From these and other data it has been concluded that "cyanine"[8] is a derivative of 4,4-diquinolyl-methane and "isocyanine" of 4,2-diquinolyl-methane. It needs hardly to be stated that the hydrogens (1) and (1′) must be replaced to permit the formation of dyes capable of existence in alkaline solution.

The formation of a dye with alkali and quinaldine alkyl halides alone is explained as a condensation of the 2-methyl and 4-hydrogen, respectively,

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[1] It is now known that other quaternary addition compounds react similarly but the earliest dyes of all the types mentioned were halides.

[2] Benzene-substituted quinolines react similarly.

[3] *I. e.*, 4-methyl quinoline; benzene-substituted lepidines react similarly.

[4] C. Greville Williams, *Chem. News*, **1**, 15 (1860).

[5] *I. e.*, 2-methyl quinoline. Benzene-substituted quinaldines react similarly.

[6] Spalteholz, *Ber.*, **16**, 1849 (1883). Hoogewerff and V. Dorp, *Rec. trav. chim.* **2**, 28, 41 (1883); **2**, 317–26 (1883); **3**, 336–62 (1884).

[7] The results obtained with this combination appear to be nowhere recorded in the literature available to us; since the blue solution thus prepared is a mixture of at least 5 dyes, no one of which can be obtained crystalline, this omission is hardly to be wondered at.

[8] This nomenclature was first suggested by Hoogewerff and V. Dorp, *loc. cit.* A more detailed explanation, together with a more complete bibliography, will be given in a paper from this laboratory by L. E. Wise.