[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NORTHWESTERN UNIVERSITY]

Conjugation of Methylsulfonyl and Nitro Groups with the Mercapto Group in Thiophenols[1]

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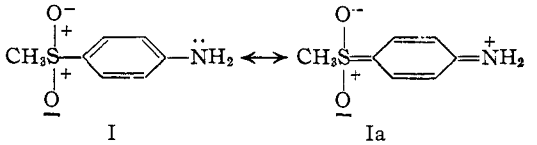
The acidity constants of thiophenol and eight *m*- and *p*-substituted thiophenols were measured in 48% alcohol. With these data together with seven additional pK values from the literature, ρ and pK_0 in the Hammett equation were calculated to be +2.578 and 7.699. From these figures σ-constants for p-CH_3SO_2 and p-NO_2 of +0.82 and +1.00 were obtained. The fact that the σ-value for p-CH_3SO_2 determined from the acidity of thiophenols is significantly larger than that from benzoic acids but smaller than that from phenols or anilines is rationalized by assuming varying degrees of resonance interactions (involving expansion of the valence shell of sulfur to ten electrons).

It is generally accepted that most strong electron-attracting substituents (NO_2, CN, CH_3CO, etc.) can enter into resonance interactions with amino, hydroxyl and similar groups situated in a para position. These interactions in some instances may be reflected in enhanced values for dipole moments or shifts in absorption spectra maxima.[2] Perhaps the most reliable indication is obtained, however, from the enhanced values for acidity constants obtained when these interlocking groups are situated in para (but not meta) positions. In terms of Hammett σ-constants,[3] considerably larger values are needed to express the electronic effects of these para (but not meta) electron-attracting groups in the reactions of anilines and phenols than in the reactions of benzoic acids. Thus, the difference in these two sets of σ-values amounts to 0.49 for p-NO_2,[3] 0.44 for p-CH_3CO,[4] and 0.34 for *p*-CN.[5] These differences are significant since the mean probable error for the whole table of 28 σ-constants given by Hammett[3] is only ±0.07.

Recently it has been found that not only do the σ-constants for the p-CH_3SO_2 group for reactions of phenols and anilines differ from that for reactions of benzoic acid, but that they are significantly different from each other.[4] These results suggest resonance interactions in the ground state between the p-CH_3SO_2 group and a –OH or $-NH_2$, which involve an expanded valence shell for sulfur.[6] The fact that the σ-values of the CH_3SO_2 group for the reactions of phenols and anilines differ from one another is not difficult to reconcile, since there is no *a priori* reason to expect the resonance contributions in the two instances to be the same. In order to obtain further evidence concerning the conjugative ability of the CH_3SO_2 group and other groups capable of strong resonance, the relative acidities of a number of *m*- and *p*-substituted thiophenols have been determined. A further objective was to measure the ability of the –SH group to enter into resonance interactions as compared to the –OH and $-NH_2$ groups.


I Ia

The acidity constants of twenty *o*-, *m*- and *p*-substituted thiophenols in 48.9% alcohol (by volume) and in 95% alcohol have previously been determined by Schwarzenbach and Egli[7] using a hydrogen electrode. No data on thiophenols containing strongly electron-attracting groups were obtained, however. In the present investigation the acidity of thiophenol and of *m*-Br, m-CH_3, *p*-Br and p-CH_3 thiophenols in 48% alcohol were measured in order to compare with the previous results,[7] and the method was then extended to m-CH_3SO_2, p-CH_3SO_2, m-NO_2 and p-NO_2 thiophenols.

The thiophenols were prepared by methods similar to those reported in the literature. Preparation of *m*-methylsulfonylthiophenol by reduction of *m*-methylsulfonylbenzenesulfonyl chloride with lithium aluminum hydride was, in our hands, more convenient and superior to reduction with tin and hydrochloric acid. Purification of *p*-nitro and *p*-methylsulfonylthiophenols was effected by way of the disulfides.

The determinations of the apparent ionization constants in 48% alcohol (prepared by dilution of ordinary 96% alcohol to twice its volume) were carried out by measuring the *p*H of solutions which had been approximately 20, 40 and 60% neutralized. The pK_a values were computed using the Henderson equation,[8] $pK_a = pH + \log(ArSH)/(ArS^-)$; the spread in pK_a values was usually no greater than 0.02–0.03 pK unit for the three determinations.

The thiophenols were observed to undergo rapid oxidation in the presence of air, particularly in alkaline solution, so precautions were taken to

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[1] This investigation was supported by the American Petroleum Institute under Project 48B and the Office of Naval Research under Contract No. N7onr-45007.

[2] G. W. Wheland, "The Theory of Resonance," John Wiley and Sons, Inc., New York, N. Y., 1944, Chapters V and VI.

[3] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, Chapter VIII.

[4] F. G. Bordwell and G. D. Cooper, THIS JOURNAL, **74**, 1058 (1952).

[5] J. D. Roberts and E. A. McElhill, *ibid.*, **72**, 628 (1950).

[6] The formulas show a representation involving the amino group and methylsulfonyl group wherein the sulfur shell is expanded to ten electrons. It is, of course, also possible to write structures in which one or both sulfur–oxygen bonds are double bonds, whereby the valence shell of sulfur is expanded to ten or twelve in both I and Ia. The prevailing opinion appears to be that doubly covalent sulfur-oxygen bonds contribute more to the hybrid structure of sulfones than do semi-polar sulfur–oxygen bonds (see D. Barnard, J. M. Fabian and H. P. Koch, *J. Chem. Soc.*, 2442 (1949), for a discussion). Our work has no bearing on this point except that it provides strong evidence that the sulfur atom *is capable* of expanding its shell in the sulfone structure.

[7] (a) G. Schwarzenbach and H. A. Egli, *Helv. Chim. Acta*, **17**, 1176 (1934); (b) H. Egli, Doctoral Dissertation, University of Zurich, 1935.

[8] S. Glasstone, "The Electrochemistry of Solutions," Methuen and Company, Ltd., London, 1930, p. 207.

minimize contact of the solutions with air. To correct for the presence of disulfides or other impurities in the thiophenols, the stoichiometric quantity of thiophenols present at the time of the pH measurement was determined by titration of an aliquot of the solution with iodine.

The results obtained in the present investigation for thiophenol and the eight *m*- and *p*-substituted thiophenols are summarized in Table I together with values for seven additional thiophenols calculated from the data of Schwarzenbach and Egli.[7] For *p*-CH_3, *m*-CH_3 and *p*-Br thiophenols and for thiophenol itself, the agreement in the relative values between our results in 48% alcohol at 25° and those of Schwarzenbach and Egli, which were obtained in 48.9% alcohol at 20°, is excellent. Our results, which are those listed in the table, were almost uniformly about 0.05 pK unit higher. For *m*-bromothiophenol our value of 6.77 is significantly different from their value of 6.91.

Table I

Apparent Acidity Constants for Thiophenols in 48% Alcohol at 25°

Substituent	pK_a	Substituent	pK_a
p-HO	8.30^b	*p*-I	6.94^b
p-CH_3	$8.03^{a,b}$	*m*-I	6.82^b
p-CH_3O	7.99^b	*m*-Br	6.77^a
m-CH_3	$7.96^{a,b}$	*m*-Cl	6.74^b
H	$7.76^{a,b}$	*m*-NO_2	5.90^a
m-CH_3O	7.45^b	*m*-CH_3SO_2	5.88^a
p-Br	$6.99^{a,b}$	*p*-CH_3SO_2	5.57^a
p-Cl	6.96^b	*p*-NO_2	5.11^a

[a] Present investigation. [b] Schwarzenbach and Egli.[7]

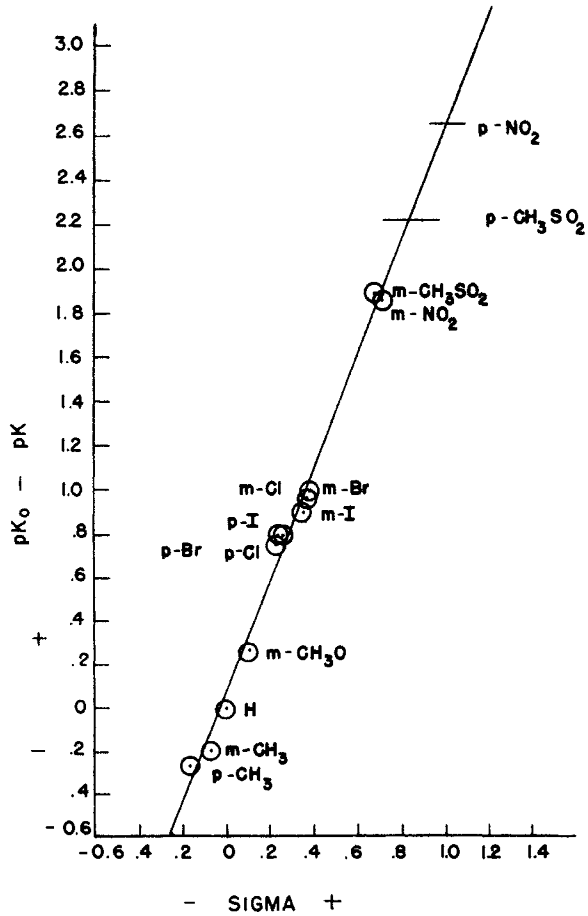


Fig 1.—Determination of ρ for thiophenols.

A plot of $pK_0 - pK$ *versus* the σ-values[3] for the substituents listed in Table I, *excluding* *p*-HO, *p*-CH_3O, *p*-CH_3SO_2 and *p*-NO_2 gave an excellent straight line (Fig. 1). The pK_a value of 6.91 for *m*-bromothiophenol would have given a point farther from the line than did our value of 6.77 which was used. The slope of the line, ρ in the Hammett equation ($pK = \sigma\rho + pK_0$) was determined by the method of least squares to be +2.578; pK_0 7.699. The average deviation from the line of the pK values was ±0.055. The probable error was ±0.045, which compares favorably with that in other reactions.[8] The position of the *p*-NO_2 and *p*-CH_3SO_2 groups on the line (Fig. 1), as obtained from the pK_a data, is indicated.

Discussion

σ-Values for *p*-CH_3SO_2 and *p*-NO_2 Groups.—Values of σ for *p*-CH_3SO_2 and *p*-NO_2 calculated using $\rho = +2.58$ and $pK_0 = 7.70$ and the pK values listed in Table I are +0.82 and +1.00, respectively. Table II summarizes the σ-values that have been determined in this laboratory from the acidity constants of benzoic acids,[4] thiophenols, phenols[4] and anilinium ions.[4]

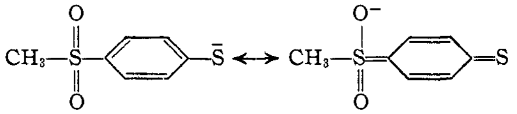
Table II

σ-Values for *m*- and *p*-Methylsulfonyl Groups from Acidity Constants

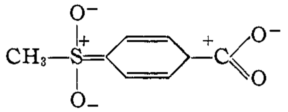
Compound	σ	Compound	σ
m-$CH_3SO_2C_6H_4COOH$	$+0.65^a$	*p*-$CH_3SO_2C_6H_4COOH$	$+0.72^a$
m-$CH_3SO_2C_6H_4SH$	$+.71^b$	*p*-$CH_3SO_2C_6H_4SH$	+.82
m-$CH_3SO_2C_6H_4OH$	$+.70^d$	*p*-$CH_3SO_2C_6H_4OH$	$+.98^c$
m-$CH_3SO_2C_6H_4\overset{+}{N}H_3$	+.69	*p*-$CH_3SO_2C_6H_4\overset{+}{N}H_3$	$+1.13^d$

[a] C. C. Price and J. J. Hydock, This Journal, **74**, 1942 (1952), obtained +0.65 for *m*-CH_3SO_2 and +0.76 for *p*-CH_3SO_2 from the rates of alkaline hydrolysis of the ethyl benzoates. H. J. Backer and H. Kloosterziel, *Rec. trav. chim.*, **71**, 295 (1952), give values of +0.56, +0.65 and +0.63 for *m*-CH_3SO_2 from the acidity constants of the benzoic acids in water and 50% alcohol and the rate of reaction of the acid with diphenyldiazomethane in alcohol; the values for *p*-CH_3SO_2 from acidity constants in water and alcohol were +0.68 and +0.75. [b] Determined from the data used for Fig. 1 excluding that for *m*-CH_3SO_2 and using the method of least squares. [c] Backer and Kloosterziel (ref. *a*) gave a value of +1.16 for σ from *p*-$CH_3SO_2C_6H_4OH$, but Kloosterziel, Doctoral Dissertation, University of Groningen, July, 1952, reported this to be in error and states that a redetermination of the acidity constant gave a check with our value.[4] A copy of our previous manuscript[4] was given to Kloosterziel in September of 1951. [d] Backer and Kloosterziel (ref. *a*) gave +0.68 for *m*-CH_3SO_2 and +1.14 for *p*-CH_3SO_2.

The spectrum of σ-values for *p*-CH_3SO_2 is striking when contrasted with the constancy of the values for *m*-CH_3SO_2. The differences for the former are all outside the range of experimental error. The larger σ required for *p*-CH_3SO_2 to describe the acidity of the thiophenol as compared to the benzoic acid supports the previous observations with phenols and anilines[4] and again may be attributed to acid strengthening resonance effects in the thiophenols, such as that shown, which are absent in the benzoic acid. Further evidence is thus obtained for the expansion of the valence shell



of sulfur in the methylsulfonyl group. Furthermore, the progressively larger σ-values for *p*-CH_3SO_2 as determined from the acidity constants of benzoic acids, thiophenols, phenols and anilinium ions may well reflect the increasing disparity in the amount of resonance interaction between the *p*-CH_3SO_2 group and the dissociated *versus* the undissociated forms in each of these systems. That is, the difference in resonance of $\overset{+}{N}H_3$ and NH_2 with *p*-CH_3SO_2, is greater than the difference in resonance of OH and O^- with *p*-CH_3SO_2, which in turn is greater than the difference in resonance of SH and S^- with *p*-CH_3SO_2. The *p*-CH_3SO_2 group cannot enter into direct resonance interactions with $-COOH$ and $-COO^-$, but structures such as that shown probably make some contribution.



Judging from the results with *p*-CH_3SO_2, similar para groupings (NO_2, CN, $COOCH_3$, etc.) would also be expected to show varying degrees of resonance interactions depending on the reaction concerned. In accordance with this the σ-values for *p*-NO_2 (in contrast to those of the *m*-NO_2 group) become increasingly great when determined for benzoic acids (σ 0.778),[3] thiophenols (σ 1.00) and phenols (σ 1.22, see below),[4] but the value from the acidity constant of anilinium ions appears to be almost the same (σ 1.27) as that obtained from phenols.[3]

Experimental

Materials.—Each compound was freshly distilled or recrystallized just before measuring. Thiophenol, *p*-thiocresol and *m*-thiocresol were Eastman Kodak Co. white label samples. The preparations of the other thiophenols are described in the sections which follow.

m-**Bromothiophenol.**—The method used was similar to that described by Wiley[9] for *m*-carboxythiophenol. Forty-three grams (0.25 mole) of *m*-bromoaniline was diazotized at 5° with 49 ml. of concd. hydrochloric acid and 17.2 g. (0.25 mole) of sodium nitrite in 110 ml. of water. The solution of the diazonium salt was added over a 1.5-hr. period to a solution of 40 g. (0.25 mole) of potassium ethyl xanthate and 33 g. (0.3 mole) of sodium carbonate in 250 ml. of water maintained at 70°. The mixture was maintained at this temperature for an additional hour, the resulting oil separated, the aqueous phase washed twice with ether, and the ether added to the oil. The ether was removed on the steam-bath in a stream of nitrogen, and the residual oil added to a solution of 40 g. (1 mole) of sodium hydroxide in 250 ml. of methanol and 40 ml. of water. The mixture was refluxed for 2 hours under nitrogen, diluted with 4 l. of water, and acidified with hydrochloric acid. The resulting oil was separated, the aqueous phase washed with methylene chloride, and the latter combined with the oil and dried over anhydrous sodium sulfate. Distillation yielded 19.1 g. (40%) of material, b.p. 100–104° at 10 mm. On redistillation the b.p. was 123–124° at 40 mm., n^{20}_D 1.6338.

Anal. Calcd. for C_6H_4SBr: C, 38.11; H, 2.67. Found: C, 37.89; H, 2.68.

Schwarzenbach and Egli[7a] gave no physical properties or analysis for this compound, and Egli[7b] reports only the b.p. (100° at 10 mm.). Reinboldt[10] also prepared this compound but gave no constants or analysis.

p-**Bromothiophenol.**—*p*-Bromobenzenesulfonyl chloride was reduced with zinc and sulfuric acid, following the procedure of Senear, Rapport and Koepfli[11] for the preparation of *p*-chlorothiophenol. The yield was 51%, m.p. 73–75°; a m.p. of 75° has been reported.[12]

m-**Methylsulfonylthiophenol.**—Twist and Smiles[13] report the preparation of this compound by the reduction of the corresponding sulfonyl chloride with tin and hydrochloric acid, and report a m.p. of 69°. Attempts to repeat their work failed; apparently we obtained a mixture of disulfide, thiol and tin mercaptide. Finally the sulfonyl chloride (obtained by Twist and Smiles' procedure[10]) in 60% yield, m.p. 92–94°, was reduced with lithium aluminum hydride to the thiophenol.[14] We were, however, unable to crystallize this compound; it was purified by distillation.

Three and eight-tenths grams (0.1 mole) of lithium aluminum hydride was dissolved in 150 ml. of dry ether and connected to a Soxhlet extractor (continuous type) containing 7.7 g. (0.03 mole) of *m*-methylsulfonylbenzenesulfonyl chloride, which is rather sparingly soluble in ether. Refluxing the ether one-half hour was sufficient to carry all the sulfonyl chloride into the reaction flask, after which the mixture was refluxed one hour more. Ten ml. of ethyl acetate was added to decompose the excess hydride, followed by 125 ml. of 2 *N* sulfuric acid. After about two hours the ether layer was separated, washed thrice with water, dried over sodium sulfate, and the ether removed *in vacuo* to leave a residue of 3.4 g. (61% yield) of a light colored oil. Repeated attempts to crystallize this oil failed. The material remaining was then distilled in a short path apparatus at a bath temperature of about 200° at 1 mm. yielding 1.05 g. of *p*-methylsulfonylthiophenol as a colorless liquid. The distillation left practically no residue.

Anal. Calcd. for $C_7H_8O_2S_2$: C, 44.66; H, 4.28. Found: C, 44.59; H, 4.34.

m-**Nitrothiophenol.**—Fifty-five and two-tenths grams (0.4 mole) of *m*-nitroaniline was diazotized according to the procedure of reference 15. This was then carried through the xanthate process as described under the preparation of *m*-bromothiophenol, using sufficient sodium carbonate (106 g., 1 mole) to keep the mixture alkaline during the reaction. Hydrolysis of the xanthate ester was carried out under nitrogen, as was the subsequent acidification. The resulting emulsion was decanted from some solid tar, and extracted with chloroform. The chloroform solution was treated with silica gel, filtered, and the chloroform removed *in vacuo* on the steam-bath to leave 25 g. (40% as crude) of dark red oil. Five grams of this material was charged to a short-path still and distilled at a bath temperature of about 200° at 1 mm. to yield 1 g. of *m*-nitrothiophenol as a straw-colored oil. The remainder of the charge pyrolyzed to a black tar. On two attempts to analyze this substance it was observed to explode and a value about 1% low in carbon was obtained.

This compound has been previously reported prepared by the same route by Leuckart and Holtzapfel[16] as a dark red oil, and by Bennett and Berry[17] who did not isolate the compound as such.

p-**Methylsulfonylthiophenol.**—Following essentially the procedure of Bourgeois and Abraham,[18] phenyl methyl sulfide in refluxing carbon tetrachloride was treated with an equimolar amount of bromine and refluxed 15 hours. The mixture was washed with water, sodium bisulfite solution, and water again. It was dried over calcium chloride, and the solvent stripped off *in vacuo* to yield *p*-bromophenyl methyl sulfide, m.p. 34–37°, in 96% yield as crude product. One recrystallization from alcohol gave pure product, m.p. 37–38°, 77% yield based on phenyl methyl sulfide.

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(9) P. F. Wiley, *J. Org. Chem.*, **16**, 810 (1951).

(10) H. Reinboldt, *Ber.*, **59**, 1311 (1926).

(11) A. E. Senear, M. M. Rapport and J. B. Koepfli, *J. Biol. Chem.*, **167**, 232 (1947).

(12) H. Hubner and J. Alsberg, *Ann.*, **156**, 327 (1870).

(13) R. F. Twist and S. Smiles, *J. Chem. Soc.*, **127**, 1248 (1925).

(14) J. Strating and H. J. Backer, *Rec. trav. chim.*, **69**, 638 (1950); C. S. Marvel and F. D. Caeser, THIS JOURNAL, **72**, 1033 (1950); L. Field and F. A. Grunwald, *J. Org. Chem.*, **16**, 946 (1951).

(15) W. A. Hartman and M. R. Brethen, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 162.

(16) R. Leuckart and W. Holtzapfel, *J. prakt. Chem.*, **41**, 197 (1890).

(17) G. M. Bennett and W. A. Berry, *J. Chem. Soc.*, 1669 (1927).

(18) E. Bourgeois and A. Abraham, *Rec. Trav. Chim.*, **30**, 407 (1911).

Oxidation of *p*-bromophenyl methyl sulfide in acetic acid solution with hydrogen peroxide (refluxing one hour) followed by dilution with water yielded *p*-bromophenyl methyl sulfone, m.p. 102–104°, in 84% yield. The reported m.p. is 102.5–103.0°.[18]

p-Bromophenyl methyl sulfone was converted to *p*-methylsulfonylthiophenol by displacement of the bromine with disulfide ion and reduction. Twenty-seven grams (0.2 mole) of 60% sodium sulfide flakes and 6.4 g. (0.2 mole) of sulfur were dissolved in 150 ml. of water on the steam-bath. To this was added 12 g. (0.05 mole) of *p*-bromophenyl methyl sulfone dissolved in 50 ml. of warm alcohol, and the mixture refluxed 13 hours. The alcohol was distilled off, the mixture cooled and filtered (to remove any unreacted starting material) into a mixture of 50 ml. of concd. hydrochloric acid and ice. Both the thiophenol and sulfur are thereby precipitated, and, unfortunately, most of the former adheres to the latter, which agglomerates in a lump. Extraction of this material with boiling alcohol or chloroform results in isolation of the corresponding disulfide, m.p. 190–192°, apparently by oxidation of the thiophenol by sulfur. The yield of disulfide was 6.5 g. (68%).

The disulfide was reduced to the thiophenol by treatment with glucose and sodium hydroxide, following the procedure of Lecher and Simon.[19] Four grams (0.0107 mole) of disulfide and 5.4 g. (0.03 mole) of glucose were mixed in 15 ml. of alcohol. While this was maintained at 60°, a solution 2.4 g. (0.06 mole) of sodium hydroxide in 6 ml. of water was added gradually. The mixture was then kept at 60–70° for 15 minutes, diluted with several volumes of water, and filtered into a mixture of 10 ml. of concd. hydrochloric acid and ice. The product separated as an oil which soon solidified on keeping at 0°; it then melted at 56–60° and weighed 2.55 g. (64% yield as crude). It was dissolved in chloroform and treated with silica gel, then precipitated by dilution with pentane to yield material melting 65–67°. Finally, crystallization from 75% ethanol yielded 1.6 g. (40%) of *p*-methylsulfonylthiophenol melting at 66–68°.

Anal. Calcd. for $C_7H_8O_2S_2$: C, 44.66; H, 4.28. Found: C, 44.72; H, 4.31.

***p*-Nitrothiophenol.**—This compound was prepared by reduction of the disulfide[20] with glucose and sodium hydroxide as described under the preparation of *p*-methylsulfonylthiophenol. The yield of crude product was 32%, m.p. 72–80°. Recrystallization from 50% ethanol raised the m.p. to 76–78°. The reported m.p. is 77°.[21] The compound is not very soluble in boiling 50% ethanol, but by filtering the boiling solution all disulfide present can be removed without loss of much of the thiophenol. Care must be taken to prevent oxidation to disulfide during the work-up.

Measurement of Acidity Constants.—Three samples of each thiophenol were weighed into 50-ml. volumetric flasks which had previously been swept out with nitrogen. To minimize atmospheric oxidation, this nitrogen atmosphere was maintained while each flask was promptly processed, one at a time, according to the following procedure. Twenty-five ml. of 96% ethanol at 25° was added from a pipet, and the flask again swept out with nitrogen before agitating to dissolve the sample. Sufficient standard carbonate-free sodium hydroxide solution was then measured from a buret into the flask to partially neutralize (about 20, 40 or 60% in turn) the thiophenol. The solution was then made up to the mark with carbonate-free water, and again swept with nitrogen before inverting to mix. An aliquot was then withdrawn and added to an excess of standard iodine solution. While this was allowed to stand for a few minutes, another sample was withdrawn and the *p*H measured immediately with a Beckman Model G *p*H meter. The iodine solution was then titrated with thiosulfate so that the exact -SH content of the solution could be calculated. The pK_a was then computed using the Henderson equation,[8] $pK_a = pH + \log (ArSH/ArS^-)$. The value from the iodine titration was used for the stoichiometric concentration of thiophenol, and the concentration of anion was taken as equal to that of the sodium hydroxide added; the concentration of un-ionized thiophenol could then be obtained by difference. The compounds were measured at concentrations of 0.01 to 0.05 *M*, depending on their solubility. The data are summarized in Table III.

TABLE III

MEASUREMENT OF ACIDITY CONSTANTS FOR THIOPHENOLS IN 48% ALCOHOL AT 25°

Substituent	Stoichiometric concn., *M*	ArS^-	Neutralized, %	*p*H obsd.	pK_a	pK_a aver.
H	0.0510	0.0108	21.2	7.20	7.77	
	.0461	.0216	46.9	7.70	7.75	7.76
	.0510	.0324	63.6	8.00	7.76	
m-CH_3	.0572	.0108	18.9	7.35	7.98	
	.0450	.0216	48.0	7.90	7.93	7.96
	.0490	.0324	66.2	8.25	7.96	
p-CH_3	.0414	.0108	26.1	7.58	8.03	
	.0441	.0216	49.1	8.03	8.05	8.03
	.0593	.0324	54.7	8.10	8.02	
p-Br	.0177	.0043	24.3	6.49	6.99	
	.0186	.0108	58.1	7.14	7.00	6.99
	.0217	.0151	62.8	7.33	6.97	
m-Br	.0207	.0043	20.9	6.18	6.76	
	.0223	.0108	48.5	6.75	6.78	6.77
m-CH_3SO_2	.0175	.0108	61.9	6.08	5.87	
	.0178	.0065	36.5	5.65	5.89	5.88
p-NO_2	.00528	.00433	82.1	5.78	5.11	
	.00528	.00217	41.1	4.95	5.11	5.11
p-CH_3SO_2	.0101	.0022	21.8	5.03	5.59	
	.0157	.0065	41.5	5.39	5.34	5.57
	.0152	.0108	71.1	5.97	5.58	
m-NO_2	.00826	.00217	26.2	5.39	5.84	
	.00771	.00433	56.3	6.07	5.97	5.90

Sample calculation, using data from first line of Table III

$$
\begin{aligned}
pK_a &= pH + \log (ArSH)/(ArS^-) \\
&= 7.20 + \log (0.0510 - 0.0108)/(0.0108) \\
&= 7.77
\end{aligned}
$$

EVANSTON, ILLINOIS

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[19] R. Lecher and K. Simon, *Ber.*, **55**, 2427 (1922).

[20] Prepared according to the procedure in "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., p. 220.

[21] C. Willgerodt, *Ber.*, **18**, 331 (1885).