1-Cyclopropylethyl S-Methyl Xanthate.—A general procedure for xanthate preparation[16] was employed. From 46.2 g. (0.495 mole) of 1-cyclopropylethanol, n^{25}_{D} 1.4292, there was obtained 1-cyclopropylethyl S-methyl xanthate boiling at 70° (0.2 mm.), 45.7 g., 52.3%, n^{25}_{D} 1.5454, d^{25}_{4} 1.0878, C–H absorptions at 3005 and 3082 cm.$^{-1}$, additional absorptions at 1225 and 1050(s) cm.$^{-1}$.

Anal. Calcd. for $C_7H_{12}OS_2$: C, 47.69; H, 6.86. Found: C, 47.84; H, 7.02.

Pyrolysis of 1-Cyclopropylethyl S-Methyl Xanthate.—1-Cyclopropylethyl S-methyl xanthate was pyrolyzed[10,12] as previously described for 1-cyclopropylethyl acetate. From 21 g. (0.119 mole) of 1-cyclopropylethyl S-methyl xanthate, n^{25}_{D} 1.5454, and at 200–245°, 3.7 g., 46%, of material boiling at 25–40° (755 mm.) was obtained. The latter material was washed with 50 ml. of cold 5% aqueous sodium bicarbonate, dried over calcium hydride and distilled from sodium metal to yield 1.1 g. of a 3-component olefin mixture.

Alternatively, 1-cyclopropylethyl S-methyl xanthate (116.8 g., 0.66 mole) was boiled in a small distillation assembly. Ebullition commenced at a pot temperature of 130° and the temperature slowly rose to a steady 230° value at which it was maintained for an additional 2 hr. The distillate was treated as above to yield 20 g., 44.5%, of an olefin mixture consisting of vinylcyclopropane, 95%, 1,4-pentadiene, trace amount, and an unidentified olefin, trace amount. Rectification through a 90 theoretical plate concentric tube column yielded vinylcyclopropane boiling at 40.5–40.8° (755 mm.), n^{25}_{D} 1.4104, d^{25}_{4} 0.7157, C–H absorptions at 3005, 3019, 3083, 1645(s), 1020(s), and 905(s) cm.$^{-1}$ [lit.[7] b.p. 40.19° (760 mm.), n^{20}_{D} 1.4138, d^{20}_{4} 0.72105, 54% from 1-cyclopropylethanol by dehydration over alumina].

Anal. Calcd. for C_5H_8: C, 88.16; H, 11.84; *M*D, 23.34. Found: C, 88.03; H, 12.02; *M*D, 23.60.

1-Cyclopropylethyl Methyl Dithiolcarbonate.—The pot residue, S-methyl xanthate, above, was a two-component mixture as evidenced by G.P.C. Pyrolysis at 360° failed to cleave this material. Distillation of 61.8 g. of this material through a 7" Vigreux column followed by rectification through a 14' packed column yielded a yellow oil boiling at 236–237° (759 mm.), 25.2 g., n^{25}_{D} 1.5358, d^{25}_{4} 1.0908, which was pure in G.P.C. Absorptions at 3002 and 3082 cm.$^{-1}$ indicated that the cyclopropyl group had remained intact, and additional absorptions at 1645(s) and 868(s) cm.$^{-1}$ were noted for 1-cyclopropylethyl methyl dithiolcarbonate.

Anal. Calcd. for $C_7H_{12}OS_2$: C, 47.69; H, 6.86; S, 36.37. Found: C, 47.54; H, 7.00; S, 36.20.

1-Cyclopropylethanethiol.—1-Cyclopropylethyl methyl dithiolcarbonate (14 g., 0.079 mole), n^{25}_{D} 1.5334, was saponified essentially according to the procedure of Shriner, *et al.*[30] The mixture was acidified with acetic acid since mineral acids could open the cyclopropyl group. The aqueous phase was extracted with ether and the organic phase, after washing with 5% aqueous sodium bicarbonate and drying, was distilled to yield 1-cyclopropylethanethiol boiling at 115–115.5° (758 mm.), 2.5 g., 31%, n^{25}_{D} 1.4626, d^{25}_{4} 0.8836, C–H absorptions at 3004 and 3079 cm.$^{-1}$.

Anal. Calcd. for $C_5H_{10}S$: C, 58.76; H, 9.86; S, 31.37; *M*D, 31.50. Found: C, 58.85; H, 9.50; S, 31.78; *M*D, 31.83.

1-Cyclopropylethanethiol was treated with 2,4-dinitrofluorobenzene essentially according to the procedure of Bost, *et al.*,[26] and an orange-yellow crystalline sulfide melting at 74.5–75° was obtained.

Acknowledgment.—The assistance given by Miss M. Caldera, Mr. S. Abramowitz and Dr. R. Bauman in obtaining and interpreting infrared data was deeply appreciated. This research was supported by the United States Air Force under Contract No. AF 33(616)-5253, monitored by the Materials Laboratory, Wright Air Development Center, Wright–Patterson Air Force Base, Ohio.

Summary.—(1) 1-Cyclopropylethyl acetate was prepared and pyrolysis of this material yielded cyclopentene and smaller amounts of vinylcyclopropane and 1,4-pentadiene. (2) 1-Cyclopropylethanol yielded vinylcyclopropane, 2-methyltetrahydrofuran and small amounts of both 1,4-pentadiene and cyclopentene when subjected to sulfuric acid-catalyzed dehydration. (3) 1-Cyclopropylethyl S-methyl xanthate was prepared and pyrolysis of this material yielded vinylcyclopropane and 1-cyclopropylethyl methyl dithiolcarbonate.

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(30) R. L. Shriner, R. C. Fuson and D. Y. Curtin, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., Fourth Ed., 1956, p. 236.

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA, MINNEAPOLIS 14, MINN.]

Inductive Effects on the Acid Dissociation Constants of Mercaptans[1]

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The acid dissociation constants of a number of mercaptans have been measured by a variety of methods. These constants, along with some taken from the literature, have been correlated with the Taft σ^*-parameters. The correlation holds for eleven mercaptans but fails for thiophenol and hydrogen sulfide. The former is attributed to a resonance effect, the latter to a steric effect on solvation.

A knowledge of the acid dissociation constants of simple mercaptans is fundamental to an understanding of the chemistry of these compounds for two reasons. First, many important reactions of mercaptans may proceed through the mercaptide ions, and secondly the acid dissociation constants can give important information about the distribution of electrons in mercaptans.[2] In spite of this, there seem to be only a small number of such constants available,[2-10] and most of these are

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(1) This research was supported, in part, by the U. S. Army Medical Research and Development Command through contract DA-49-193-MD-2027 and in part by the National Science Foundation through grant No. N.S.F.-G5434. Reproduction in whole or in part is permitted for any purpose of the United States Government.

(2) M. Calvin in S. Colowick, *et al.*, "Glutathione," Academic Press, Inc., New York, N. Y., 1954, Chap. I.

(3) G. Schwarzenbach, *Helv. Chim. Acta*, **15**, 1468 (1932).

(4) G. Schwarzenbach and H. A. Egli, *ibid.*, **17**, 1176 (1934).

(5) G. Schwarzenbach and A. Epprecht, *ibid.*, **19**, 169 (1936).

(6) G. Schwarzenbach and H. A. Egli, *ibid.*, **22**, 260 (1939).

(7) D. L. Yabroff, *Ind. Eng. Chem.*, **32**, 257 (1940).

(8) W. H. Fletcher, THIS JOURNAL, **68**, 2726 (1946).

(9) J. Maurin and R. A. Paris, *Compt. rend.*, **232**, 2428 (1951).

(10) F. G. Bordwell and H. M. Anderson, THIS JOURNAL, **75**, 6019 (1953).

not in completely aqueous solutions.[10a] The present paper reports the determination of a number of such constants in dilute aqueous solution by *p*H titration, a spectrophotometric method, and a gas solubility method. A number of previously available constants have been redetermined. Both the new and the old data are correlated quite nicely by eq. 1, in which K is an ionization constant, σ^* is Taft's inductive parameter, characteristic of

$$\log K = \sigma^* \rho^* - \alpha \qquad (1)$$

the R group in RSH, ρ^* is a parameter characteristic of the reaction, and α is the log of the predicted ionization constant of methyl mercaptan.[11]

Results

Dissociation constants were calculated by means of eq. 2 at points corresponding to approximately 25, 50 and 75% neutralization. In all cases the temperature was held at 25 ± 1°. In the *p*H titrations the hydrogen ion concentration is that given by a Beckman model H-2 meter.

$$K = \frac{(\mathrm{H}^{\oplus})(\mathrm{RS}^{\ominus})f_{\pm}^{2}}{(\mathrm{RSH})} \qquad (2)$$

The total mercaptan concentration was determined from the end-point on the titration curves. The mercaptide ion concentration was taken from the known amount of sodium hydroxide that had been added and the neutral mercaptan concentration was obtained by difference.

In the spectrophotometric determinations the hydrogen ion concentration was established by using a buffered solution. The mercaptide ions have a moderately intense absorption around 2400 Å. which is nearly absent in the neutral mercaptans and this was used to determine the mercaptide ion concentration. Total mercaptan concentration was determined by iodine titration and neutral mercaptan concentration was obtained by difference.

For low-boiling mercaptans, the Henry's law constant was determined manometrically in the absence of base and was then used to evaluate neutral mercaptan concentration. In basic solutions the total mercaptan concentration was determined from the solubility of the gas and the mercaptide ion concentration was obtained by difference. The hydrogen ion concentration was established by using basic buffers.

The mean ion activity coefficient, $f_{\pm}$, was in all cases evaluated by the use of eq. 3,[12] in which Γ is the ional strength, S_f is a parameter given by

$$\log f_{\pm} = -\frac{S_f\sqrt{\Gamma}}{1 + A\sqrt{\Gamma}} \qquad (3)$$

Harned and Owen,[13] while A is a function of the dielectric constant,[14] the temperature, and the mean ionic radius. The latter quantity was assumed to be 6 Å. for all mercaptans, which does not seem unreasonable for ions of this general type. The mean ionic radius for acetic acid is 2.6 Å.[15] No systematic dependence of K on the ionic strength could be detected in any case. The resulting constants are, nevertheless, not thermodynamic dissociation constants because the cells used to determine buffer *p*H values were not free of liquid junctions.[16] It is not likely that they deviate from thermodynamic dissociation constants by more than their experimental uncertainty, however.[16]

In most of the present experiments the mercaptan was introduced as a solution in ethanol. As a result the solvent in these experiments actually contained up to 1% ethanol. Within the accuracy of the present values it is not likely that this has any effect on the measured dissociation constants. The addition of 10% methanol changes the dissociation constant of propionic acid from 1.336×10^{-5} to 0.947×10^{-5}.[17]

Table I shows the dissociation constants obtained by these various methods. Values previously available are also included for comparison and in one case two values obtained for a single compound by different methods are included. In all cases the values are the same within their uncertainties.

The values in Table I attributed to Yabroff were determined at 20° from liquid–liquid extraction data. It is likely that the corresponding values at 25° are somewhat higher. Boric acid has an acid dissociation constant of 5.26×10^{-10} at 20° and 5.79×10^{-10} at 25°.[18]

Discussion

If eq. 1 governs the dissociation constants, a plot of log K *vs.* σ^* should be linear. Figure 1 shows such a plot. Newly determined dissociation constants were used in preference to values taken from the literature in all cases except that of ethyl mercaptan. A line of very reasonable precision is produced by all the points except those for H_2S and thiophenol. It has a slope, ρ^*, of 3.402, an intercept, α, of −10.168 moles l.$^{-1}$, and a correlation coefficient of 0.991, all determined by the method of least squares.[19] There are eleven points on this line with a total spread of a little over three powers of ten in K. The average deviation of a point from the line is 0.120 log unit, which corresponds to a 32% deviation in K. The largest deviation is 0.264 log unit. These deviations are probably somewhat larger than would be expected from the uncertainties in K but the fit is about as good as can be hoped for, since eq. 1 is not expected to be exact.[11]

In constructing Fig. 1 Taft's σ^*-values were used for the C_6H_5, H, CH_3COCH_2, $C_6H_5CH_2$, C_2H_5,

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[10a] NOTE ADDED IN PROOF.—After the submission of this manuscript a paper containing a number of mercaptan acid dissociation constants appeared (J. P. Danehy and C. F. Noel, THIS JOURNAL, **82**, 2511 (1960)). The values reported are in general agreement with those given here for 2-mercaptoethanol, methylmercaptoacetate, and ethylmercaptan but the two values for thiophenol differ by over a power of 10.

[11] R. W. Taft in M. S. Newman, "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., Chap. 13.

[12] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corp., New York, N. Y., 1958, pp. 34-37.

[13] *Ibid.*, p. 105.

[14] *Ibid.*, p. 161.

[15] H. S. Harned, *J. Phys. Chem.*, **43**, 275 (1939).

[16] R. G. Bates, "Electrometric *p*H Determinations," John Wiley and Sons, Inc., New York, N. Y., 1954, Chap. 3.

[17] Reference 12, p. 761.

[18] Reference 12, p. 755.

[19] C. A. Bennett and N. L. Franklin, "Statistical Analysis in Chemistry and the Chemical Industry," John Wiley and Sons, Inc., New York, N. Y., 1954, pp. 36-40.

TABLE I

ACID DISSOCIATION CONSTANTS OF MERCAPTANS, RSH

R	K	Method
C_6H_5	$3.0 \pm 0.8 \times 10^{-7}$	Spec.
H	9.5×10^{-8a}	
$CH_3\overset{O}{\overset{\|}{C}}CH_2$	$1.37 \pm 0.10 \times 10^{-8}$	*p*H tit.
$C_2H_5OCOCH_2$	$1.11 \pm 0.07 \times 10^{-8}$	*p*H tit.
$C_2H_5OCOCH_2$	$1.17 \pm 0.14 \times 10^{-8}$	Spec.
CH_3OCOCH_2	1.6×10^{-8b}	
$C_6H_5CH_2$	$3.75 \pm 0.18 \times 10^{-10}$	Spec.
$C_2H_5OCH_2CH_2$	$4.15 \pm 0.14 \times 10^{-10}$	*p*H tit.
$HOCH_2CH_2$	$3.74 \pm 0.20 \times 10^{-10}$	*p*H tit.
$HOCH_2CH_2$	3.2×10^{-10b}	
$HOCH_2CH(OH)CH_2$	$3.09 \pm 0.05 \times 10^{-10}$	*p*H tit.
$HOCH_2CH(OH)CH_2$	2.2×10^{-10c}	
$CH_2{=}CHCH_2$	$1.1 \pm 0.4 \times 10^{-10}$	Gas sol.
C_2H_5	$\sim 1.3 \times 10^{-11}$	Gas sol.
C_2H_5	2.52×10^{-11d}	
n-C_3H_7	2.26×10^{-11d}	
n-C_4H_9	2.21×10^{-11d}	
t-C_4H_9	0.89×10^{-11d}	
t-C_5H_{11}	0.62×10^{-11d}	

[a] A. J. Ellis and R. M. Golding, *J. Chem. Soc.*, 127 (1959); divided by a symmetry factor of two. [b] Ref. 2. [c] B. Sjoberg, *Ber.*, **75**, 18 (1942). [d] Ref. 7.

n-C_3H_7, n-C_4H_9 and t-C_4H_9 groups.[11] The σ^* for $CH_2{=}CHCH_2$ has been assumed equal to that for $CH_3CH{=}CHCH_2$. Values for $C_2H_5OCOCH_2$, $C_2H_5OCH_2CH_2$ and $HOCH_2CH_2$ were obtained by dividing those for the groups having one less methylene group by 2.8.[11,20] The σ^* for the *t*-amyl group was obtained by subtracting 0.015 (the difference between the σ^* for a propyl group and that for an ethyl group) from the σ^* for the *t*-butyl group. A reliable σ^* value could not be obtained for the $HOCH_2CH(OH)CH_2$ group so the point for this substituent is not included in Fig. 1. Its σ^* should probably be about the same as that for the β-hydroxyethyl substituent, however, and the acid dissociation constant to which it gives rise is appropriate to such a σ^*.

The failure of H_2S to obey eq. 1 (even after correction for the symmetry factor)[21] is very likely due to a steric effect on solvation. The HS^- ion is probably surrounded by a solvent shell of almost spherical symmetry. The solvation of the mercaptide ions from the direction of the alkyl group is effectively inhibited. Among the various alkyl groups studied, no further steric differences are discernible; but it should be noted that the groups studied do not present the widest possible variation in steric requirements.

The failure of thiophenol to obey eq. 1 must be largely due to a resonance effect. The delocalization of the negative charge onto the *o*- and *p*-positions of the benzene ring enhances the stability of the thiophenolate ion. The corresponding resonance of the neutral molecule involves charge separation and is less important. The resulting enhancement of the acid dissociation constant, $\Delta pK\psi$, amounts to 1.57 log units. This is a much smaller value than that for phenol (variously estimated as 4.5 log units[22] and 6 log units[23]). The enhancement of the acidity of thiophenol definitely seems real, however, contrary to a previous view.[2]

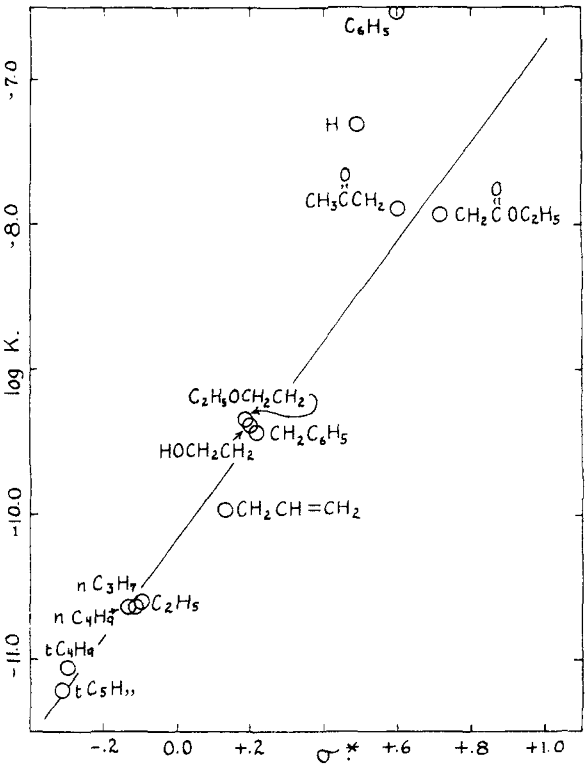

Fig. 1.—Correlation of the acid dissociation constants of mercaptans by eq. 1.

These results are in qualitative agreement with those of Bordwell and Andersen,[10] who correlated the acid dissociation constants of *m*- and *p*-substituted phenols in 48% ethanol with the Hammett σ-values. They found $\rho = 2.58$. They noted that σ-values obtained for the *p*-methanesulfonyl group and the *p*-nitro group are intermediate between those obtained from the ionization constants of carboxylic acids and those obtained from the ionization constants of phenols. This is consistent with a resonance stabilization of the thiophenolate ion which is real but smaller than that of the phenolate ion.

Reactions which are subject to resonance effects are also frequently subject to Baker–Nathan effects.[24,25] In the present series no such effect is detected. The Baker–Nathan effect per α-hydrogen atom is usually about one-tenth of the resonance effect due to a phenyl group.[24-26] The only two mercaptans in the present series which have other than two α-hydrogen atoms are the two tertiary alkyl mercaptans, which have none. These should be off the line defined by the other points by about 0.3 log unit. Actually they fit about as

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(20) In addition, values for methyl derivatives were assumed to be the same as those for ethyl derivatives in the first two cases.

(21) S. W. Benson, THIS JOURNAL, **80**, 5151 (1958).

(22) G. E. K. Branch and M. Calvin, "The Theory of Organic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1941, p. 245.

(23) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1948, p. 205.

(24) M. M. Kreevoy and R. W. Taft, Jr., THIS JOURNAL, **79**, 4016 (1957).

(25) M. M. Kreevoy, *Tetrahedron*, **5**, 233 (1959).

(26) M. M. Kreevoy and H. Eyring, THIS JOURNAL, **79**, 5121 (1957).

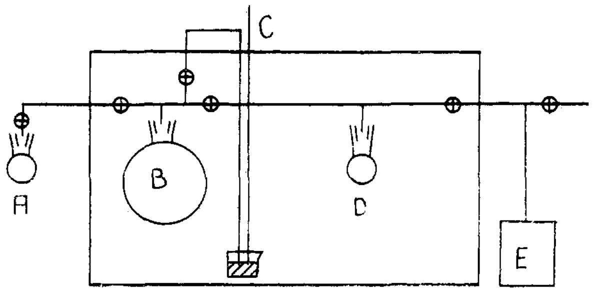

Fig. 2.—The gas solubility apparatus.

well as any other points but the predicted deviation is only about three times the *average* deviation of points from the line. In order to evaluate the possible Baker–Nathan effect on this reaction, it will be necessary to study a substantial number of compounds with other than two α-hydrogen atoms.

Acid dissociation constants recently have been reported for a number of alcohols in water.[27–29] Acid dissociation constants for monosubstituted methanols, RCH_2OH, obey eq. 1 with a ρ^* of 1.42. Since σ^* for a group RCH_2 can be estimated from σ^* for the group R by multiplying the latter by $^1/_{2.8}$, a ρ^* of about 3.9 is implied for dissociation constants of alcohols, ROH, very similar to the present value for mercaptans. The ρ^* for dissociation of alkylammonium ions, RNH_3^+, also has a similar value (3.14).[30]

Experimental

pH Titrations.—The pH meter was calibrated and pH measurements were made by the method suggested by Bates.[31] The solution was stirred and its oxygen content kept low by continuous bubbling with nitrogen. This nitrogen previously had been passed through a solution of the same mercaptan concentration to prevent it from gassing the mercaptan out of the test solution. Sodium hydroxide (0.25 N) was added and the pH was measured at regular intervals. About twenty pH measurements were made in each determination. The end-point was determined visually. Temperature control was maintained by immersing the titration flask in a beaker of water of the proper temperature during the titration.

Spectrophotometric Determinations.—The method is essentially that of Robinson.[32] The bulk of the solution, without the mercaptan, was made up in a volumetric flask and nitrogen was bubbled through it for 0.5 hour to remove oxygen. The mercaptan then was added as a stock solution in ethanol. The solution was made up quickly to volume and optical densities were measured in a Beckman DU spectrophotometer with a thermostated cell compartment. The spectrum of the anion was obtained in $\sim$0.1 M NaOH, and that of the neutral mercaptan was obtained in neutral or acid solution. Wave lengths for dissociation constant determinations were chosen so as to approximately maximize the ratio of the extinction coefficients of the ion and the neutral molecule. In all determinations measurements were made at at least two wave lengths. At the wave lengths used the mercaptide extinction coefficient was about ten times that for the neutral mercaptan. In all the basic solutions there was a noticeable change in optical density on standing, due to the air oxidation of the mercaptan, so optical densities were measured as rapidly as possible after the solutions were made up.

In determining the acid dissociation constants, basic buffers were needed. These were made up to approximately the required pH using the components recommended by Bates.[31] The pH of these solutions was determined potentiometrically,[33] using a hydrogen electrode and a Leeds and Northrup student potentiometer, before the addition of the mercaptan.

Gas Solubility Measurements.—Gas solubility measurements were made in a straightforward manner using the apparatus shown in Fig. 2. The mercaptan was placed in flask A, the water or aqueous buffer was placed in flask D, and both were cooled with Dry Ice–acetone. The whole system was then pumped down to a pressure of $\sim$0.1 mm., as read on the McLeod gauge, E. The system showed no leakage at this pressure over a period of several days. The aqueous solution was then permitted to warm up to 25° and the vapor pressure over it was read on the manometer, C. Water vapor was also admitted to the reservoir, B. (Liquid and vapor temperatures were controlled by keeping the whole apparatus in a large, electrically heated, ice-cooled air thermostat.) Mercaptan vapor then was admitted to the reservoir, B, and its vapor pressure measured. The mercaptan vapor now was admitted to D, which was stirred magnetically, and its solubility in the aqueous solution was determined from the drop in pressure and the known volumes of the various parts of the system.

The preparation and standardization of the buffer solutions is described under spectrophotometric determinations.

Materials.[34]—Thiophenol was Mathieson, reagent grade, and was redistilled before use (b.p. 55–56° (10 mm.)). Ethyl mercaptoacetate was Eastman Kodak Co., practical grade, and was redistilled (b.p. 68–69° (32 mm.)). Mercaptoacetone was prepared by the method of Hromatka and Engel[35] (m.p. 95–100°). 2-Ethoxyethanethiol was prepared by the method of Swallen and Boord[36] (b.p. 127°). 2-Mercaptoethanol was obtained from Union Carbide Chemicals Co. and redistilled under water-pump vacuum. It had n^{25}_{D} 1.4975. Bennett[37] reports n^{20}_{D} 1.4996. Monothioglycerol was obtained from Evans Chemetics Inc. as a 46% solution in water and was used without further purification. Benzyl mercaptan was a gift from Evans Chemetics Inc. It had an assay of 95.5% and was used without further purification. Allyl mercaptan was obtained from Aldrich Chemical Co. and ethanethiol from Eastman Kodak Co. Both were of the best grade supplied by these firms and were used without purification, except that they were distilled into the gas solubility apparatus.

Acknowledgment.—The authors are grateful to the U. S. Army Medical Research and Development Command and to the National Science Foundation for support of this work and to Evans Chemetics, Inc., for the gift of chemicals.

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(27) P. Ballinger and F. A. Long, This Journal, **82**, 795 (1960).

(28) P. Ballinger and F. A. Long, *ibid.*, **81**, 2347 (1959).

(29) P. Ballinger and F. A. Long, *ibid.*, **81**, 1050 (1959).

(30) H. K. Hall, *ibid.*, **79**, 5441 (1957).

(31) Reference 16, p. 191.

(32) R. A. Robinson in W. J. Hamer, "The Structure of Electrolytic Solutions," John Wiley and Sons, Inc., New York, N. Y., 1959, p. 253.

(33) Reference 16, p. 253.

(34) All boiling points are uncorrected; all melting points are corrected.

(35) O. Hromatka and E. Engel, *Monatsh.*, **78**, 32 (1948).

(36) L. C. Swallen and C. E. Boord, This Journal, **52**, 655 (1930).

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