[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Conjugative Effects of Dimethylsulfonio [$(CH_3)_2S^+$] and Trimethylammonio [$(CH_3)_3N^+$] Groups[1,2]

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RECEIVED MARCH 10, 1955

Acidity constant measurements of phenols and thiophenols containing the $(CH_3)_3N^+$ group, and of benzoic acids and phenols containing the $(CH_3)_2S^+$ group have demonstrated the ability of the $(CH_3)_2S^+$ group, but not the $(CH_3)_3N^+$ group to conjugate with a *p*-hydroxyl group. This conclusion was supported by ultraviolet absorption spectral measurements with these compounds. The ultraviolet absorption spectra revealed a remarkable correspondence between the effect of the $(CH_3)_2S^+$ and CH_3SO_2 groups on the position of absorption maxima in benzene derivatives. The similarity in conjugative effects of $(CH_3)_2S^+$ and CH_3SO_2 groups shows that the sulfur–oxygen bonds of the latter are not required for conjugation.

In continuing our efforts to assess the conjugative ability of various sulfur groupings[4] we have extended our investigations to include the dimethylsulfonio group.[1] The strongly electron-attracting $(CH_3)_3N^+$ and $(CH_3)_2S^+$ groups are particularly interesting to include in such a study, since the $(CH_3)_3N^+$ group cannot enter into conjugation in a conventional manner, and the $(CH_3)_2S^+$ group can do so only by expanding its valence shell to ten electrons. At about the time this research program was initiated Roberts, Clement and Drysdale[5] published their study of the electrical effect of the $(CH_3)_3N^+$ group. The σ- constants reported[5] for the *m*-$(CH_3)_3N^+$ group from several reactions showed a much wider variation than is usual for *meta* σ- constants. This, and our desire to have a direct comparison of the two groups from measurements made in the same laboratory, prompted us to supplement the work of Roberts, Clement and Drysdale[5] by measuring the acidity of *m*- and *p*-trimethylammoniophenols and thiophenols.

Hydroxyphenyl- and mercaptophenyltrimethylammonium *p*-toluenesulfonates or *p*-bromobenzenesulfonates were readily prepared by reaction of the proper dimethylaminophenol or thiophenol with methyl *p*-toluenesulfonate or *p*-bromobenzenesulfonate in refluxing benzene solution.

Formation of the sulfonium salts required a higher temperature than formation of the ammonium salts and this was achieved by using refluxing toluene solution, or by heating the reactants at 100–150° in the absence of a solvent. For the phenols the *p*-toluenesulfonate salts were too low melting to be purified readily. The picrates were high melting but too slightly soluble for acidity constant measurements in water. The *p*-bromobenzenesulfonates proved to be satisfactory on both counts.

The acidity constant of *p*-mercaptophenyltrimethylammonium iodide has been measured in 48.9% ethanol at 20–22° by Schwarzenbach and Rudin[6] using a conductivity method. Their *pK* value of 5.60 agrees well with our value of 5.68 obtained with the *p*-toluenesulfonate in 48% ethanol at 25°. The calculated σ- values are +0.81 and +0.78. For *p*-nitrothiophenol the reported *pK* values are 4.99[6] and 5.11.[4b] Our results and those of Roberts, Clement and Drysdale[5] are summarized in Table I.

TABLE I

σ-CONSTANTS FOR THE $(CH_3)_3N^+$ AND $(CH_3)_2S^+$ GROUPS

Acidity constant of	Solvent	log K_0	ρ	σmeta	σpara	$\sigma_m - \sigma_p$
Trimethylammonio Group [$(CH_3)_3N^+$]						
Benzoic acids[a]	50% EtOH			+1.02	+0.88	+0.14
Anilinium ions[a]	H_2O			+ .85	+ .75	+ .10
Dimethylanilinium ions[a]	H_2O			+ .67	+ .65	+ .02
Phenols	H_2O	−9.95	2.29[b]	+ .83	+ .70	+ .13
Thiophenols	48% EtOH	−7.70	2.58	+ .86	+ .78[c]	+ .08
Dimethylsulfonio Group [$(CH_3)_2S^+$]						
Benzoic acids	H_2O	−4.20	1.00	+1.00	+0.90	+0.07
Phenols	H_2O	−9.95	2.29[b]	+1.00	+1.16	− .16

[a] Reference 5. [b] This ρ-value was calculated by the least squares method using the data reported in ref. 4a, but omitting values for *p*-nitrophenol and *p*-methoxyphenol. [c] Schwarzenbach and Rudin[6] have measured the *pK* of the iodide in 48.9 and 95% alcohol. The σ-constants calculated from these measurements using the ρ and log K_0 values computed by Jaffé [H. H. Jaffé, *Chem. Revs.*, **53**, 191 (1953)] are +0.96 (48.9%) and +1.15 (95%). Many of the other σ-values calculated from these ρ and log K_0 vaues are high, however [*e.g.* σ_{m-Cl} +0.55 (48.9% alcohol) and +0.42 (95% alcohol) as compared to Hammett's value of +0.37].

The present results on the $(CH_3)_3N^+$ group augment those of Roberts, Clement and Drysdale.[5] It is significant that the *para* σ- constants for the $(CH_3)_3N^+$ group, as determined from the measure-

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(1) The nomenclature suggested by J. F. Bunnett, THIS JOURNAL, **75**, 642 (1953), for these groups has been adopted.

(2) Presented at the Meeting of the American Chemical Society in Chicago, Ill., September, 1953; see Abstracts p. 81-O.

(3) Texas Company Research Fellow, 1952–1954.

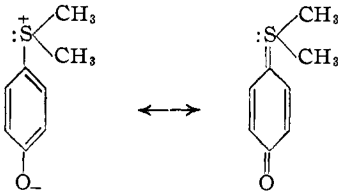
(4) (a) F. G. Bordwell and G. D. Cooper, THIS JOURNAL, **74**, 1058 (1952); (b) F. G. Bordwell and H. M. Andersen, *ibid.*, **75**, 6019 (1953).

(5) J. D. Roberts, R. A. Clement and J. J. Drysdale, *ibid.*, **73**, 2181 (1951).

(6) G. Schwarzenbach and E. Rudin, *Helv. Chim. Acta*, **22**, 360 (1939). This paper was overlooked when we reported our previous results,[4b] and was kindly brought to our attention by Prof. Schwarzenbach.

ment of acidity constants of anilinium ions, dimethylanilinium ions, phenols and thiophenols, are all *smaller* than that determined from the benzoic acid. If the $(CH_3)_3N^+$ group were able to conjugate effectively with *para* NH_2, $N(CH_3)_2$, O^- or S^- groups, these values would be considerably *larger* than that of the benzoic acid. The fact that the *meta* σ- constants are in every instance larger than the *para* σ- constants supports the viewpoint that no alternating inductive effect is present,[5] but instead the inductive effect of the $(CH_3)_3N^+$ group decreases with distance. The recent work of Roberts and Moreland[7] indicates that this effect is to a considerable extent a field effect.

The benzoic acids with ammonium and sulfonium groups in *meta* or *para* positions are of about comparable acidities, the *meta* isomer being the stronger acid in each pair.[5] The ability of the $(CH_3)_2S^+$ group to influence the acidity of a *p*-hydroxyl contrasts sharply, however, with that of the $(CH_3)_3N^+$ group. Whereas the *meta* isomer is about twice as acidic as the *para* isomer in the trimethylammoniophenols, the reverse is true in the dimethylsulfoniophenols, the *para* isomer being over twice as acidic as the *meta* isomer. The greater acidity of the *para* isomer in the latter instance appears to be best accounted for by assuming a conjugative interlocking between the $-S^+(CH_3)_2$ and O^- groupings, which is represented in the resonance terminology by forms such as Ia and Ib. This result is similar to that obtained for the CH_3SO_2- group.[4] The increase in σ- constant required for phenols over those for benzoic acids for these compounds may be taken as an approximate measure of conjugative ability. These differences are *p*-NO_2, $+0.49$; *p*-$COCH_3$, $+0.44$; *p*-SO_2CH_3, $+0.26$; *p*-$(CH_3)_2S^+$ $+0.26$; *p*-$(CH_3)_3N^+$, -0.19.



Ia Ib

Ultraviolet Absorption Spectra.—The investigations of Doub and Vandenbelt[8] first clearly demonstrated that conjugative effects existing in the ground state of *para* substituted benzenoid derivatives are frequently reflected in the excited states of their ultraviolet absorption spectra by shifts of absorption maxima to longer wave lengths. This test of conjugative ability was applied to the sulfonamide group by Doub and Vandenbelt,[8] and to the sulfone group by Fehnel and Carmack[9] and by Koch.[10] A comparison of the conjugative effects of $(CH_3)_3N^+$ and $(CH_3)_2S^+$ groups, as indicated by their ultraviolet absorption spectra, is of particular interest since $(CH_3)_3N^+$ and H_3N^+ groups are taken as classical examples in this field of groups without resonance effects. The ammonium groups have virtually no effect on the position of the absorption maximum of the primary band of benzene itself, nor do they greatly affect the absorption maximum when substituted into a position *para* to an electron-releasing group, such as hydroxyl.

The sulfonium *p*-toluenesulfonates and *p*-bromobenzenesulfonates cannot be used for ultraviolet absorption spectral measurements, since the anions exhibit absorption in the region in which we are interested. The methods used to prepare the iodides, methyl sulfates and perchlorates, upon which these measurements were made, are given in the Experimental section.

The results concerning the conjugative effect of the $(CH_3)_2S^+$ group from ultraviolet absorption spectra measurements were found to complement nicely those from acidity constant measurements. The primary band[8] of benzene is shifted from 203.5 to 220 mμ by substituting a $(CH_3)S^+$ group into benzene, and a further shift to 242 mμ is observed for this band in *p*-$(CH_3)_2S^+$-C_6H_4OH. Both of these results indicate conjugation.

The $(CH_3)_2S^+$ group is remarkably like the CH_3SO_2 group in its effect on the ultraviolet absorption spectra of benzene derivatives. The CH_3SO_2 group shifts the primary band of benzene to 217 mμ,[9a] while with the $(CH_3)_2S^+$ group the shift is to 220 mμ. Substitution of *m*-OH, *p*-OH and *p*-NO_2 groups into the benzene ring of methyl phenyl sulfone cause shifts in the primary band to longer wave lengths amounting to 6, 22 and 31 mμ, respectively. Comparable substitution in the benzene ring of the sulfonium compound causes shifts of 6, 22 and 32 mμ. Close correspondence is also observed in the positions of the secondary bands and in the intensity of absorption of sulfones and sulfonium compounds. A summary of the positions of the absorption maxima for a number of compounds pertinent to the problem are given in Table II.

The shifts in absorption bands with substitution of a hydroxyl group in the *para* positions of the benzene ring of the phenyldimethylsulfonium ion is characteristic of electron-withdrawing groups which can enter into resonance interactions,[8] and differs from the non-participation of the $-^+NH_3$ group in such interactions. The further shifts to longer wave lengths when the *p*-hydroxy sulfone and *p*-hydroxy sulfonium salt are placed in alkaline medium can be correlated with increased conjugation,[9b] since the shifts are larger for *para* isomers than for *meta* isomers or phenol itself. This is consistent with the behavior of similar compounds, such as *p*- and *m*-$HOC_6H_4COCH_3$ and *p*- and *m*-HOC_6H_4CHO.[8]

Neutralization of the *p*-hydroxyphenyldimethylsulfonium ion gives a species which may exist in the form of a dipolar ion Ia or a neutral molecule Ib. If form Ib makes a major contribution to the structure it might be anticipated that the substance would be colored. Actually, the neutralized solution is colorless, and showed no absorption in or near the visible. The spectrum was very

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[7] J. D. Roberts and W. T. Moreland, Jr., THIS JOURNAL, **75**, 2167 (1953).

[8] L. Doub and J. M. Vandenbelt, *ibid.*, **69**, 2714 (1947); **71**, 2414 (1949).

[9] (a) E. A. Fehnel and M. Carmack, *ibid.*, **71**, 231 (1949); (b) **72**, 1292 (1950).

[10] H. P. Koch, *J. Chem. Soc.*, 408 (1949).

TABLE II

COMPARISON OF THE ULTRAVIOLET ABSORPTION SPECTRA OF BENZENE DERIVATIVES CONTAINING $(CH_3)_2S^+$, CH_3SO_2 AND RELATED SUBSTITUENTS

Compound	Ref.	Primary band λ_{max}	Primary band log ε	Secondary band λ_{max}	Secondary band log ε	(λ_{max}-203.5)
Benzene	8	203.5	3.87	254	2.31	. . .
Anilinium ion	8	203	3.87	254	2.20	−0.5
Dimethylanilinium ion	[a]	<210	3.00	256	2.2	
Phenol	8	210.5	3.79	270	3.16	7.0
Methyl phenyl sulfone	9a	217	3.83	264	2.99	13.5
m-Hydroxyphenyldimethylsulfonium iodide (0.01 *N* NaOH)		218.5[b]	4.34	312	3.41	
Phenyldimethylsulfonium perchlorate		220	3.94	265	3.04	16.5
m-Hydroxyphenyl methyl sulfone		223	3.82	286	3.50	19.5
m-Hydroxyphenyldimethylsulfonium iodide		226	4.10	286	3.27	22.5
Aniline	8	230	3.93	280	3.15	26.5
Phenol (0.01 *N* NaOH)	8	235	3.97	287	3.41	31.5
p-Hydroxyphenyl methyl sulfone	9b	239	4.25	(268)	3.22	35.5
p-Hydroxyphenyldimethylsulfonium methyl sulfate		242	4.08	(262–267)	3.6	38.5
m-Hydroxyphenyl methyl sulfone (0.01 *N* NaOH)		248	3.92	314	3.60	44.5
p-Nitrophenyl methyl sulfone		248	4.05			44.5
Dimethylaniline	[a]	250	4.14	292	3.25	46.5
p-Nitrophenyldimethylsulfonium methyl sulfate		252	4.28			48.5
p-Hydroxyphenyl methyl sulfone (0.01 *N* NaOH)	9b	268	4.31			64.5
p-Hydroxyphenyldimethylsulfonium methyl sulfate (0.01 *N* NaOH)		269	4.29			65.5

[a] A. Wohl, *Bull. soc. chim.*, 6, 1312 (1939). [b] In view of the close correspondence of the spectra of the sulfonium compounds and sulfones, and the shifts to longer wave lengths for all phenols in alkaline solution, the spectrum of *m*-hydroxyphenyldimethylsulfonium iodide in alkaline solution is unusual. It seems probable that fusion of several bands may have led to an erroneous assignment of band positions.

similar to that of the anion of *p*-hydroxyphenyl methyl sulfone.

The data from acidity constant and ultraviolet absorption spectra measurements strongly indicate that the conjugative effects of the $(CH_3)_2S^+$ and CH_3SO_2 groups are similar. Since conjugation with the $(CH_3)_2S^+$ group[11] is restricted to the sulfur atom, these results suggest that conjugation in the CH_3SO_2 group also involves primarily the sulfur atom, and that the presence of sulfur–oxygen bonds is incidental. This is not surprising, since it seems unlikely that the strong inner stabilizing influences existing in groups like carboxyl, nitro and sulfone are disturbed very much by conjugation with a *para* group.

Experimental[12]

***p*-(Methylthio)-benzoic Acid.**—Sodium *p*-mercaptobenzoate was prepared by the method described by Allen and MacKay[13] for sodium *o*-mercaptobenzoate, and the alkaline solution treated with an equimolar quantity of methyl sulfate. After a reflux period of 30 min. the solution was cooled and acidified. The product was collected and recrystallized from 50% methanol to give material melting at 189–190.5°. Price and Hydock[14] report m.p. 191–192°. Modification of this preparation by use of sodium hydrosulfite rather than zinc and acetic acid for the reduction step[15] was much more convenient and increased the yield on a 0.5-mole run from 42 to 83% (based on *p*-aminobenzoic acid).

***m*-(Methylthio)-benzoic Acid.**—*m*-(Methylthio)-benzoic acid, m.p. 126–127°, was prepared in a comparable manner by the zinc–acetic acid reduction. A melting point of 126–127° has been reported.[14]

***m*-Dimethylaminophenol.**—A solution of 25 g. (0.184 mole) of technical *m*-dimethylaminophenol was extracted with 100 cc. of 10% aq. sodium hydroxide. The basic extract was acidified with concd. hydrochloric acid, washed with 100 cc. of ether, and then neutralized to a *p*H of 7–8 with 25% sodium hydroxide. The resulting mixture was extracted with ether and the extracts combined and dried over magnesium sulfate. The ether was distilled and the resulting oil fractionated to give 20.0 g. of a product, b.p. 102–104° at 0.04 mm. This oil crystallized spontaneously. It was recrystallized from ligroin to give colorless plates, m.p. 84–85°. A melting point of 87° and a boiling point of 153° have been reported.[16] *m*-Dimethylaminophenol oxidizes rapidly in air and turns black. When dissolved in base, its solution acquires a bluish tinge and fluoresces.

***p*-N,N-Dimethylanisidine.**—Fifty-two grams (0.41 mole) of methyl sulfate was added dropwise to 50.0 g. (0.41 mole) of *p*-anisidine and 60 cc. of water. The mixture was stirred until homogeneous, then neutralized with a 25% aqueous potassium hydroxide solution. This procedure was repeated using two additional 52.0-g. portions of methyl sulfate. The resulting mixture was allowed to stand at room temperature for 12 hours, then extracted with 500 cc. of ether in 4 portions. The ether extracts were combined and dried over solid potassium hydroxide. Distillation of the ether followed by fractionation of the residual oil gave 26.0 g. (43%) of a colorless oil, b.p. 125–125.5° at 20 mm. This oil was refluxed for 3 hours with 25 cc. of acetic anhydride and refractionated to give 24.0 g. of a colorless oil, b.p. 124–126° at 20–21 mm., m.p. 48–49°. A melting point of 49° has been reported.[17]

***p*-Dimethylaminophenol.**—A solution of 18.5 g. (0.12 mole) of *p*-N,N-dimethylanisidine and 100 cc. of constant boiling hydroiodic acid was refluxed 10 hours, cooled, made basic and finally washed with ether. The basic extract was neutralized to a *p*H of 7–8, and extracted with ether. The ether extract was dried over magnesium sulfate, then filtered. Distillation of the ether followed by fractionation of the residue gave 12.8 g. (78%) of a colorless oil, b.p. 101–103° at 0.5 mm., which crystallized in the receiver. Recrystallization of this material from ether-hexane gave large rhombic colorless crystals, m.p. 77.5–78°. A melting point of 76°

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[11] Recent work of W. E. Doering and K. C. Schreiber, THIS JOURNAL, **77**, 514 (1955), and W. E. Doering and A. K. Hoffmann, *ibid.*, **77**, 521 (1955), also demonstrates the ability of a sulfonium group to enter into conjugation, as contrasted with an ammonium group.

[12] Microanalyses were by Misses J. Sorenson, C. White, H. Beck (Northwestern University) and Mr. C. W. Beazley(Microtech. Laboratories, Skokie, Ill.).

[13] C. F. H. Allen and D. D. MacKay, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1948, p. 581.

[14] C. C. Price and J. J. Hydock, THIS JOURNAL, **74**, 1943 (1952).

[15] C. Hansch and H. G. Lindwall, *J. Org. Chem.*, **10**, 383 (1945).

[16] H. Heckel and R. Adams, THIS JOURNAL, **47**, 1715 (1925).

[17] H. Wieland, *Ber.*, **43**, 720 (1910).

and a boiling point of 127–128° at 0.4–0.5 mm. have been reported.[16,18]

***m*-Bromodimethylaniline.**—Alkylation of *m*-bromoaniline with methyl sulfate by the method of Gilman and Banner[19] gave 56% yield of material, b.p 147–148° at 30 mm., m.p. 10–10.5°. These authors[19] reported a boiling point of 118–119° at 8 mm. and a melting point of 11°.

***m*-Dimethylaminothiophenol.**—Nineteen grams (0.25 mole) of propylene sulfide in 100 cc. of dry ether was added slowly (exothermic reaction) to a lithium reagent made from 50.0 g. (0.25 mole) of *m*-bromodimethylaniline, 3.85 g. (0.55 mole) of lithium metal and 200 cc. of dry ether, according to the method of Bordwell, Andersen and Pitt.[20] The preparation of the lithium reagent and the addition of propylene sulfide were carried out under a nitrogen atmosphere. The reaction mixture was poured into 400 cc. of ice-water, the layers were separated, and the ether layer was washed with 100 cc. of 10% aqueous sodium hydroxide. The combined aqueous solutions were neutralized to a *p*H of 7, and the resulting mixture was extracted with 300 cc. of ether in four portions. The ether extracts were combined and dried over sodium sulfate. The ether was distilled and the resulting residue fractionated to give 17.5 g. (46%) of a colorless oil, b.p. 82–83° at 0.6 mm., $n^{25}D$ 1.6173, which decolorized iodine, and gave a positive test for mercaptan.

Anal. Calcd. for $C_8H_{11}NS$: C, 62.71; H, 7.23; neut. equiv., 153. Found: C, 62.46; H, 7.23; neut. equiv., 157.

A second fraction, b.p. 135–137° at 0.6 mm., $n^{25}D$ 1.6100, weighing 6.4 g., gave a negative test for mercaptan and was identified as *m*-dimethylaminophenyl disulfide. A boiling point of 162–166° at 16 mm. has been reported.[21]

***p*-Dimethylaminothiophenol.**—Addition of propylene sulfide to *p*-dimethylaminophenyllithium according to the procedure previously described for the *meta* isomer gave a 77% yield of *p*-dimethylaminothiophenol as a colorless oil, b.p. 74–75° at 0.2 mm. This oil crystallized spontaneously to give a material, m.p. 33.5–33.7°. A melting point of 28.5° and a boiling point of 122° at 2 mm. have been reported.[22]

Anal. Calcd. for $C_8H_{11}NS$: C, 62.71; H, 7.23. Found: C, 62.89; H, 7.37.

The method of Gilman and Fullhart,[22] *i.e.*, addition of powdered sulfur to *p*-dimethylaminophenyllithium, gave in one trial 28% of a material b.p. 85–86° at 0.8 mm.

Ammonium Salts.—Aryltrimethylammonium *p*-bromobenzenesulfonates and *p*-toluenesulfonates were readily prepared by the method of Marvel, Scott and Amstutz.[23] In general, 1 g. of the tertiary amine was refluxed for 15–30 minutes in 10 ml. of dry benzene with 1.5 molar quantity of methyl *p*-bromobenzenesulfonate or methyl *p*-toluenesulfonate. The reaction mixture was cooled and the product was collected on a filter, washed with ether and recrystallized from mixtures of ethanol–ethyl acetate or ethanol–ether.

***m*-Mercaptophenyltrimethylammonium *p*-Bromobenzenesulfonate.**—The reaction between 1.53 g. (0.01 mole) of *m*-dimethylaminothiophenol and 3.77 g. (0.015 mole) of methyl *p*-bromobenzenesulfonate gave 1.95 g. (48%) of white plates m.p. 139–140°. Recrystallization from ethanol–ethyl acetate brought the melting point to 140–141°.

Anal. Calcd. for $C_{15}H_{18}O_3NS_2Br$: C, 44.57; H, 4.48. Found: C, 44.81; H, 4.68.

***p*-Mercaptophenyltrimethylammonium *p*-Toluenesulfonate.**—A 76% yield of white plates, m.p. 210–211°, was obtained after two recrystallizations from ethanol–ethyl acetate.

Anal. Calcd. for $C_{16}H_{21}O_3NS_2$: C, 56.60; H, 6.23. Found: C, 56.73; H, 6.17.

***m*-Hydroxyphenyltrimethylammonium *p*-Toluenesulfonate.**—The crude reaction product was recrystallized from ethanol–ethyl acetate to give 55% yield of white shiny needles, m.p. 142–144°.

Anal. Calcd. for $C_{16}H_{21}O_4NS$: C, 59.42; H, 6.54. Found: C, 59.48; H, 6.52.

***p*-Hydroxyphenyltrimethylammonium *p*-Toluenesulfonate.**—The crude product obtained in 85% yield was crystallized from ethanol–ethyl acetate to give large white plates, m.p. 110–111°. The drying of this material at 80° and 0.1 mm. was accompanied by an apparent change of crystalline form: partial melting followed by resolidification took place. The product obtained, m.p. 150–170°, was recrystallized from ethanol–ethyl acetate to give long needles, m.p. 178–179°, which were not affected by further drying. The melting point of a sample of this compound which stood in an open bottle for a few days was lowered to 150–175°. Drying raised this m.p. to 178–179°.

Anal. Calcd. for $C_{16}H_{21}O_4NS$: C, 59.42; H, 6.54. Found: C, 59.31; H, 6.69.

Sulfonium Salts.—The aryl methyl sulfide was heated with a 2-molar quantity of methyl *p*-toluenesulfonate or methyl *p*-bromobenzenesulfonate for 1–2 hours in refluxing toluene or at 100–150° in the absence of a solvent. In the latter method, which gave 15–35% better yields, the product was washed free of starting materials with ether, and was recrystallized from mixtures of ethanol–ethyl acetate or ethanol–ether.

***m*-Carboxyphenyldimethylsulfonium *p*-Toluenesulfonate.**—Without solvent a 96% yield of white crystalline material, m.p. 196–197°, was obtained after two recrystallizations from ethanol–ethyl acetate.

Anal. Calcd. for $C_{16}H_{18}O_5S_2$: C, 54.22; H, 5.12; neut. equiv., 354.4. Found: C, 54.24; H, 5.20; neut. equiv., 356.7.

***p*-Carboxyphenyldimethylsulfonium *p*-Toluenesulfonate.**—By conducting the reaction without a solvent an 80% yield of white material, m.p. 176–177°, was obtained.

Anal. Calcd. for $C_{16}H_{18}O_5S_2$: C, 54.22; H, 5.12; neut. equiv., 354.4. Found: C, 54.67; H, 4.91; neut. equiv., 353.8.

***m*-Hydroxyphenyldimethylsulfonium *p*-Bromobenzenesulfonate.**—The reactants were refluxed for two hours in toluene to give 83% of white plates, m.p. 103–104°.

Anal. Calcd. for $C_{14}H_{15}O_4S_2Br$: C, 42.97; H, 3.86. Found: C, 43.14; H, 3.87.

***p*-Hydroxyphenyldimethylsulfonium *p*-Bromobenzenesulfonate.**—The crude product of the reaction was crystallized from ethanol–ethyl acetate to give 80% of a material, m.p. 77–78°. Dried at 65° at 10 mm. this material partially melted, then solidified to give a higher melting form, m.p. 124–125°. Seeding the low melting form with a crystal of the high melting material gave a product, m.p. 124–125°, which was stable on drying.

Anal. Calcd. for $C_{14}H_{15}O_4S_2Br$: C, 42.97; H, 3.86. Found: C, 42.71; H, 3.73.

***p*-Hydroxyphenyldimethylsulfonium *p*-Toluenesulfonate.**—A white crystalline material, m.p. 76–78°, was obtained in 90% yield after crystallization from ethanol–ethyl acetate. Attempts to dry the sample at 65° at 10 mm. resulted in a glassy amorphous mass which on recrystallization gave back the original material, m.p. 76–78°. Mixed melting points showed no depression; analysis suggested the presence of a molecule of water of crystallization.

Anal. Calcd. for $C_{15}H_{18}O_4S_2 \cdot H_2O$: C, 52.31; H, 5.85. Found: C, 52.82; H, 5.94.

The pK_a values obtained from the hydrated *p*-toluenesulfonate and the anhydrous *p*-bromobenzenesulfonates were identical. Roberts, Clement and Drysdale[5] reported that *m*- and *p*-dimethylaminophenyltrimethylammonium chloride retained water of crystallization tenaciously.

***m*-Hydroxyphenyldimethylsulfonium Picrate.**—The material obtained by treating 1.4 g. (0.01 mole) of *m*-hydroxyphenyl methyl sulfide with 4.5 g. (0.025 mole) of methyl *p*-toluenesulfonate was added to a solution containing 2.29 g. (0.01 mole) of picric acid in 50 cc. of ethanol. The solution was refluxed 30 minutes and the material which crystal-

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(18) This cleavage proceeds well despite the fact that the concentration of oxonium ions in solution must be very low. This probably means that attack of iodide ion occurs on the species p-$(CH_3)_2\overset{+}{N}HC_6H_4$-$OCH_3$ giving p-$(CH_3)_2\overset{+}{N}HC_6H_4O^- + CH_3I$. A similar result has been reported with hydrobromic acid in acetic acid by K. H. Slotta and R. Behnisch, *J. prakt. Chem.*, **135**, 235 (1932).

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lized on cooling was recrystallized from ethanol to give 2.3 g. (60%) of flaky, yellow material, m.p. 175–176°. This salt is very slightly soluble in water, or cold ethanol.

Anal. Calcd. for $C_{14}H_{13}O_8N_3S$: C, 43.86; H, 3.41. Found: C, 44.22; H, 3.48.

***p*-Hydroxyphenyldimethylsulfonium Picrate.**—The method previously described, starting with the *p*-toluenesulfonate salt, gave 86% yield of bright, yellow plates, m.p. 184–185°. As in the case of the *meta* isomer, this salt was almost insoluble in water or cold ethanol.

Anal. Calcd. for $C_{14}H_{13}O_8N_3S$: C, 43.86; H, 3.41. Found: C, 43.93; H, 3.45.

***m*-Hydroxyphenyldimethylsulfonium Iodide.**—The method of Zincke and Ebel[24] gave a 70% yield of a hard crystalline material, m.p. 96–96.5°. These authors[24] have reported a melting point of 97–98°.

***p*-Hydroxyphenylmethylsulfonium Methyl Sulfate.**—One and four-tenths grams (0.01 mole) of *p*-hydroxyphenyl methyl sulfide was heated at 100° for 2 hours with 2.52 g. (0.02 mole) of methyl sulfate. The reaction mixture was cooled, methanol was added and the solid which separated was filtered and washed with ether. Recrystallization from methanol–ethyl acetate gave 2.2 g. (83%) of white crystalline material, m.p. 92–93°.

Anal. Calcd. for $C_9H_{14}O_5S_2$: C, 40.59; H, 5.29. Found: C, 40.64; H, 5.36.

***p*-Nitrophenyldimethylsulfonium Methyl Sulfate.**—Two and four-tenths grams (0.014 mole) of *p*-nitrophenyl methyl sulfide was heated at 100° for 1 hour with 2.52 g. of methyl sulfate. After two recrystallizations from ethanol, 3.7 g. (95%) of cream colored plates, m.p. 157–158.5°, was obtained. A melting point of 157–158.5° has been reported.[25]

Dimethylphenylsulfonium Perchlorate.—The material obtained by heating 1.24 g. (0.01 mole) of phenyl methyl sulfide and 2.52 g. (0.02 mole) of methyl sulfate at 100° for two hours was added to 50 cc. of water and 28 g. (0.2 mole) of 70% perchloric acid. The clear solution was allowed to stand 3 days at 10°. The large colorless plates which separated out were filtered, washed with ether and dried to give 1.90 g. (80%) of a material which decomposed at 158–160°. A decomposition point of 160° has been reported.[26]

Acidity Constants Measurements.—The acidity constants of the phenols, thiophenols and benzoic acids were determined potentiometrically with a Beckman *p*H meter model G standardized against Beckman buffers. The phenols and carboxylic acids were dissolved in water and processed by the method of Bordwell and Cooper.[4a] The apparent ionization constants of the thiophenols in 48% ethanol were measured by a procedure described earlier.[4b] The *p*H's of these compounds were also followed to complete neutralization as the titration curves obtained furnished a convenient method of checking their purity.

The ionization constants of the substituted phenols and thiophenols were calculated by the Henderson equation,[27] $pK_a = pH + \log C_a/C_b$, and are summarized in Tables III and IV. Because of the relatively large dissociation of *m*- and *p*-dimethylsulfoniobenzoic acids, the concentration of undissociated acid, C_a, and the concentration of salt, C_b, had to be corrected for the ionization occurring, and the equation $pK_a = pH + \log(C_a - [H^+])/(C_b + [H^+])$ was used.[28] The data are summarized in Table III.

TABLE III

ACIDITY CONSTANTS

Substituents	*C* mole/liter	*C*b mole/liter	*p*H obsd.	*pK*a	*pK*a average
	Phenols in water at 25°				
p-$(CH_3)_2S^+$–	0.01426	0.00268	6.65	7.29	
(*p*-$CH_3C_6H_4SO_3^-$)	.01462	.00534	7.06	7.30	
	.01733	.01069	7.51	7.30	7.30
p-$(CH_3)_2S^+$–	.01467	.00322	6.75	7.30	
(*p*-$BrC_6H_4SO_3^-$)	.01405	.00616	7.20	7.31	
	.00544	.00322	7.45	7.29	7.30
m-$(CH_3)_2S^+$–	.01918	.00429	7.13	7.67	
(*p*-$BrC_6H_4SO_3^-$)	.01615	.00643	7.49	7.67	
	.01826	.01072	7.83	7.68	7.67
p-$(CH_3)_3N^+$–	.01734	.00881	8.37	8.35	
(*p*-$CH_3C_6H_4SO_3^-$)	.02003	.00979	8.31	8.33	
	.01560	.00685	8.24	8.34	8.34
m-$(CH_3)_3N^+$–	.01051	.00443	7.89	8.03	
(*p*-$CH_3C_6H_4SO_3^-$)	.01327	.00690	8.08	8.04	
	.01327	.00394	7.67	8.04	8.04
	Benzoic acids in water at 25°				
p-$(CH_3)_3S^+$–	0.02214	0.00858	3.13	3.27	
(*p*-$CH_3C_6H_4SO_3^-$)	.02498	.01501	3.51	3.31	
	.02770	.00956	3.09	3.31	3.30
m-$(CH_3)_2S^+$–	.02366	.00962	3.11	3.22	
(*p*-$CH_3C_6H_4SO_3^-$)	.01866	.01283	3.55	3.18	
	.01909	.00428	3.82	3.20	3.20

TABLE IV

APPARENT ACIDITY CONSTANTS OF SUBSTITUTED THIOPHENOLS IN 48% ETHANOL AT 25°

Substituents	*C* mole/liter	*C*b mole/liter	*p*H obsd.	*pK*a	*pK*a average
p-$(CH_3)_3N^+$–	0.01215	0.00246	5.08	5.67	
(*p*-$CH_2C_6H_4SO_3^-$)	.01272	.00493	5.49	5.69	
	.01064	.00601	5.79	5.68	5.68
m-$(CH_3)_3N^+$–	.00564	.00148	5.01	5.46	
(*p*-$BrC_6H_4SO_3^-$)	.00595	.00246	5.33	5.48	
	.00601	.00345	5.60	5.47	5.47

Ultraviolet Absorption Spectra.—The ultraviolet absorption spectra of the sulfonium salts prepared for this investigation were measured in water at 25 ± 1° with a Cary recording spectrophotometer equipped with a hydrogen discharge tube and 1-cm. quartz cells. The absorption spectra of *m*- and *p*-hydroxyphenyldimethylsulfonium ions were also measured in 0.01 *N* sodium hydroxide solution.

A sample of the compound to be measured was weighed in a 100-ml. volumetric flask which was subsequently filled to the mark. A few milliliters of this stock solution, approximately $10^{-3}M$ in concentration, were withdrawn with a pipet, quantitatively diluted several fold, thoroughly mixed and thermostated to give a solution which could be used in the spectrophotometer. The results obtained have been summarized in Table II, together with the absorption spectra of *m*-hydroxyphenyl methyl sulfone in neutral and basic solutions measured by the method of Fehnel and Carmack[29] in 48% ethanol.

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