[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PENNSYLVANIA]

Effects of Dimethylsulfonio and Trimethylammonio Groups on the Dissociation of Substituted Phenols

BY SHIGERU OAE AND CHARLES C. PRICE

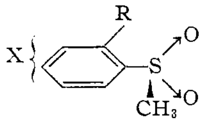
RECEIVED MAY 29, 1957

A methyl group *ortho* to the dimethyl sulfonio group *meta* and *para* in phenol seems to exert relatively small effects on either pK_a or ultraviolet spectra.

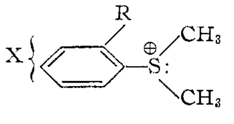
There have been many reports of the conjugative ability of the sulfone group[1] and it has become a well recognized fact that the sulfur atom in a sulfone group may stabilize unshared electrons on an adjacent carbon atom, perhaps in part through conjugation using its *d*-orbitals. Recently Bordwell and Boutan[2] presented evidence that the sulfur atom in the dimethylsulfonio group shows a similar interaction with adjacent carbon atoms, by showing that the *p*-substituted phenol is a stronger acid than the *m*-isomer and that the *p*-isomer shifts its ultraviolet maxima to longer wave lengths than the *meta*.

While much has been known about the steric or angular requirement for *p,p*-orbital overlapping for resonance, little information is available on the nature of the angular requirement for *p,d*-overlap of the C–S bond for resonance.[1g,3] However, most of the work seems to indicate that there is little if any angular requirement for *p,d*-overlap.

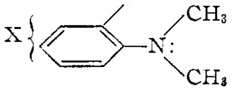
Our present investigation was planned to add more information about the steric or angular requirement for *p,d*-orbital overlap between the C–S bond in the dimethylsulfonio group attached to the benzene ring.



I



II



III

Earlier conclusions have been reached largely from a study of sulfone interaction. Because of the tetrahedral nature of the sulfur in sulfones, it is not clear whether steric hindrance by R would restrict rotation to a particular preferred conformation in I. With sulfonium salts, having only two substituents on the sulfur, steric hindrance to rotation should clearly lead to a preferred conformation, *i.e.*, to an arrangement with the methyl groups in II out of the plane of the ring. An additional factor of interest in sulfonium salt is their electronic similarity to amines (III), where much clear evidence of steric inhibition of resonance exists.[4] Because of the positive charge on the sulfur atom in II, electron donation to form a π-bond to carbon would seem unimportant. However, formation of a π-bond by donation of one or two electrons from carbon to sulfur, with promotion of the ninth or tenth unshared outer valence electron to a *d*-orbital seems a reasonable possibility for II, but *not* for I, III or the quaternary derivative of III.

We have, therefore, prepared *p*- and *m*-hydroxyphenyldimethylsulfonium halides, 2-methyl-4-hydroxyphenyldimethylsulfonium chloride and 2-methyl-5-hydroxyphenyldimethylsulfonium chloride and compared their acidity constants, as well as their ultraviolet spectra, to those for analogous aryltrimethylammonium chlorides.

Experimental

4-Methyl-3-dimethylaminophenol.—2-Methyl-5-aminodimethylaniline[5] (30 g.) was diazotized in an ice-water solution of sulfuric acid (170 g. of ice and 75 ml. of sulfuric acid) with 15 g. of sodium nitrate, keeping the temperature below −5°. The diazotized solution was dropped into a boiling solution of dilute sulfuric acid solution (114 ml. of sulfuric acid in 100 ml. of water) at 150–160°. After neutralizing with sodium carbonate. the whole solution was extracted in a Soxhlet liquid–liquid extractor with ether. After evaporating ether from the dried ether extract. the residue was distilled *in vacuo* and 15 g. (50%). b.p. 102–103° (2.5 mm.), was collected. It crystallized at room temperature. giving a yellow solid which melted at 68–70°. Recrystallization from Skellysolve gave cubic crystals. m.p. 72–72.5°.

Anal. Calcd. for $C_9H_{13}NO$: C. 71.53; H, 8.61; N. 9.27. Found: C, 71.47; H, 8.55; N, 9.36.

4-Hydroxyphenyltrimethylammonium iodide was made according to the method previously used,[6] starting from *p*-aminophenol. methyl iodide and sodium carbonate. and the crystals obtained were recrystallized repeatedly from alcohol and the colorless compound, m.p. 195° dec., was collected. **3-Hydroxyphenyltrimethylammonium iodide**[7] was made by the same procedure as described above. The colorless crystals, m.p. 179°, were collected and used.

2-Methyl-4-hydroxyphenyltrimethylammonium Iodide.—3-Methyl-4-aminophenol (12.5 g., 0.1 mole), 45 g. (0.3 mole) of methyl iodide and 11 g. (0.1 mole) of anhydrous sodium carbonate were placed in 150 ml. of water and the mixture was refluxed for six hours. After evaporating 50

---

[1] (a) E. A. Fehnel and M. Carmack, THIS JOURNAL, **71**, 231 (1949); **72**, 1292 (1950); (b) H. P. Koch, *J. Chem. Soc.*, 387, 394 (1949); (c) C. C. Price and J. J. Hydock, THIS JOURNAL, **74**, 1943 (1952); (d) F. G. Bordwell and G. D. Cooper, *ibid.*, **74**, 1058 (1952); (e) F. G. Bordwell and H. M. Anderson, *ibid.*, **75**, 6019 (1953); (f) A. Kotch, L. H. Krol, P. E. Verkade and B. M. Wepster, *Rec. trav. chim.*, **71**, 108 (1952); (g) H. Kloosterziel and H. J. Backer, *ibid.*, **72**, 185 (1953); (h) *ibid.*, **72**, 655 (1953); (i) W. E. Doering and L. K. Levy, *ibid.*, **73**, 509 (1955).

[2] F. G. Bordwell and P. J. Boutan, *ibid.*, **78**, 87 (1956). This paper appeared after our work had been initiated.

[3] (a) G. E. Kimball, *J. Chem. Phys.*, **8**, 188 (1940); (b) W. E. Moffitt, *Proc. Roy. Soc. (London)*, **A200**, 409 (1950); (c) H. P. Koch and W. E. Moffitt, *Trans. Faraday Soc.*, **47**, 7 (1951); (d) W. v. E. Doering and L. K. Levy, THIS JOURNAL, **77**, 509 (1955); (e) W. v. E. Doering and K. Hoffman, *ibid.*, **77**, 521 (1955).

[4] See, *e.g.*, C. C. Price and D. C. Lincoln, *ibid.*, **73**, 5838 (1951).

[5] F. Ullmann, M. Rozenband and B. Muhlhauser, *Ber.*, **35**, 326 (1902).

[6] H. v. Pezchmann, *ibid.*, **32**, 3682 (1899).

[7] A. Hantsch and W. B. Davidson, *ibid.*, **29**, 1533 (1896).

ml. of water, the solution was cooled and the crystals precipitated were collected and dried; yield 14.5 g. (50%). It was recrystallized twice from ethanol and the colorless crystals, m.p. 194.8–195° dec., were collected.

Anal. Calcd. for $C_{10}H_{16}ONI$: C, 40.96; H, 5.46; I, 43.34. Found: C, 41.10; H, 5.24; I, 43.20.

2-Methyl-5-hydroxyphenyltrimethylammonium Iodide.—4-Methyl-3-dimethylaminophenol (3 g.) and 3 g. of methyl iodide were mixed in 20 ml. of ethanol and the solution was refluxed overnight, and then half the ethanol was removed. When the solution was cooled, colorless crystals appeared; yield 4 g., m.p. 176° dec.

Anal. Calcd. for $C_{10}H_{16}NIO$: C, 40.96; H, 5.46; N, 4.78. Found: C, 41.34; H, 5.74; N, 4.95.

***p*-Hydroxyphenyldimethylsulfonium Iodide.**—The method of Zincke and Ebel[8] gave colorless fine needles, m.p. 122–123°. in 60% yield.

2-Methyl-4-hydroxyphenyl Methyl Sulfide.—3-Methyl-4-amino-phenol (31 g., 0.25 mole) was diazotized with 18 g. of sodium nitrite in a mixture of 50 ml. of concentrated hydrochloric acid and 150 g. of ice. Methyl mercaptan (24 g., 0.5 mole) was added dropwise in 200 ml. of 20% sodium hydroxide solution under cooling and then, after warming to 70–75°, the diazotized solution was added during the period of one hour with vigorous stirring. After the addition, the temperature was raised to 90°. The reaction mixture was cooled and extracted with ether. After the ether was removed, the residue was distilled *in vacuo* and the fraction of b.p. 120° (3.5 mm.) was collected. Only 6 g. (16%) was obtained. It solidified at room temperature and, after recrystallization from Skellysolve, the colorless crystals melted at 55–56°.

Anal. Calcd. for $C_8H_{10}S$: C, 62.34; H, 6.49; S, 20.78. Found: C, 62.28; H, 6.75; S. 20.74.

2-Methyl-4-hydroxyphenyldimethylsulfonium Iodide.—A mixture of equimolar amounts of 2-methyl-4-hydroxyphenyl methyl sulfide and methyl iodide was heated in a sealed tube for six hours at 100°. By the method of Zincke and Ebel,[8] colorless crystals were obtained in 40% yield after one recrystallization from methanol–ether, m.p. 110–111° dec.

Anal. Calcd. for $C_9H_{13}SOI$: C, 36.49; H, 4.39; S, 10.81. Found: C, 36.80; H, 4.52; S, 10.80.

2-Methyl-5-nitrophenyl Methyl Sulfide.—Seventy grams (0.46 mole) of 2-methyl-5-nitroaniline was diazotized with 30 g. (0.47 mole) of sodium nitrite in a mixture of 100 ml. of concentrated hydrochloric acid and 300 g. of ice. The diazotized solution was decomposed by dropping it into 400 ml. of 20% sodium hydroxide solution, containing 30 g. (0.625 mole) of methyl mercaptan at 70–75°. Then the mixture was steam distilled and 45 g. (50%) of yellow crystalline solid, m.p. 76–77°, was obtained. Recrystallization from alcohol gave yellow crystals, m.p. 81–82°.

Anal. Calcd. for $C_8H_9NSO_2$: C, 52.46; H, 4.92; N. 7.65; S. 17.49. Found: C. 52.52; H, 5.05; N, 7.58; S, 17.31.

2-Methyl-5-aminophenyl Methyl Sulfide.—Thirty grams of 2-methyl-5-nitrophenyl methyl sulfide was dissolved in 600 ml. of 50% acetic acid. Into the boiling solution, 45 g. of reduced iron was added portionwise in 45 minutes and heating and refluxing were continued for 2.5 hours additionally. After making alkaline with sodium hydroxide, the whole solution was steam distilled and 20 g. (80%) of white crystalline solid, m.p. 42°, was obtained. It was recrystallized from alcohol, giving colorless crystals, m.p. 48°.

Anal. Calcd. for $C_8H_{11}SN$: C, 62.73; H, 7.19; N, 9.15; S. 20.92. Found: C, 63.11; H, 7.44; N, 9.06; S, 20.48.

2-Methyl-5-hydroxyphenyl Methyl Sulfide.—Fifteen grams of 2-methyl-5-aminophenyl methyl sulfide was diazotized with 10 g. of sodium nitrite in a mixture of 40 ml. of sulfuric acid and 1400 ml. of ice-water. After excess nitrite was decomposed by adding urea, the solution was gradually added to hot boiling diluted sulfuric acid solution (100 ml. of sulfuric acid in 800 ml. of water). When nitrogen ceased to evolve, an oil appeared at the bottom. This was extracted with ether and the ether extract was dried. After removing ether, the residue was distilled *in vacuo* and 7 g. (50%) of a constant boiling fraction, b.p. 110° (1 mm.), was obtained. It solidified at room temperature and was recrystallized from Skellysolve, m.p. 41°.

Anal. Calcd. for $C_8H_{10}SO$: C, 62.49; H, 6.49; S, 20.77. Found: C, 62.07; H, 6.24; S, 20.92.

2-Methyl-5-hydroxyphenyldimethylsulfonium Iodide.—An equimolar mixture of 2-methyl-5-hydroxyphenyl methyl sulfide and methyl iodide was heated in a sealed tube at 100° for four hours. After one recrystallization from methanol and ether, colorless needles, m.p. 109–110°, were obtained in 46% yield.

Anal. Calcd. for $C_9H_{13}SOI$: C, 36.49; H, 4.39; S, 10.81. Found: C, 36.51; H, 4.54; S, 10.64.

Acidity Constant Measurements.—The acidity constants of the substituted phenols were determined potentiometrically with a Beckman glass electrode *p*H meter model H2, standardized against Beckman buffers. The phenols were dissolved in purified water and the *p*H of partially neutralized solutions were determined. The ionization constants of the substituted phenols were calculated by the Henderson equation,[9] $pK_a = p\text{H} - \log C_a/C_b$, where C_a and C_b are the concentrations of undissociated acid and of salt, respectively. The data are summarized in Table I.

TABLE I

ACIDITY CONSTANTS OF SUBSTITUTED PHENOLS

Substituents	C. mole l.	C_b. mole l.	*p*H obsd.	*pK*a	*pK*a average
$p\text{-}(CH_3)_2\overset{\oplus}{S}\text{-}\overset{\ominus}{I}$	0.02000	0.01002	7.30	7.30	
	.01498	.00503	7.00	7.30	7.30
$m\text{-}(CH_3)_2\overset{\oplus}{S}\text{-}\overset{\ominus}{I}$	.02000	.01002	7.67	7.67	
	.01598	.00503	7.37	7.67	7.67
$p\text{-}(CH_3)_2\overset{\oplus}{S}\text{-}\overset{\ominus}{I}$, *m*-$CH_3$	.02000	.01002	7.60	7.60	
	.01501	.00503	7.60	7.60	7.60
$m\text{-}(CH_3)_2\overset{\oplus}{S}\text{-}\overset{\ominus}{I}$, *p*-$CH_3$	.01894	.01009	8.05	8.00	
	.01509	.00503	7.70	8.01	8.01
$p\text{-}(CH_3)_3\overset{\oplus}{N}\text{-}\overset{\ominus}{I}$	.02000	.01002	8.21	8.21	
	.01503	.00503	7.91	8.21	8.21
$m\text{-}(CH_3)_3\overset{\oplus}{N}\text{-}\overset{\ominus}{I}$	.01989	.01002	8.04	8.04	
	.01522	.00503	7.71	8.02	8.03
$p\text{-}(CH_3)_3\overset{\oplus}{N}\text{-}\overset{\ominus}{I}$. *m*-$CH_3$	.02000	.01002	8.34	8.34	
	.01500	.00503	8.04	8.34	8.34
$m\text{-}(CH_3)_3\overset{\oplus}{N}\text{-}\overset{\ominus}{I}$. *p*-$CH_3$	.02000	.01002	8.26	8.26	
	.01497	.00503	7.96	8.26	8.26

Ultraviolet Absorption Spectra.—The ultraviolet absorption spectra of the sulfonium and ammonium salts were measured in water at 25 ± 1° with a Process and Instruments recording spectrophotometer. The absorption spectra of these salts also were measured in 0.01 *N* sodium hydroxide solution. The concentrations of these salts were approximately 2.5×10^{-5} *M* and the results obtained are summarized in Table II. The calculations of σ values for acid constants were made using log K_0 and ρ of phenol as −9.95 and 2.29, respectively. The values were listed in Table III.

Discussion

The σ-constant data in Table III indicate very little effect of the adjacent methyl group on the effect of the trimethylammonio group in either the *m*- or *p*-position to the hydroxyl. However, the effect of the dimethylsulfonio group, particularly in the *p*-position, is decreased appreciably by the adjacent methyl group. This would be in accord with the concept that the resonance interaction proposed by Bordwell and Boutan has angular dependence, as would be expected if it involves a 2p-3p π-bond between carbon and sulfur.

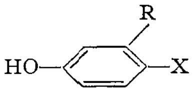
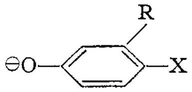
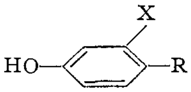
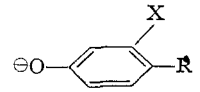
---

[8] T. H. Zincke and C. E. Ebel, *Ber.*, **47**, 923 (1914).

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

TABLE II

PRIMARY (λ) AND SECONDARY (λ') ULTRAVIOLET ABSORPTION BANDS (mμ)[a]

									
R	X	λ_{max} (log ϵ)	λ'_{max} (log ϵ)	λ_{max} (log ϵ)	λ'_{max} (log ϵ)	λ_{max} (log ϵ)	λ'_{max} (log ϵ)	λ_{max} (log ϵ)	λ'_{max} (log ϵ)
H	H[10]	211(3.79)	270(3.16)	235(3.97)	287(3.41)	211(3.79)	270(3.16)	235(3.97)	287(3.41)
CH_3	H	214(3.73)	272(3.13)	238(3.91)	289(3.51)	219(3.71)	275(3.22)	236(3.89)	295(3.50)
H	$\oplus NMe_3$[b]	221(3.98)	269(3.33)	244(4.15)	284(3.60)	220(3.85)	272(3.36)	238(4.06)	293(3.60)
CH_3	$\oplus NMe_3$	221(3.86)	271(3.08)	243(4.04)	289(3.37)	224(4.01)	277(3.41)	243(4.08)	298(3.55)
H	$\oplus SMe_2$[c]	242(4.03)[d]	264(3.66)	269(4.20)	....	215(4.17)[e]	283(3.56)	217(4.35)	304(3.62)
CH_3	$\oplus SMe_2$	245(4.00)[f]	271(3.46)	274(4.11)	....	215(4.06)	295(3.54)	218(4.25)[g]	324(3.58)

[a] All iodides were converted to chlorides by agitation of solutions with a tenfold excess of silver chloride and then filtration. The earlier data of Bordwell and Boutan[2] on iodide salts must be considered with caution in view of the strong absorption for iodide ion in the region involved: λ_{max} 226.5(4.07); λ_{max} 291(2.74). [b] We find for $(C_6H_5)N^+Me_3Cl^-$: λ_{max} 203(3.83), λ'_{max} 255(2.45). [c] Bordwell and Boutan[2] report λ_{max} 220(3.94), λ'_{max} 265(3.04) for $(C_6H_5)S^+Me_2ClO_4^-$. [d] There was an additional peak at 214(3.68). [e] There was an additional peak at 248(3.62). [f] There were additional peaks at 215-(4.02) and 280(3.37). [g] There was an additional shoulder at 243(3.81).

TABLE III

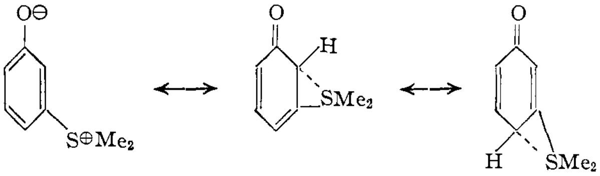
σ-CONSTANTS FOR THE $(CH_3)_3N^{\oplus}$ AND $(CH_3)_2S^{\oplus}$ GROUPS FROM THE DISSOCIATION CONSTANTS OF SUBSTITUTED PHENOLS IN WATER SOLUTION

Substituent	σ_{meta}	σ_{para}	$\sigma_m - \sigma_p$
CH_3	−0.03	−0.10	0.07
$(CH_3)_3N\oplus-$	0.84	0.76[c]	.08
$(CH_3)_3N\oplus(o\text{-}CH_3-)$	0.84[a]	0.73[b]	.11
$(CH_3)_2S\oplus-$	1.00	1.16[d]	− .16
$(CH_3)_2S\oplus(o\text{-}CH_3-)$	0.95[a]	1.00[b]	− .05

[a] $\sigma_{obsd} - \sigma_{p-CH_3}$ (−0.10). [b] $\sigma_{obsd} - \sigma_{m-CH_3}$ (−0.03). [c] Bordwell and Boutan[2] reported 0.83 and 0.70, respectively. [d] Bordwell and Boutan[2] reported 1.00 and 1.16, respectively.

If we assume, with Bordwell and Boutan,[2] that the bands near 240 mμ in the *p*-sulfoniophenol and near 270 mμ in the *p*-phenolate ions correspond to the primary band of Doub and Vandenbelt,[10] we may conclude that the methyl group adjacent to the sulfonio group has very little influence on the conjugative characteristics of the group. The small shifts to longer wave length are probably only what would be expected from the normal red shift (3 mμ) due to the methyl group.

The considerably enhanced red shift in the secondary bands of the *m*-sulfonio compounds by incorporation of an adjacent methyl group is of some interest. Since no direct resonance interaction of the type proposed for the *p*-isomers is possible, and since the *m*-sulfonio compounds do show a red shift whereas the ammonio compounds do not, we wish to suggest that the interaction in the *m*-position may involve contribution from canonical structures with three-membered rings, particularly in the excited state.



Such forms, involving interaction across an intervening carbon atom, have been indicated by the ultraviolet spectra of dithioformals, benzyl sulfide and allyl sulfides.[11]

The geometry for such structures, if it involves a tetrahedral arrangement at the sulfur atom, would have the methyl groups perpendicular to the ring. Since this conformation would be more favorable with a methyl group adjacent to the sulfonio group, this may explain the enhanced red shift, both for the phenol (13 mμ, *vs.* 20 mμ) and for the phenolate (17 mμ *vs.* 29 mμ).

PHILADELPHIA 4, PENNSYLVANIA

---

(10) L. Doub and J. M. Vandenbelt, THIS JOURNAL, **69**, 2714 (1947).

(11) M. Carmack and E. A. Fehnel, *ibid.*, **71**, 84 (1949).