and appropriate values for the other parameters, he finds a^* to be 0.18 cm. in the first experiment and 0.16 cm. in the second. Since there are a number of disturbing factors which will cause departure from the ideal theory the agreement with experiment must be considered good.

The amount of transport achieved in the experiments is small but significant. An apparatus with a narrower and longer channel should be capable of making practical separations.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Conjugative Effects of Methylsulfonyl and Methylthio Groupings[1]

BY F. G. BORDWELL AND GLENN D. COOPER

The effect of *m*- and *p*-CH_3SO_2 and CH_3S groups on the acid dissociation constants of benzoic acid, phenol and the anilinium ion have been determined. The necessity for using a larger Hammett sigma constant to express the effect of the *p*-CH_3SO_2 group on the acidity of phenol and the anilinium ion than for its effect on the acidity of benzoic acid is interpreted as evidence for an appreciable resonance effect (involving ten-electron structures). The CH_3S group resembles CH_3O in increasing the acidity of benzoic acid when substituted in the meta position and decreasing the acidity when in the para position, which points to a resonance effect for CH_3S similar to that for CH_3O but smaller in magnitude.

Chemical evidence, such as the ability of the CH_3SO_2 group to increase the acidity of α-hydrogens, its power in promoting addition of basic reagents to an α,β-carbon–carbon double bond, its strong accelerating effect on the loss of carbon dioxide from a β-carboxyl group, and its role as a meta director in aromatic substitution, suggests a close similarity in electronic effects between the CH_3SO_2 group and CH_3CO, CN, NO_2, etc., groups. Until recently it has been felt, however, that the CH_3SO_2 group differed in that it must exert its influence primarily through induction rather than by resonance. The recent physical evidence which may be interpreted as indicating considerable double bond character for the sulfur–oxygen bond in CH_3SO_2, etc., groups[2] has led to a reconsideration and renewed interest in the ability of the sulfur in such groups to expand its valence shell and to conjugate with other unsaturated groupings.

The present investigation of the acid dissociation constants of *m*- and *p*-CH_3SO_2 and CH_3S benzoic acids, phenols and anilinium ions was undertaken with two objectives in mind. First, the determinations would furnish quantitative data as to the electronic effects of CH_3SO_2 and CH_3S relative to that of other groups. Second, it should provide additional evidence as to the conjugative effect of CH_3SO_2, since it is known that para groups which can enter into strong resonance interaction with the $-O^-$ and $-NH_2$ groupings, such as NO_2, increase the acidity of phenol and the anilinium ion much more than would be expected from their acidifying effect on benzoic acid (where resonance is a minor factor).[3] As a result of this resonance effect, two Hammett sigma constants are needed to describe the electronic effect of the *p*-NO_2 group (and similar groups) one for reactions of benzoic acids and other benzene derivatives, and one for reactions of phenols and anilines (σ = 0.778 and 1.27, respectively).[3-5] The difference in sigma constants for the *p*-CH_3SO_2 group determined for benzoic acids *vs.* phenols and anilines should then be indicative of the ability of this group to conjugate with $-O^-$ and NH_2. Determinations were also made for the CH_3CO group to serve as a comparison.

Experimental

Preparation of Materials.—The compounds used were, for the most part, either Eastman Kodak Co. White Label products, further purified by recrystallization or rectification, or compounds obtained by procedures given in the literature. In a few instances new synthetic routes were used, and these are given below.

***p*-Methylsulfonylbenzoic Acid.**—Twenty grams (0.145 mole) of methyl *p*-tolyl sulfide and 100 g. of potassium permanganate were refluxed in 800 ml. of water to which 10 ml. of 10% sodium hydroxide was added. After two hours the mixture was cooled, acidified with 96% sulfuric acid, and decolorized with sodium bisulfite. The precipitate was collected and dissolved in 200 ml. of 2 *N* sodium hydroxide solution; this solution was treated with charcoal and filtered. The filtrate was acidified and the colorless needles of *p*-methylsulfonylbenzoic acid were collected on a filter and recrystallized from glacial acetic acid; yield 18 g. (62%), m.p. (uncor.) 264–265°.

***m*-Methylsulfonylbenzoic Acid.**—*m*-Methylsulfonylbenzoic acid, m.p. 234–235° (uncor.), was obtained in 72% yield by oxidation of methyl *m*-tolyl sulfide by the procedure described above.

***p*-Methylsulfonylphenol.**—Eight and eight-tenths grams (0.05 mole) of *p*-methylsulfonylanisole was refluxed for two hours with 50 ml. of 48% hydrobromic acid. The solution was cooled and extracted with a total of 250 ml. of chloroform in 50-ml. portions. Evaporation of the chloroform left a white solid which on crystallization from benzene yielded 6.5 g. (40%) of colorless needles of *p*-methylsulfonylphenol, m.p. 95.5–96.5°.

***m*-Methylsulfonylphenol.**—One and seven-tenths grams (0.01 mole) of *m*-methylsulfonylaniline was diazotized and the diazonium salt decomposed in aqueous sulfuric acid according to the directions given for the preparation of *m*-nitrophenol.[6] The reaction mixture was extracted with chloroform and the chloroform extracted with 5% sodium hydroxide solution. The sodium hydroxide solution was acidified and extracted with chloroform. Evaporation of the chloroform and crystallization of the residue from ben-

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[1] This investigation was supported by the Office of Naval Research under Contract No. N7onr-45007. An account of this work was presented at the Conference on Organic Sulfur Compounds held at Indiana University, Aug. 29–Sept. 1, 1951.

[2] G. M. Phillips, J. S. Hunter and L. E. Sutton, *J. Chem. Soc.*, 146 (1945); D. Barnard, J. M. Fabian and H. P. Koch, *ibid.*, 2442 (1949).

[3] G. E. K. Branch and M. Calvin, "The Theory of Organic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1941, pp. 257, 417.

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

[5] Using σ = 0.778 and a rho value for phenols determined for groups having small resonance effects (ρ = 2.0), the calculated K_A for p-$NO_2C_6H_4OH$ is less than one-tenth the observed value.

[6] H. Gilman, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 404.

zene yielded 0.70 g. (40%) of *m*-methylsulfonylphenol, m.p. 84–85°.

Acidity of Phenols.—Stock solutions of the phenols (0.02 *M*) were prepared by dissolving a weighed portion of phenol in freshly boiled distilled water at 25° in a volumetric flask. Two hundred-milliliter portions of the stock solutions were partially neutralized with freshly prepared carbonate-free sodium hydroxide solution. The *p*H of the solutions was measured at 25°, using a glass electrode and a Beckman Model G *p*H meter. The pK_A values were calculated from the Henderson equation[7] and are the average of three determinations at approximately 20, 40 and 60% neutralization; the spread in pK_A was generally 0.02 to 0.03. Table I gives the pK_A values for the phenols measured. In Fig. 1 log K/K_0 is plotted against σ for ten phenols. Application of the method of least squares gives ρ = 2.091, log K_0 = −9.861. The average deviation is 0.055.[8]

TABLE I

ACIDITY CONSTANTS OF PHENOLS IN WATER AT 25°

Substituent	pK_A	Substituent	pK_A
H	9.98	*m*-CH_3	10.08
m-CH_3O	9.65	*p*-CH_3	10.25
p-CH_3O	10.20	*m*-CH_3CO	9.19
p-Br	9.34	*p*-CH_3CO	8.05
m-Cl	9.08	*m*-CH_3S	9.53
p-Cl	9.42	*p*-CH_3S	9.53
m-NO_2	8.38	*m*-CH_3SO_2[a]	9.33
p-NO_2	7.16	*p*-CH_3SO_2	7.83

[a] Measured only at half-neutral point.

Apparent Ionization Constants of Benzoic Acids in 50% Ethanol.—Apparent ionization constants for the substituted benzoic acids were obtained in the same way as for the phenols; the solvent was 1:1 (by volume) ethanol–water. Roberts, McElhill and Armstrong[9] find ρ = 1.464 for this reaction. The acidity constants thus measured are listed in Table II.

TABLE II

APPARENT pK_A VALUES OF BENZOIC ACIDS IN 50% ETHANOL AT 25°

Substituent	pK_A	Substituent	pK_A
H	5.73	*m*-CH_3SO_2	4.78
m-CH_3S	5.53	*p*-CH_3SO_2	4.68
p-CH_3S	5.74	*m*-CH_3CO	5.21
		p-CH_3CO	5.10

Acidity Constants of Anilinium Ions.—The acidities of *m*-methylsulfonylaniline and *p*-methylsulfonylaniline were measured in dilute sulfuric acid solution at 25° using a Beckman Model DU spectrophotometer equipped with a constant temperature jacket, by the method of Hammett.[10] *m*-Methylmercaptoaniline and *p*-methylmercaptoaniline were measured by potentiometric titration of the hydrochlorides in the manner described above for the phenols. The results are summarized in Table III.

TABLE III

ACIDITY CONSTANTS OF ANILINIUM IONS

Substituent	*C* (moles/liter × 10^5)	λ	D_{ArNH_2}	$D_{ArNH_3^+}$	*D*	pK_A
p-NO_2	3.30	381	0.435	0.003	0.394	(1.11)
m-CH_3SO_2	3.40	242	.212	.024	.067	2.681
p-CH_3SO_2	3.23	263	.551	.033	.448	1.484
m-CH_3S						4.05
p-CH_3S						4.40

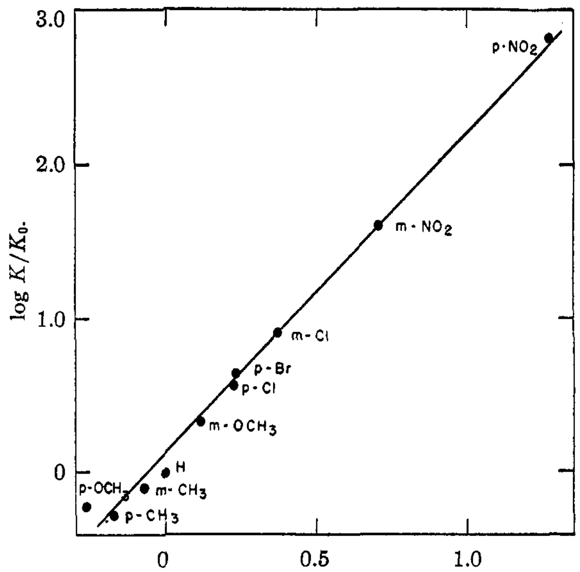


Fig. 1.—Relationship between ionization of phenols and Hammett sigma constants.

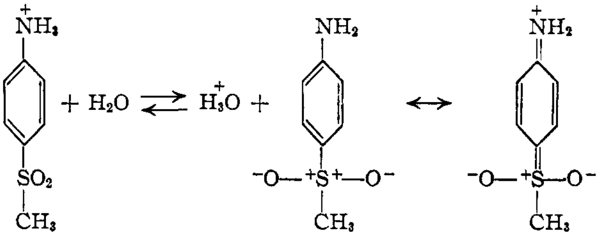
Discussion

The data concerning the electronic effects of the CH_3SO_2, CH_3S and CH_3CO groups can be expressed concisely by means of the sigma constant calculated from Hammett's equation[4]

$$\rho\sigma = \log K - \log K_0$$

The results are summarized and compared with those of other investigators in Table IV.

From Table IV it is apparent that the effect of *m*-CH_3SO_2 in reactions of benzoic acids, phenols and anilines is accurately described by a single σ constant, whereas the values for *p*-CH_3SO_2 differ by 0.26 (phenols) and 0.42 (anilinium ion). These differences are comparable to those observed for *p*-CH_3CO (0.44), and to those reported for *p*-NO_2 (0.049[4] and *p*-CN (0.34).[11] The present evidence, therefore, points to appreciable conjugative ability for the CH_3SO_2 group (involving ten electrons); one possible representation is shown.



This interpretation is strengthened by a recent study of the electrical effect of the $(CH_3)_3N^+$ group,[12] which cannot exert direct conjugative effects. The data, showing that σ is greater for *m*-$(CH_3)_3N^+$ than for *p*-$(CH_3)_3N^+$, and that the difference $\sigma_{para} - \sigma_{meta}$ is nearly constant for reactions of benzoic acids, phenols and anilines, are consistent with the view of an inductive effect without appreciable conjugation.[12] The evidence

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(7) S. Glasstone, "The Electrochemistry of Solutions," Methuen and Co., Ltd., London, 1930, p. 207.

(8) The recorded values (ref. 4, p. 189) for this reaction (ρ = 2.008, log K_0 = −9.941) are based on ionization constants of five phenols measured by a different technique.

(9) J. D. Roberts, E. A. McElhill and R. Armstrong, THIS JOURNAL, 71, 2923 (1949).

(10) Ref. 4, Chapter IX.

(11) J. D. Roberts and E. A. McElhill, THIS JOURNAL, 72, 628 (1950).

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

TABLE IV

CONSTANTS FOR THE METHYLMERCAPTO, METHYLSULFONYL AND ACETYL GROUPS

Reaction	m-CH_3S	p-CH_3S	m-CH_3SO_2	p-CH_3SO_2	m-CH_3CO	p-CH_3CO
Apparent ionization constants of benzoic acids, 50% ethanol, 25°	+0.14	−0.01	+0.65	+0.72	+0.35	+0.43
Alkaline hydrolysis of ethyl benzoates, 56% acetone, 25°[a]	+ .10[b]	− .07[b]	+ .65	+ .76		
Ionization of phenols, water, 25°	+ .16	+ .16	+ .70	+ .98	+ .32	+ .87
Acidity constants of anilinium ions, water 25°	+ .19	+ .06	+ .69	+1.13		
Hydrolysis of arylsulfuric acids, water 78.6°[c]					+ .31[c]	+ .87[c]

[a] C. C. Price and J. J. Hajduk, private communication. [b] Measured at 0°, a previous value of −0.047 was recorded for p-CH_3S, see ref. 4, p. 188. [c] Ref. 4, p. 188.

from sigma constants indicates, therefore, that the CH_3SO_2 group should be classified electronically with resonating groups such as CH_3CO, CN, etc., rather than with the $(CH_3)_3N^+$ group.

Recently Koch and Moffitt[13] have reviewed the evidence for conjugative effects of the $-SO_2-$ group, and have suggested that the existing rather contradictory data can be made consistent by assuming that only a weak conjugation is possible in a sulfone only one of whose carbon atoms is part of an unsaturated or conjugated system, but that a strong conjugation is possible in systems where both carbons are unsaturated such as the thiophene 1-dioxides. An analysis using the molecular orbital theory was found to be consistent with this hypothesis. The spectroscopic evidence for conjugation in alkyl aryl sulfones[14] was rationalized by assuming that conjugation of groups with CH_3SO_2 may be important in excited states or transition states but not in ground levels. The present data indicate that conjugative effects may be appreciable in sulfones only one of whose carbons is unsaturated even in the ground state.[15]

The fact that m-CH_3S increases the acidity of benzoic acid whereas p-CH_3S decreases the acidity, can be interpreted as being due to an acid-weakening resonance for the para group,[16] $p\text{-}CH_3\overset{\curvearrowright}{S}\text{—}\overset{\curvearrowright}{C_6H_4}\text{—}\overset{\curvearrowright}{C(OH)}{=\!=}O$. This effect is similar to that observed for p-CH_3O, but smaller in magnitude.[17] It seemed possible *a priori* that p-CH_3S might exert a resonance effect comparable to that of p-CH_3SO_2 in conjunction with O^- and NH_2 groups, *i.e.*,  In line with this the sigma constants of p-CH_3S determined for phenols and anilinium ions are somewhat more positive than those for benzoic acids. Similar effects are noted, however, with p-CH_3O, and a better interpretation is probably that the more positive sigma value reflects a resonance effect which is present in the p-CH_3O and p-CH_3S benzoic acids, but absent in the corresponding phenols and anilines.

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(13) H. P. Koch and W. E. Moffitt, *Trans. Faraday Soc.*, **47**, 7 (1951); see also ref. 2.

(14) E. A. Fehnel and M. Carmack, THIS JOURNAL, **71**, 231 (1949); *ibid.*, **72**, 1292 (1950); H. P. Koch, *J. Chem. Soc.*, 408 (1949).

(15) Note, however, that the sulfonyl group does not appear to be able to conjugate with an odd electron (C. C. Price and J. Zomlefer, THIS JOURNAL, **72**, 14 (1950); C. G. Overberger, D. E. Baldwin and H. P. Gregor, *ibid.*, **72**, 4864 (1950)).

(16) C. K. Ingold, *J. Chem. Soc.*, 1124 (1933), first used this explanation for the m- and p-CH_3O benzoic acids.

(17) The order of resonance effects $CH_3O > CH_3S$ is in line with the similar order observed for the halogens, F > Cl, Br > I. Other evidence pointing to a lesser resonance effect of –S– than –O– is found in the lack of shortening of the C–S bond in CH_3COSH (W. Gordy, *J. Chem. Phys.*, **14**, 560 (1946)).

EVANSTON, ILLINOIS RECEIVED SEPTEMBER 14, 1951

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NEW YORK UNIVERSITY]

Stereospecificity of Hydrogen Migration in the Pinacol Rearrangement

BY KURT MISLOW AND MAURICE SIEGEL[1]

The synthesis and resolution of 2-methylbenzilic acid are described. Reduction of the optically active acid to 1-phenyl-1-o-tolylglycol, followed by acid-catalyzed rearrangement to optically active phenyl-o-tolylacetaldehyde, substantiates that hydrogen migration in the rearrangement is stereospecific.

The stereospecificity of the pinacol–pinacolone rearrangement seems well established[2]; in many instances the rearrangement of optically active glycols or aminoalcohols has yielded optically active ketones, the migrating group in those cases being phenyl or benzyl.[3] Of particular interest is the work done on the optically active tolylhydrobenzoins. It was shown[4] that the rearrangement of the o- and m-tolyl isomers, but not of the p-isomer, led to the corresponding optically active tolyldesoxybenzoins, results which were taken as evidence for the stereospecific 1,2-shift of hydrogen. The interpretation of these data was, however, made with some reservations: the product of the more critical rearrangement, α-phenyl-α-o-tolylacetophenone, was never definitely identified, and

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[1] The major portion of this material was abstracted from the thesis submitted by Maurice Siegel to the Graduate School of New York University in partial fulfillment of the requirements for the degree of Master of Science, 1951.

(2) E. R. Alexander and D. C. Dittmer, THIS JOURNAL, **73**, 1665 (1951), and references given therein.

(3) R. Roger and A. McKenzie, *Ber.*, **62**, 272 (1929); A. McKenzie and W. S. Dennler, *ibid.*, **60**, 220 (1927); A. McKenzie, R. Roger and G. O. Wills, *J. Chem. Soc.*, 779 (1926); H. J. Bernstein and F. C. Whitmore, THIS JOURNAL, **61**, 1324 (1939); S. Kanao, *J. Pharm. Soc. Japan*, **64**, 137 (1944) [*C. A.*, **45**, 5136 (1951)].

(4) A. McKenzie, R. Roger and W. B. McKay, *J. Chem. Soc.*, 2597 (1932); R. Roger and W. B. McKay, *ibid.*, 332 (1933).