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The Basicities of Substituted Diphenyl Sulfoxides[1]

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The basicities of nine *meta*- and *para*-substituted diphenyl sulfoxides have been determined spectrophotometrically in sulfuric acid media. The pK_{BH^+} values thus obtained indicate that these sulfoxides possess rather weak basicities (pK_{BH^+}; -3.67—-5.74). and these pK_{BH^+} values gave a good correlation with Brown-Okamoto's σ^+ values, ($\rho=-2.00$), instead of σ-values. These observations seem to suggest a considerable conjugative interaction between phenyl groups and sulfoxide group of these diphenyl sulfoxides.

Sulfoxides have been considered to be weakly basic because of their physical and chemical behavior, the remarkable solvating power of cationic species, semipolar nature of the S–O linkage, *etc.* But the basicities of only a few alkyl sulfoxides have hitherto been determined.[2]

Recently, Andersen and his co-workers[3] determined the basicities of *meta*- and *para*-substituted phenyl methyl sulfoxides by the potentiometric titration in acetic anhydride, and gave the pK_{BH^+} values which can be nicely correlated by Hammett's σ values with a large ρ value of -3.79. More recently, Haake and Cook[4] determined the pK_{BH^+} values of phenyl methyl sulfoxide and dimethyl sulfoxide, -3.45 and -2.7 respectively, by the measurements of NMR chemical shift of methyl group and they showed the values to be considerably larger than those of Andersen's[3] and earlier workers'.

During the course of our studies on the acid-catalyzed oxygen exchange reactions,[5] we were interested in the basicities of diaryl sulfoxides and synthesized nine substituted diphenyl sulfoxides and determined their basicities. The measurements of the basicities of these substituted diphenyl sulfoxides were carried out spectrophotometrically in sulfuric acid media in a fashion similar to that described by Hammett[6] and other workers,[7] taking advantage of our earlier finding that sulfoxides ionize in a concentrated sulfuric acid in a following manner,[8] since the UV spectra of diaryl sulfoxides are quite different from those of the corresponding protonated species.

$$R_2SO + H_2SO_4 \rightleftarrows R_2\overset{+}{S}OH + HSO_4^- \qquad (i\text{-facter}=2) \qquad (1)$$

The pK_{BH^+} values for the substituted diphenyl sulfoxides thus obtained are listed in Table 2, and are found to be nicely correlated by Brown-Okamoto's[9] σ^+ values, with ρ value of -2.00.

Experimental and Results

The Substituted Diphenyl Sulfoxides were prepared by the oxidation of the corresponding sulfides with the bromine complex of pyridine and water in acetic acid according to the same procedure as described in our previous paper.[10] Their melting and boiling points (°C) were *p*-CH_3O, 60—60.5°C, lit,[11] 55—57°C; *p*-C_2H_5O, 71— 72°C; *p*-CH_3, 69—70°C, lit,[11] 71—72°C; *m*-CH_3, 44.5—45.5°C, lit,[11] 46—47°C; H, 70—71°C, lit,[11] 71°C; *p*-Cl, 44—45°C, lit,[11] 45—46°C; *p*-I, 106—107°C, lit,[12] 106°C; *p*-Br, 62—62.5°C; *m*-Cl, 165—

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[1] Paper XXXII on Sulfoxides.

[2] P. Nylén, *Z. Anorg. Allgem. Chem.*, **246**, 227 (1941).

[3] K. K. Andersen, W. H. Edward, J. B. Biasotti and R. A. Strecker, *J. Org. Chem.*, **31**, 2859 (1966).

[4] a) P. Haake and D. Cook, *Tetrahedron Letters*, **1968** 427; b) S. Oae, K. Sakai and N. Kunieda, unpublished work.

[5] a) S. Oae, T. Kitao and Y. Kitaoka, *Chem. & Ind.*, **1961**, 291; b) S. Oae, T. Kitao, T. Kitaoka and S. Kawamura, This Bulletin, **38**, 546 (1965); c) S. Oae and N. Kunieda, *ibid.*, **41**, 696 (1968).

[6] a) L. P. Hammett and A. J. Deyrup, *J. Am. Chem. Soc.*, **54**, 2721 (1932); b) L. A. Flexser, L. P. Hammett and A. Dingwall, *ibid.*, **57**, 2103 (1925).

[7] a) A. R. Katritzky, A. J. Waring and K. Yates, *Tetrahedron*, **19**, 465 (1963); b) K. Yates and H. Wai, *Can. J. Chem.*, **43**, 2131 (1965).

[8] S. Oae, T. Kitao and Y. Kitaoka, This Bulletin, **38**, 543 (1965).

[9] H. C. Brown and Y. Okamoto, *J. Am. Chem. Soc.*, **80**, 4979 (1959).

[10] S. Oae, Y. Ohnishi, S. Kozuka and W. Tagaki, This Bulletin, **39**, 364 (1966).

[11] G. Modena, *Gazz. Chem. Ital.*, **89**, 834 (1959).

[12] D. L. Hammick and B. Wiliams, *J. Chem. Soc.*, **1938**, 211.

167°C/1.5 mmHg, lit,[11] 190—192°C/5 mmHg; *p*-NO_2, 106—107°C, lit.[11] 106—107°C.

Sulfuric Acid. Concentrations of sulfuric acid - water media were determined by titrating with a standard alkali solution. The H_0 values used here are Long and Paul's[13] with the corrections above 60% of concentrations given by Jorgensen and Harter.[14]

Measurement of pK_{BH^+}. The UV spectra of the sulfoxides in sulfuric acid media ranging from 0% to 91.3% acid were measured with a Hitachi EPS-2U model Spectrophotometer. The wave lengths and intensities of the absorption maxima of the unprotonated (A_B) and protonated (A_{BH^+}) forms of the sulfoxides are listed in Table 1. We can see from these UV charts, for example, shown in Fig. 1 that the intensities of the absorption maxima of the unprotonated sulfoxides increase while those of the protonated sulfoxides decrease with the decrease of the concentration of sulfuric acid.

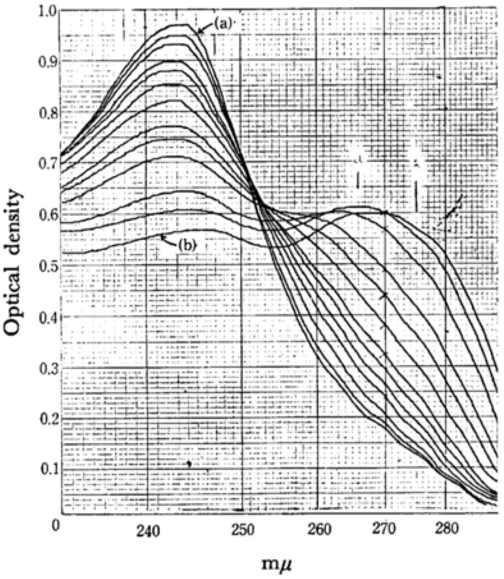

Fig. 1. UV chart of *p*-bromophenyl phenyl sulfoxide in sulfuric acid.
(a), in water and (b), in 90.2% sulfuric acid

TABLE 1. WAVE LENGTH MAXIMA FOR SUBSTITUTED DIPHENYL SULFOXIDES ($X-C_6H_4-SO-C_6H_5$)

Substituent (X)	λ_{max} in water) mμ	λ_{max} in water) log ε	λ_{max} in 91.3 % sulfuric acid mμ	λ_{max} in 91.3 % sulfuric acid log ε
p-CH_3O	245	4.21	281	4.05
p-C_2H_5O	246	4.22	283	4.11[b]
p-CH_3	237	4.20	264	4.02
m-CH_3	234	4.13	253	3.88
H	233	4.15	255	3.91
p-Cl	240	4.23	262	4.07
p-I	240	4.40	263	4.19[b]
p-Br	243	4.28	268	4.07[b]
m-Cl	232	4.10	245	3.94[b]

a) The values of UV spetcra in water in this column had close resemblance to those in ethanol solution.
b) In 90.2% sulfuric acid.

Hammett used the following equation (Eq. (2)) to estimate the pK_{BH^+} values of such weak bases as acetophenone, benzoic acid and others in sulfuric acid media,[6a] but the equation could not be used for the measurement of pK_{BH^+} values of several other compounds[15] which do not behave as ideal Hammett bases,[7a,16] since a gradient of log $[BH^+]/[B]$ *vs.* $-H_0$ for a non-Hammett base is not unity.

$$pR_{BH^+} = H_0 - \log \frac{[BH^+]}{[B]} \qquad (2)$$

Although numerous compounds have been shown to behave as Hammett bases, many compounds are not so, and our compounds were also found to be non-Hammett bases. In such cases it is more prudent to use the following equation (Eq. (3)) for the pK_{BH^+} calculation of the non-Hammett bases,[7a,16] namely substituted sulfoxides in this case.

$$pK_{BH^+} = H_0 - n \log \frac{[BH^+]}{[B]} \qquad (3)$$

Incidentally this equation has been used for the estimation of pK_{BH^+} values of amides,[7a,b] acetophenone,[7b] benzoic acid,[7b] benzaldehyde,[7b] phosphine oxides,[16] phosphine sulfides,[16] and phenyl methyl sulfoxide,[4] *etc.*

In the spectrophotometric determination, $[BH^+]$ and $[B]$ can be rewritten as $[A-A_{BH^+}]$ and $[A_B-A]$ respectively, where A is an absorbance of a sulfoxide in sulfuric acid media of an adequate concentration. When the values of $\log[BH^+]/[B]$ obtained are plotted against H_0 values according to Eq. 3, one gets a straight line from which n and the pK_{BH^+} value can be obtained. This method was quite useful for the determination of pK_{BH^+} of most of the sulfoxides. However, we could not measure the pK_{BH^+} values of *para*- and *meta*-nitrophenyl phenyl sulfoxides by this method, since the absorption maxima of the UV spectra for the unprotonated and protonated forms of these sulfoxides are too near to be measured with reliable accuracy.

The n-values for the substituted diphenyl sulfoxides were found to be larger (1.8—2.4) than unity, like those for benzamide (1.51),[7b] acetophenone (1.37),[7b] benzaldehyde (1.22),[7b] benzoic acid (1.20),[7b] phosphine oxides

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[13] M. A. Paul and F. A. Long, *Chem. Revs.*, **57**, 1 (1957).

[14] M. J. Jorgenson and D. R. Harter, *J. Am. Chem. Soc.*, **85**, 878 (1963).

[15] a) For the uracil; A. R. Katritzky and A. H. Wuring, *J. Chem. Soc.*, **1962**, 1540; b) For the substituted benzamide; J. T. Edward, H. S. Chang, K. Yates and R. Stewart, *Can. J. Chem.*, **38**, 1518 (1960); c) R. Stewart and M. R. Granger, *ibid.*, **39**, 2508 (1961).

[16] Recently, Haake and his co-workers have used this equation for the pK_{BH^+} measurement of phosphine oxides and others by NMR with less confusion; P. Haake, R. D. Cook and G. H. Hurst, *J. Am. Chem. Soc.*, **89**, 2650 (1967).

TABLE 2. THE pK_{BH^+} VALUES AND H_0 DEPENDENCE OF SUBSTITUTED DIPHENYL SULFOXIDES

Substituent	$-pK_{BH^+}$	$n^{a)}$	Wavelength for detn. $m\mu^{b)}$
p-CH_3O	3.67 ± 0.18	1.81 ± 0.20	240—290
p-C_2H_5O	3.67 ± 0.16	1.81 ± 0.20	240—290
p-CH_3	4.40 ± 0.22	2.19 ± 0.11	235—274
m-CH_3	4.73 ± 0.13	1.68 ± 0.20	231—270
H	4.92 ± 0.18	2.39 ± 0.12	230—265
p-Cl	5.15 ± 0.18	2.26 ± 0.11	238—270
p-I	5.13 ± 0.26	2.19 ± 0.20	235—270
p-Br	5.24 ± 0.10	2.24 ± 0.20	238—275
m-Cl	5.74 ± 0.04	2.27 ± 0.23	231—270
Benzophenone$^{c)}$	6.23 ± 0.10	1.75 ± 0.10	259—345
Acetophenone$^{c)}$	6.30 ± 0.18	1.50 ± 0.11	250—310

a) The correlation coefficient of all these values gave more than 0.990.
b) This is the wave length of UV spectra used to determine A.
c) These compounds were used as the standard of the pK_{BH^+} values of the sulfoxides.

(1.43—2.21),[16] *etc.*, indicating that the diphenyl sulfoxides also do not behave as Hammett bases. Recently Haake and Cook[4] also reported large n-values for phenyl methyl sulfoxide (1.62) and dimethyl sulfoxide (1.61).

All our pK_{BH^+} data of the substituted diphenyl sulfoxides obtained are listed in Table 2. Although we have also calculated the pK_{BH^+} values of our compounds by the method described by Davis and Geissmann,[17] these values are identical to those in Table 2.

Stretching Frequency of S–O Bond for Substituted Diphenyl Sulfoxides. The infrared spectra were determined in a set of 0.20 mm fixed path cells by means of JASCO-IR-C Infrared Spectrophotometer while the concentration of a sulfoxide was maintained as 0.05 mol/l in carbon tetrachloride. The stretching vibrations of S–O bonds of these substituted diphenyl sulfoxides obtained are listed in Fig. 2, and are found to be in a good correlation with Hammett σ values, with a correlation coefficient, $r=0.990$.

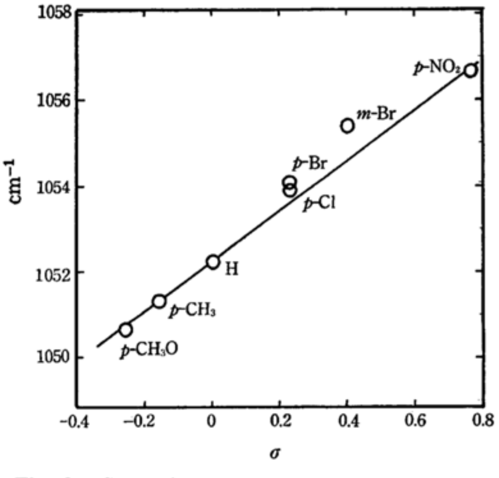

Fig. 2. Stretching frequencies of the S–O bond substituted diphenyl sulfoxides plotted against σ values.

Discussion

The pK_{BH^+} values of the diphenyl sulfoxides listed in Table 2 reveal that these sulfoxides possess rather weak basicities, and even the strongest base of this series, *i. e.*, p-anisyl phenyl sulfoxide, has its pK_{BH^+} of only -3.67. Recently, the pK_{BH^+} values of diphenyl sulfoxide has been measured in acetic anhydride by titration with perchloric acid by Andersen and his co-workers,[3] but their pK_{BH^+} value (-3.58) is considerably larger than that of ours (-4.97).[20] The pK_{BH^+} values of several other organic oxides are also listed in Table 3 for comparison.

TABLE 3. pK_{BH^+} VALUES OF ORGANIC OXIDES

Compound	pK_{BH^+}		
$(C_6H_5)_2SO$	$-4.97^{a)}$	$-3.58^{b)}$	
$(C_6H_5)S(O)CH_3$	$-0.488^{b)}$	$-3.45^{c)}$	$-3.60^{d)}$
$(CH_3)_2SO$	$0.911^{b)}$	$0^{f)}$	$-2.7^{c)}$
$(C_6H_5)_2P(O)CH_3$	$-3.2^{c)}$		
$(C_6H_5)C(O)CH_3$	$-6.15^{e)}$	$-6.30^{a)}$	$-6.51^{c)}$
$(C_6H_5)_2CO$	$-6.18^{e)}$	$-6.23^{a)}$	
$(CH_3)_3NO$	$4.65^{f)}$		
$(CH_3)_3AsO$	$3.75^{f)}$		

a) This work.
b) By potentiometric titration method (Ref. 3).
c) By NMR method (Ref. 4a, 16).
d) Our unpublished work, by NMR (Ref. 4b).
e) By a similar method to ours (Ref. 18, 19).
f) Ref. 2.

The basicities of the sulfoxides resemble more closely those of the carbonyl compounds and phosphine oxides than those of the amine and arsine oxides. Probably a substantial 2p–3dπ interaction may be in operation between the two ends of the S–O bond to diminish the basicities of the sulfoxide as in the cases of carbonyl compounds and phosphine oxides. It is known incidentally that the basicity of an oxide would be diminished

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[17] C. T. Davis and T. A. Geissmann, *J. Am. Chem. Soc.*, **76**, 3507 (1954).

[18] A. Fischer, B. A. Grigor, J. Packer and J. Vanghan, *ibid.*, **83**, 4208 (1962).

[19] R. Stewart and K. Yates, *ibid.*, **80**, 6355 (1959).

[20] The pK_{BH^+} value for phenyl methyl sulfoxide of Haake and Cook[4a] and ours[4b] which was measured by NMR in sulfuric acid media, are also smaller than that of Andersen and his co-workers'[3] which was measured by potentiometric titrations in acetic anhydride.

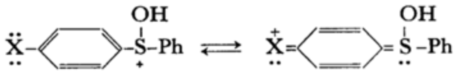
not only the semipolar character but also by the π-bonding character of the oxide bond.[21]

For example, the C–O bond of the carbonyl compounds which display the weakest basicities among several organic oxides possess almost complete π-bonding character, while the N–O and As–O bonds of amines and arsine oxides are known to be of a semipolar nature and quite basic.

It is interesting to note that the basicities of diphenyl sulfoxide is markedly smaller than that of dimethyl sulfoxide. In the case of dimethyl sulfoxide,[22] perhaps both electron-donating inductive and hyperconjugative effects of two methyl groups increase the electron density of the sulfoxide S–O linkage to enhance the basicity, while the low basicity of diphenyl sulfoxide may be due to the electron-withdrawing inductive effect of two phenyl groups which reduce the electron density of the S–O bond.

When the pK_{BH^+} values for the *meta*- and *para*-substituted diphenyl sulfoxides thus obtained were plotted against Brown–Okamoto's[9] σ^+ values, a good straight line was obtained with the correlation coefficient $r=0.990$, and the ρ value of -2.00.[24] Incidentally it is known that the plotting of the same pK_{BH^+} values against Hammett's σ values gives a very poor correlation, $r=0.920$.

These σ^+-correlations and the magnitude of ρ value of the diphenyl sulfoxides closely resembled those of substituted acetophenones (For $\sigma^+-pK_{BH^+}$; $\rho=-2.17$ ($r=0.983$). For $\sigma-pK_{BH^+}$; $\rho=-2.22$ ($r=0.903$))[19] and benzaldehydes (for $\sigma^+-pK_{BH^+}$; $\rho=-1.85$ ($r=0.994$)).[25] This suggests that similar resonance effects by the same substituents are possible for all these compounds. The two extremely delocalized formula for the protonated form of *p*-substituted diphenyl sulfoxides would be depicted as shown below.



Since the sulfur atom can expand its valence shell beyond octet using its 3d orbitals, the C–S bond between the aromatic carbon atom and the sulfur atom could have another π bonding (2p–3d type) upon the protonation to create a discrete positive charge on the sulfur atom and the formation of this 2p–3dπ bonding may call for a large resonance effect of the substituent.

In the case of the unprotonated sulfoxides, however, such a large demand for resonance effect of substituent would be negligible, since the sulfur atom bears only a fraction of a positive charge and hydrogen bonding to the terminal oxygen atom would give only a perturbation on the electron localization along the C–S linkage. Therefore, the S–O stretching frequency would be very slightly affected by the resonance effect of the substituents.

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[21] The bond moment; average value $\mu_{SO}=3.0$ D and the shorter bond length; 1.45 Å (average) also indicate a considerable double bonding of sulfoxides. [See C. C. Price and S. Oae, "Sulfur Bonding," Chapter 4, Ronald Press Co., New York, N. Y. (1962).]

[22] The dipole moments of diphenyl sulfoxide and dimethyl sulfoxide were 4.08 (D)[12] and 4.3 (D)[23] respectively, which also show a larger inductive effect of methyl substituents.

[23] A. J. Parker, "The Use of Dipolar Aprotic Solvents in Organic Chemistry," in "Advances in Organic Chemistry," Vol. 5, ed. by R. A. Raphael, E. C. Taylor and H. Wynberg, Interscience Publishers, N. Y. (1965), p. 3.

[24] The value for *p*-anisyl phenyl sulfoxide was found to be slightly lower than that predicted by the σ^+ values. This deviation would be caused by the solute-solvent hydrogen bonding in sulfuric acid acting to reduce the resonance effect of *p*-CH_3O group.[5a]

[25] K. Yates and R. Stewart, *Can. J. Chem.*, **37**, 664 (1959).