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EVALUATION OF THE BASICITY OF SULFOXIDES BY MEASUREMENTS OF CHEMICAL SHIFTS IN AQUEOUS SULFURIC ACID (1,2)

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Reported data for the basicity of sulfoxides are misleading (4,5,6,7). We wish to report preliminary results which give reliable acidity constants for the conjugate acids of sulfoxides in aqueous solutions.

Terjesen and Sandved (4) titrated diethyl sulfoxide in propionic acid with perchloric acid and found that the basicity was between acetanilide and acetamide which in aqueous solutions have pK's of approximately 0 to -1 (8). However, they also found that trimethylphosphine oxide and diethyl sulfoxide have similar basicity in this solvent; we have shown that phosphine oxides are weak bases, pK_{BH^+} = -2 to -3 (9). Although Nylen attempted to evaluate the basicity of dimethyl sulfoxide and diethyl sulfoxide, he found no measurable basicity in aqueous solutions by the methods which he used. More recently there have been measurements of the basicity of sulfoxides in acetic anhydride by titration with perchloric acid (6,7). By correlation of known pK's in aqueous solution with half-neutralization potentials in acetic anhydride, pK's of a number of sulfoxides were determined by extrapolation and are shown in Table I. All these results would lead to the conclusion that for dialkyl sulfoxides, pK_{BH^+} = 0 to 1. A value of 0 is included in Arnett's review (8).

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TABLE I

Acidity Constants and H_o Dependence for Protonated Sulfoxides[a]

			$\log BH^+/B = M(pK_{BH^+} - H_o)$				
Compound	pK_{BH^+} by Titration in Acetic Anhydride	H_o at 1/2 Protonation[b]	pK_{BH^+}[c]	M	Δ_{BH^+}[d]	Δ_B[d]	No. of Points between 5% and 95% Protonation[e]
$(CH_3)_2SO$	1.0 (6), 0.91 (7)	-2.7	-2.78 (-1.72 ± .07)	0.619 ± .02	15.0	-8.2	10
$CH_3S(O)C_6H_5$	-0.49 (7)	-3.45	-3.38 (-2.09 ± .06)	0.62 ± .015	27.8	-0.2	8

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[a] Chemical shifts of CH_3 groups were measured in our work.

[b] This is equal to pK; from sigmoid graph of Δ against H_o (9).

[c] The values in parentheses are intercepts (and their standard deviations) determined by least squares (9).

[d] Values of chemical shifts are relative to $(CH_3)_3\overset{+}{N}H$; positive indicates upfield shift.

[e] This is number of points used to determine M and pK_{BH^+} by least squares according to the method in ref. 9. More data was obtained and used to get H_o at 1/2 protonation, Δ_B, and Δ_{BH^+}.

We have used our method (9) of following chemical shifts of methyl groups as a function of sulfuric acid concentration to measure the basicity of sulfoxides. This method was shown to be valid by several methods, the most convincing of which was the determination of pK_{BH^+}'s for acetophenone and dimethylacetamide which agree well with data obtained by other methods. Our results for sulfoxides are given in Table 1. Sulfoxides in aqueous solutions are therefore some three to four powers of ten less basic than the titrations in acetic anhydride (6,7) indicate. However, our data agree with Terjesen and Sandved's data (4) indicating similar basicity of sulfoxides and phosphine oxides. We previously found $pK_{BH^+} = -2.1$ for dimethylphenylphosphine oxide (9). The titrations in propionic acid (4) plus our data in Table 1 for dimethyl sulfoxide lead to the prediction that trimethylphosphine oxide has a pK_{BH^+} of approximately -2.

We have commented on the basicity of phosphine oxides compared to arsine oxides (9). Nylen reported pK values for $(CH_3)_2SeO$ (2.6) and $(CH_3)_2TeO$ (~ 6). Therefore, it is true for Group VI as well as Group V that third period oxides are much less basic than fourth period oxides -- dimethyl sulfoxide is 5-6 powers of ten less basic than dimethyl selenoxide.

The weak basicity of dimethyl sulfoxide and the even weaker basicity of dimethyl sulfone support the view that there is considerable multiple bonding in the S-O bond (10). Protonation should cause loss of multiple bonding and therefore lowered bond energy of S-O bonds relative to more basic oxides, e.g., N-oxides and selenoxides (9,11).

The nmr spectra of dimethyl sulfoxide in the acidity range, 80% H_2SO_4 to 30% SO_3, show two signals apparently due to S-methyl groups. There are several possible explanations for this phenomenon. We hope to discover which is correct for the answer might possibly bear on the intriguing question of whether sulfoxides protonate predominantly on sulfur or on oxygen (12).

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