The Basicities of Some Aryl Methyl Sulfoxides[1]

KENNETH K. ANDERSEN, WARREN H. EDMONDS,[2] J. BRIAN BIASOTTI, AND RICHARD A. STRECKER

Department of Chemistry, University of New Hampshire, Durham, New Hampshire 03824

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Ten *meta*- and *para*-substituted phenyl methyl sulfoxides were titrated potentiometrically using perchloric acid as the titrant and acetic anhydride as the solvent. Their apparent pK_a values were determined by placing the values for the half-neutralization potentials on a straight line determined by plotting the pK_a values *vs.* the half-neutralization potential for some amines whose pK_a values were known. The pK_a values gave a good correlation with Hammett's σ constants. An analysis of the substituent effects using the procedure of Taft led to the conclusions that electron acceptance by the sulfur is more important in the protonated than the unprotonated state and that a large change in positive charge likely occurs at sulfur between the protonated and unprotonated states. This titration procedure was also used to determine the apparent pK_a values of dimethyl sulfoxide, diphenyl sulfoxide, and the S,S-dimethyl-, S,S-diphenyl-, and S-phenyl-S-methyl-N-*p*-toluenesulfonylsulfilimines.

While it is well known that sulfoxides are weakly basic, little quantitative work has been done in determining basicities of various sulfoxides.[3] In this work, ten *meta*- and *para*-substituted phenyl methyl sulfoxides were titrated potentiometrically in acetic anhydride using perchloric acid in glacial acetic acid as the titrant. The titration data led to the sulfoxides apparent pK_a values which were well correlated by Hammett's σ constants for the appropriate substituents. Specific resonance effects between the *para*-substituted phenyl group and the sulfinyl group were detected using the analytical procedure proposed by Taft.

In 1958, Streuli potentiometrically titrated a number of amines using perchloric acid in glacial acetic acid as the titrant and acetic anhydride as the solvent.[4] The pK_a values in water were known for a number of these amines. A plot of these known pK_a values against the half-neutralization potentials (HNP) gave a good straight line. This plot could then be used to determine pK_a values of amines whose pK_a values were unknown. Streuli extrapolated this method to dimethyl sulfoxide and determined its pK_a as 1.0. We have used this method to determine the pK_a values of the sulfoxides listed in Table I.[5] These pK_a values must be regarded as apparent; presumably they are proportional to the true pK_a values in water. This presumption receives reassurance from the Hammett plot data.

The pK_a values listed in Table I vary from +0.55 for *p*-anisyl methyl sulfoxide, the strongest base, to −3.51 for *p*-nitrophenyl methyl sulfoxide, the weakest base. This variation of over 4 pK_a units is large. The pK_a difference between *p*-methoxybenzamide and *p*-nitrobenzamide and between *p*-methoxybenzoic acid and *p*-nitrobenzoic acid acting as weak bases and measured in aqueous acid are both about 1.4 units.[3] The difference between *p*-methoxyacetophenone and *p*-nitroacetophenone is 3.1 pK_a units.[6] Perhaps the sulfoxides do not fall on Streuli's pK_a *vs.* HNP plot; the slope may be too steep for the sulfoxides thus leading to the wide spread in pK_a. All of the carbonyl compounds mentioned above protonate on the second atom from the benzene ring. Compounds which protonate on the first atom have larger differences in pK_a. For example, the pK_a difference between *p*-methoxy- and *p*-nitroanilinium ions[7] is 3.2 and between *p*-methoxy- and *p*-nitrobenzenethiol[8] 3.3. While the idea of a sulfoxide protonating on sulfur would help explain the large pK_a difference, it is unattractive considering current concepts of the sulfinyl group's structure. This point will be returned to later. For the moment, protonation on oxygen will be assumed.

A Hammett plot of log $K/K_0 = \rho\sigma$ gave a good straight line with $\rho = 3.79$, a correlation coefficient of 0.993, and a standard deviation of 0.169.[9]

TABLE I

Compd	HNP[a]	pK_a[b]	% error[c]
N,N-Diethylaniline	230 ± 0	6.55	+1.98
N,N-Dimethylaniline	292 ± 2	5.25	−3.39
Caffein	500 ± 1	0.49	+2.19
Substituted phenyl methyl sulfoxides			
p-CH_3O	498 ± 4	0.550	+0.76
p-CH_3	523 ± 3	0.014	+1.25
H	544 ± 2	−0.488	+1.70
m-CH_3	551 ± 2	−0.646	+2.12
m-CH_3O	575 ± 1	−1.19	−0.10
p-Cl	592 ± 1	−1.57	+1.53
m-Cl	616 ± 1	−2.11	+0.47
m-CF_3	635 ± 5	−2.54	−0.53
m-NO_2	665 ± 4	−3.22	+0.22
p-NO_2	678 ± 5	−3.51	+4.63
Dimethyl sulfoxide	482 ± 3	0.911	−1.41
Diphenyl sulfoxide	681 ± 1	−3.58	−0.32
S,S-Dimethyl-N-*p*-toluenesulfonylsulfilimine	497 ± 1	0.573	+1.74
S,S-Diphenyl-N-*p*-toluenesulfonylsulfilimine	682 ± 2	−3.60	+1.84
S-Methyl-S-phenyl-*p*-toluenesulfonylsulfilimine	609 ± 1	−1.96	+2.21

[a] Half-neutralization potential in millivolts. [b] The pK_a values for the amines are taken from Streuli.[4] The pK_a values for the sulfoxides are calculated from the equation $pK_a = 11.79 - 0.02257HNP$ derived from a least-squares treatment of the amine data. [c] Calculated from the actual volume of titrant minus the expected volume over the expected volume times 100.

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(2) Part of this work is from the B.S. thesis of W. H. Edmonds, 1965.

(3) E. M. Arnett in "Progress in Physical Organic Chemistry," Vol. 1, S. G. Cohen, A. Streitwieser, Jr., and R. W. Taft, Ed., Interscience Publishers, Inc., New York, N. Y., 1963.

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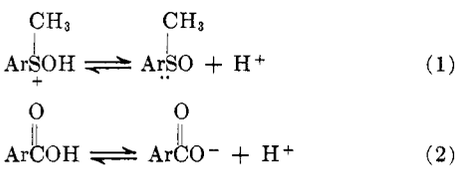
TABLE II

SPECIFIC RESONANCE EFFECTS ($\bar{\sigma} - \sigma^0$). IONIZATION REACTIONS

Subst	Protonated phenyl methyl sulfoxides[a]	Benzoic acids[b]	Anilinium ions[c]	Thiophenols[d]	Protonated acetophenones[e]
p-CH_3O	−0.26	−0.15	−0.15	+0.03	−0.59
p-CH_3	−0.08	−0.02	−0.06	+0.04	−0.24
p-Cl	−0.06	−0.04	−0.07	+0.02	−0.13
p-NO[c]	−0.07	−0.04	+0.13	+0.14	+0.03
	$\rho = 3.61$	+1.00	+2.78	+3.06	+2.01
	$r = 0.983$		1.00	0.986	0.981
	$s = 0.22$		0.026	0.108	0.128

[a] This work. [b] Difference between Hammett's σ constants and σ^0; see ref 10. [c] Reference 7. pK_a values for aniline and *m*-nitroaniline were taken from N. A. Lange, "Handbook of Chemistry," 7th ed, Handbook Publishers, Inc., Sandusky, Ohio, 1949, p 1408, and I. Heilbron, "Dictionary of Organic Compounds," Vol. 3, Oxford University Press, New York, N. Y., 1953, p 629, respectively. [d] Reference 8. [e] Reference 6. The mathematical procedure used to determine ρ, and the definitions of the correlation coefficient, r, and the standard deviation, s, are given in ref 9.

K refers to the ionization constants for the substituted and unsubstituted protonated phenyl methyl sulfoxides. The correlation with σ^+ constants is not as good. It should be recalled that ρ is defined as log (K_x/K_0) for a series of benzoic acids. The similarity between the sulfoxides and benzoic acids is shown by eq 1 and 2. The Hammett plot reveals



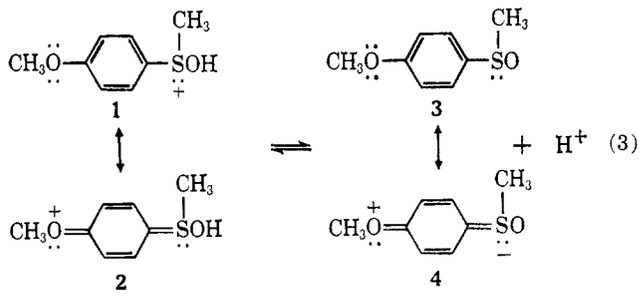
(1)

(2)

that the two equilibria are influenced similarly by the same substituents. The large value of ρ, a direct result of the large spread in pK_a values, will be commented on subsequently.

Taft[10] proposed a method for evaluating resonance effects between the substituted benzene ring and the reaction center bonded to it. This method uses a select group of *meta* substituents whose σ constants don't vary greatly for a large number of rate and equilibrium studies. Their σ constants, σ^0, are used to define the slope, ρ, of a Hammett plot, *i.e.*, log $(K_x/K_0) = \rho\sigma^0$. The substituent is considered to be the entire substituted benzene ring. The assumption is made that there is no resonance interaction between the substituted benzene ring and the reaction center involving the particular functional group attached in the *meta* position. The effective σ constants, $\bar{\sigma}$, of the *para*-substituted ring are taken from this plot, *i.e.*, $\bar{\sigma} = 1/\rho$ log (K_x/K_0). Several reactions involving compounds of the type $ArCH_2Y$ were used to define σ^0 values for the *para*-substituted rings. Resonance is assumed to be impossible between the ring and Y owing to the interposed methylene group. The difference $\bar{\sigma} - \sigma^0$ is then a measure of the specific resonance interaction between the *para*-substituted phenyl ring and the reaction center Y. This approach is useful for comparing two or more series of reactions.

The Taft method has been applied to the sulfoxides: log $K_x/K_0 = 3.61\sigma^0$. The data, with the unexplained exception of the unsubstituted case, fit the criteria proposed by Taft: at least four *meta*-substituted as well as the unsubstituted compound should be used to define ρ, no *meta*-substituted compound should deviate from the line by more than ± 0.07 σ units, and the standard error for all the substituents should be ± 0.03 or less. This method was also applied to a series of benzoic acids, anilinium ions, benzenethiols, and protonated acetophenones. These results which are independent of ρ are listed in Table II. It can be seen that the *para* resonance effects for the sulfoxides correspond best to those for the benzoic acids and not very well to those of the other three series. The large negative value of the $(\bar{\sigma} - \sigma^0)$ resonance value for the *p*-methoxyphenyl group is particularly noteworthy. This means that electron donation by the substituent is greater in the protonated than in the unprotonated form and is evidence for the expansion of sulfur's octet, or in other terms, (p → d) π bonding between sulfur and carbon. Resonance structure **2** contributes more to the resonance hybrid of the protonated molecule than **4** does to that of the unprotonated molecules.[11]



(3)

This argument for (p → d) π bonding must take into account the case of the anilinium ions (Table II). *p*-Methoxyanilium ion has a $(\bar{\sigma} - \sigma^0)$ value of −0.15, yet expansion of nitrogen's octet is unlikely. We can rationalize this resonance value as a reflection of the great polarizing power of the positive nitrogen. It is unlikely that sulfur is such a powerful polarizing atom that its $(\bar{\sigma} - \sigma^0)$ value could be due to this factor alone. For this reason, we feel that (p → d) π bonding as a concept is of real operational value.

The value of ρ is large as can be seen from the other ρ values in Table II. ρ values for acid–base equilibria, however, generally increase as one goes from aqueous to

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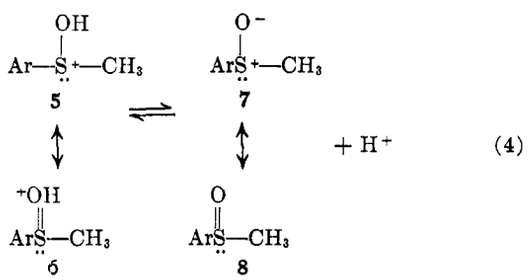
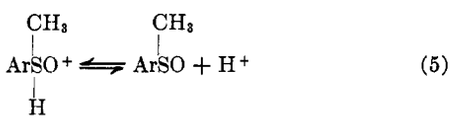
less polar nonaqueous solvents. If the wide spread in pK_a is real, the resulting magnitude of ρ supports the notion of sulfur–oxygen double-bond character, since a large change in charge at an atom adjacent to the benzene ring upon protonation is implied.[10] That is,



(4)

structure **5** is more important relative to **6** than **7** is relative to **8**.

An alternative explanation for the large ρ value is protonation on sulfur which also involves a large change in charge. While this is intuitively unattractive, since one expects protonation at the site of high-



(5)

est electron density which is the oxygen atom, one should consider this possibility in view of the existence of adducts formed utilizing the electrons on sulfur. For example, dimethyl sulfoxide and methyl iodide form $(CH_3)_3SO^+ I^-$.[12] Complexes with certain metals such as platinum and palladium also bond to sulfur.[13] These adducts follow the rules of the soft and hard acids and bases theory.[14] The sulfinyl oxygen is a hard base; the sulfur is soft. Methyl iodide and the metals are soft acids or electrophiles and consequently bond at sulfur. Since a proton is hard it should protonate the hard oxygen. On these grounds, eq 5 seems unlikely.

This is consistent with experimental evidence that sulfoxides hydrogen bond at oxygen.[15] The SO stretching frequency was shifted to lower frequencies in going from carbon tetrachloride solutions to chloroform or to carbon tetrachloride containing methanol. Such a decrease is consistent with hydrogen bond formation at oxygen rather than sulfur. It seems that sulfoxides must protonate at oxygen. Even so, the uncertain nature of ρ makes any argument based on its magnitude tentative and any interpretation of the relative importance of the resonance structures in eq 4 speculative.

N-*p*-toluenesulfonyl-substituted sulfilimines can also be titrated in acetic anhydride and then pK_a values calculated. When the pK_a values for the S,S-diphenyl, S,S-dimethyl, and S-phenyl-S-methyl-N-*p*-toluenesulfonylsulfilimines were plotted against the pK_a values for the corresponding diphenyl, dimethyl, and phenyl methyl sulfoxides a straight line was not obtained. While the reason for this is not yet known, it might be a steric effect. A series of substituted S-phenyl-S-methyl-N-*p*-toluenesulfonylsulfilimines is being investigated. Hopefully the results will make possible an explanation of the lack of correlation.

Experimental Section

Titration Procedure.—The sulfoxides and amines were dissolved in 200 ml of Fisher Certified Reagent Grade acetic anhydride contained in a 250-ml beaker. Magnetic stirring was used. The titrant, Fisher Certified Reagent Grade 0.1 *N* perchloric acid dissolved in glacial acetic acid, was delivered from a 10-ml buret. The quantity of base used required 4 to 6 ml of acid. A Beckman Model H2 pH meter equipped with a glass and a calomel electrode was used to follow the titration. The HNP and end points were obtained from a plot of potential *vs.* milliliters of acid added.

Amines.—The caffein was recrystallized from benzene and had mp 235–237°, lit.[16] mp 234–235°. The anilines were distilled shortly before use: N,N-dimethylaniline (Fisher Certified Reagent Grade), bp 49–50° (0.3 mm), lit.[17] bp 41° (1 mm); N,N-diethylaniline (Eastman Kodak Yellow Label), bp 58° (0.6 mm), lit.[17] bp 63° (2 mm).

Sulfoxides.—Commercially available diphenyl sulfoxide was recrystallized twice from petroleum ether; mp 70–71°, lit.[18] mp 70–71°. Dimethyl sulfoxide (Fischer analytical reagent) was dried over Linde Molecular Sieves No. 13X. The substituted phenyl methyl sulfoxides were prepared by oxidation of the corresponding sulfides in methanol at about −70 to −80° using *t*-butyl hypochlorite as the oxidant.[19] Phenyl methyl sulfoxide was the one exception; hydrogen peroxide in glacial acetic acid at 0° was used. All of the sulfoxides except for *m*-trifluoromethylphenyl methyl sulfoxide were known compounds. All of the sulfoxides had SO stretching bands in the infrared at about 1050 cm^{-1}. Their melting points (boiling points where pressures are given) were *p*-CH_3O, 122–123° (0.25 mm), lit.[20] 153–154° (5 mm); *p*-CH_3, 42–43°, lit.[20] 42–43°; *m*-CH_3, 109–10° (1 mm), lit.[20] 126–127° (3 mm); *m*-CH_3O, 113–115° (0.2 mm), lit.[21] 125–127° (16 mm); H, 84° (0.25 mm), lit.[22] 85° (0.5 mm); *p*-Cl, 46–48°, lit.[20] 47–48°, *m*-Cl, 125–126° (1.3 mm), lit.[20] 100–101° (0.1 mm); *m*-NO_2, 115–116°, lit.[20] 117–118°; *p*-NO_2, 148–149°, lit.[20] 148–149°.

***m*-Trifluoromethylphenyl Methyl Sulfoxide.**—A Grignard reagent was prepared from 3-(trifluoromethyl)bromobenzene (56 g, 0.25 mole) and magnesium (6.7 g, 0.28 g-atom) in anhydrous ether (100 ml). Methyl disulfide (25 g, 0.27 mole) in ether (100 ml) was added dropwise. After an additional 100 ml of ether was added, the solution was hydrolyzed with 10% hydrochloric acid. The ether layer was washed with water, dried over calcium chloride, and concentrated using a rotatory evaporator to give the presumed *m*-trifluoromethylphenyl methyl sulfide. This was distilled to give an oil (23.5 g), bp 45–49° (0.9 mm). A solution of this oil in methanol was cooled in a Dry Ice–acetone bath to about −70°. *t*-Butyl hypochlorite (13.3 g, 0.122 mole) was added dropwise over a 50-min period with stirring. Sodium bicarbonate (5 g) was added. The mixture was filtered and concentrated. The semisolid residue was extracted with ether. Concentration of the ether gave a yellow oil which was dried over calcium chloride and then distilled to give the pure sulfoxide (15.3 g, 0.0729 mole, 29% yield), bp 88–89° (0.4 mm).

Anal. Calcd. for $C_8H_7F_3OS$: C, 46.15; H, 3.39. Found: C, 46.34; H, 3.57.

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Sulfilimines.—The sulfilimines were prepared from the corresponding sulfide and chloramine-T: S,S-diphenyl-N-toluenesulfonylsulfilimine, mp 111–112°, lit.[23] 113°; S-methyl-S-phenyl-N-*p*-toluenesulfonylsulfilimine, mp 128–129°, lit.[23] mp 132°; S,S-dimethyl-N-*p*-toluenesulfonylsulfilimine, mp 158–159°, lit.[24] mp 157–158°.

Acknowledgment.—The authors wish to thank Professor R. W. Taft for some helpful comments.

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The Synthesis and Base-Catalyzed Cyclization of (+)- and (−)-*cis*-S-(1-propenyl)-L-cysteine Sulfoxides

J. F. CARSON AND LOIS E. BOGGS

Western Regional Research Laboratory,[1] *Albany, California 94710*

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S-(2-propenyl)-L-cysteine (I) has been isomerized to *cis*-S-(1-propenyl)-L-cysteine (II). Oxidation of the latter with aqueous hydrogen peroxide yielded a mixture of diastereomeric sulfoxides which was separated into the (+)- and (−)-*cis*-S-(1-propenyl)-L-cysteine sulfoxides (III). These compounds are isomers of the corresponding (+)-*trans* amino acid found in *Allium cepa* (onions). Reaction of either of the diastereomeric *cis* amino acids (III) in aqueous base produced cycloalliin (3-methyl-1,4-thiazane-5-carboxylic acid 1-oxide) (VI) and a new isomeric cyclic sulfoxide amino acid IV with unknown chirality at the sulfur atom.

S-(1-propenyl)-L-cysteine sulfoxide has been isolated from the onion (*Allium cepa*) and has been shown to be the precursor of the lachrymatory properties which result from enzyme action.[2] Recently, we have shown that the double bond of this naturally occurring amino acid has the *trans* configuration.[3] In this paper we report the synthesis of the dextro- and levorotatory *cis*-S-(1-propenyl)-L-cysteine sulfoxides (III), which are isomers of the naturally occurring amino acid, and the study of their cyclization in base.

S-(2-propenyl)-L-cysteine (I) was isomerized to *cis*-S-(1-propenyl)-L-cysteine (II)[4] by reaction with potassium *t*-butoxide in dimethyl sulfoxide. Oxidation of II with hydrogen peroxide in water yielded a mixture of diastereomeric sulfoxides III which were separated into the dextro- and levorotatory sulfoxides by fractional crystallization. The (+) isomer, which is less soluble in aqueous ethanol, has $[\alpha]^{25}D$ +118.5 (water) and the (−) isomer, which accumulates in the mother liquor, has $[\alpha]^{25}D$ −106.6.[5] The two isomers were further characterized by the preparation of N-2.4-dinitrophenyl derivatives. Both of the sulfoxides give the lachrymatory effect and onion aroma when treated with the C-S lyase enzyme of *Albizzia lophanta*.[6] Like the *trans* amino acid, the new isomers are unstable to mineral acid and to base and are very sensitive in solution to atmospheric oxygen.

The naturally occurring *trans* isomer, in the presence of dilute ammonium hydroxide, cyclizes to cycloalliin[7] for which the structure VI [3-(*S*)-methyl-1,4-thiazane-5-(*R*)-carboxylic acid 1-(*S*)-oxide] was recently established by X-ray analyses.[8] Reaction of, the *cis* amino acids with aqueous base, however is more complex. Cycloalliin is formed in yields of 10–16% and an isomeric cyclic sulfoxide (IV) is isolated in 14–24% yield. In addition, at least two other unidentified ninhydrin-reacting components are produced.

The structure of IV as a 3-methyl-1,4-thiazane-5-carboxylic acid 1-oxide was established by Raney nickel desulfurization to yield N-isopropyl-L-alanine which is also obtained on desulfurization of cycloalliin. Reduction of IV with hydriodic acid yielded the sulfide V (Figure 1), the structure of which was confirmed by nmr spectra.

The sulfide V differs from the corresponding sulfide VII obtained by reduction of cycloalliin only in the configuration of the C-methyl atom. Palmer and Lee[8] have recently shown by X-ray analyses that crystalline cycloalliin hydrochloride hydrate has the chair conformation with the sulfoxide oxygen axial and *trans* to the methyl and carboxyl groups which are equatorial. Since the carbon atom bearing the methyl group has the (*S*) configuration in cycloalliin (VI) it must have the (*R*) configuration in the isomeric sulfoxide IV and in the sulfide V. The isomer IV is therefore defined except for the sulfoxide configuration and the conformation of the molecule. IV and cycloalliin show similar ORD curves which are characterized by a positive Cotton effect at low wavelength. When the sulfoxide in cycloalliin is reduced to the sulfide, the molecular rotation in acid becomes more negative, $[M]^{25}D$ −23.6 → −47.2 while reduction of the isomeric sulfoxide IV gives a rotation less negative $[M]^{25}D$ −145 → −112.8.

Both cycloalliin and the isomeric sulfoxide IV are believed to be configurationally pure. Repeated recrystallization under varying conditions did not change the rotation or the infrared spectrum. The (+)- and (−)- and various mixtures of the *cis*-propenylcysteine sulfoxides give similar yields of cycloalliin and of the isomer IV. This suggests that the sulfoxide probably epimerizes[9] so that the same cyclic sulfoxide is produced from either configuration and that *cis–trans* isomeriza-

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(8) K. J. Palmer and K. S. Lee, *Acta. Cryst.*, **20**, 790 (1966).

(9) A reviewer has suggested that, since β,γ-unsaturated sulfoxides are energetically favored over the α,β isomers in base isomerizations [D. E. O'Connor and C. D. Broadus, *J. Am. Chem. Soc.*, **86**, 2267 (1964)], stereomutation of the double bond and of the sulfoxide group may proceed by a mechanism involving the allyl isomers in a base-catalyzed reaction.