as DMSO-d_6 or $CDCl_3$. In protic solvents such as methanol, the equatorial substituent is again destabilized by steric repulsion between the bonded solvent molecule and substituent.

In oxime hydrochlorides, in which the nitrogen atom is protonated, the positive charge on the nitrogen atom tends to stabilize the equatorial substituent, *i.e.*, $\Delta F_e < 0$. An additional steric effect, which causes $\Delta F_s > 0$, also arises from the interaction between the equatorial substituent and the proton attached to the nitrogen atom (Figure 8 (B)). The conformation energies of oxime hydrochlorides in *E* isomers are considerably reduced as compared with the parent oximes (Table V). The value of the latter compounds are estimated as 2.7 kcal/mol or larger because of the pronounced preference of the axial substituent.[37]

Assignments of Methyl Signals in Oxime Hydrochlorides. The chemical shift of the methyl signals of oximes and their hydrochlorides are listed in Table VIII together with those studied in the previous paper.[22a] From a comparison of peak intensity and the ratio of isomers studied previously, the methyl signals at higher and lower field are assigned to the *anti* and *syn* peaks, respectively. In their hydrochlorides, however, the *anti* methyl signals are shifted downfield with respect to the *syn* signals with some exceptions.[38] This is probably due to the electric field effect of the excess dipole moment produced by the formation of the hydrochloride. This interpretation has successfully explained the downfield shift due to hydrogen bond formation in aziridines[39] and also peak assignment in triazine.[40] The electric dipole moment on the nitrogen atom is directed along the N^+–H bond which replaces the former sp^2 lone-pair orbital (Figure 9), and methyl protons parallel with it suffer the largest deshielding effect by the electric field. The electric-field effect well explains all of the downfield shift of Table VIII except acetoxime and methyl ethyl ketoxime.

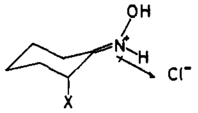

Figure 9. The electric-field effect caused by a protonation to the nitrogen atom. The arrow indicates the excess dipole moment.

Acknowledgment. We are grateful to Mr. Yuji Tanaka for his experimental assistance.

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[38] The exceptions are β-methylene proton of isophorone oxime and methyl ethyl ketoxime.

[39] H. Saitô, K. Nukada, T. Kobayashi, and K. Morita, *J. Amer. Chem. Soc.*, **89**, 6605 (1967).

[40] H. Saitô, K. Nukada, and Y. Kurita, Abstract, 21st Annual Meeting of the Chemical Society of Japan, Osaka 19319, 1968.

Acid–Base Behavior of Sulfoxides. Measurement of pK_a Values by Ultraviolet and Nuclear Magnetic Resonance Techniques

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Abstract: The protonation of several aliphatic and aromatic sulfoxides has been measured by nmr and uv techniques in aqueous sulfuric and perchloric acids. The sulfoxides do not follow the H_0 acidity function and the thermodynamic pK_a's have been calculated by the linear free energy relationship (l.f.e.r.) proposed by Bunnett and Olsen. The pK_a's range from -1.8 for DMSO to -2.9 for *p*-nitrophenylmethyl sulfoxide, and the ϕ values lie within the range 0.4–0.6. Such ϕ values are very similar to the ones reported for amides and indeed it seems that the H_A function satisfactorily represents the protonation behavior of sulfoxides. Structural effects on the basicity of the SO group are not very large; the Hammett ρ value for substituted phenyl methyl sulfoxides is $+0.85$. The evaluated thermodynamic pK_a's give good correlations with half-neutralization potentials (HNP) in acetic anhydride and with the shift of OH stretching frequencies in solutions of sulfoxides with phenol in CCl_4.

The behavior of sulfoxides as weak bases has been long recognized.[2] However there is much disagreement on the basic strength of even the most common sulfoxides.[3–8] Terjesen and Sandved[3] found by titration studies in nonaqueous media that the basicity of diethyl sulfoxide was between acetanilide and acetamide, whereas Nylen[4] found no measurable basicity of dimethyl and diethyl sulfoxide in aqueous solution (pK_a

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[2] E. Fromm, *Ann. Chem.*, **396**, 75 (1913); C. Finzi, *Gazz. Chim. Ital.*, **46**, 186 (1916).

[3] S. G. Terjesen and K. Sandved, *Kgl. Norske Videnskab. Selskabs Forh.*, 10, 117 (1937); *Kgl. Norske Videnskab. Selskabs Skrifter*, No. 7, 1 (1938). Data quoted in ref 4.

[4] P. Nylen, *Z. Anorg. Allgem. Chem.*, **246**, 227 (1941).

[5] C. A. Streuli, *Anal. Chem.*, **30**, 997 (1958).

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

[7] P. Haake and R. D. Cook, *Tetrahedron Lett.*, 427 (1968).

[8] (a) P. O. I. Virtanen and J. Korpela, *Suomen Kemistilehti, B*, **41**, 326 (1968); (b) C. Klofutar, F. Krasovec, and M. Kusar, *Croat. Chem. Acta*, **40**, 23 (1968).

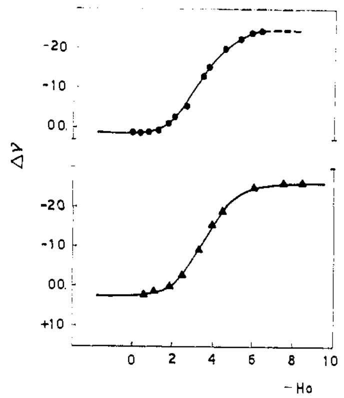

Figure 1. Correlation of $\Delta\nu$ with H_0 for phenyl methyl sulfoxide in aqueous perchloric (●) and sulfuric (▲) acids.

= 0.0 have been quoted in the Nylen's paper[4] and in the Arnett's review[9]).

More recently Streuli[5] potentiometrically titrated a series of amines, whose pK_a values in water are known, with perchloric acid in glacial acetic acid using acetic anhydride as solvent. A plot of pK_a values *vs.* the half-neutralization potentials (HNP) gave a good straight line. This plot could be used to determine the pK_a values of amines. Streuli extended this method to obtain a pK_a estimate of 1.0 for dimethyl sulfoxide.

Andersen, *et al.*,[6] extended the same method to a series of substituted phenyl methyl sulfoxides. The pK_a values ranged from +0.55 (*p*-anisyl methyl sulfoxide) to −3.51 (*p*-nitrophenyl methyl sulfoxide). The Hammett plot gave a good straight line with $\rho = 3.79$.

Recently, Haake and Cook[7] proposed a new technique to measure the basicity of sulfoxides. By plotting the chemical shifts of methyl groups of phenyl methyl or dimethyl sulfoxide against the H_0 scale, they obtained sigmoid curves. The halfway point was taken as pK_a value (DMSO −2.78; PhSOMe −3.38).

The protonation equilibria of three sulfoxides have been measured, using the H_0 function, by a partition method.[8] Virtanen and Korpela[8a] estimated the pK_a's to be −2.07 for Ph_2SO and −1.47 for Bu_2SO, whereas Klofutar, Krasovec, and Kusar[8b] reported values of −3.19 and −2.03 for Ph_2SO and $(PhCH_2)_2SO$, respectively.

The large discrepancy among the values reported is, in our opinion, due to the extrapolations involved in evaluating pK_a, referred to dilute solution in water as standard state, from measurements in nonaqueous media and to differences in behavior between sulfoxides and Hammett bases. We measured, therefore, the extent of protonation of a series of substituted phenyl methyl sulfoxides and of a few dialkyl and diaryl sulfoxides in aqueous sulfuric and perchloric acids by two independent techniques, uv and nmr. Treatment of our data by the method of Bunnett and Olsen[10] has enabled evaluation of the thermodynamic pK_a values of the compounds above.

A preliminary communication has been published.[11]

Results

Following the nmr technique proposed by Haake and coworkers,[12] we measured the chemical shifts for the CH$_3$ hydrogens of several methyl sulfoxides relative to $(CH_3)_3N^+H$ in aqueous acid solution. The trimethylammonium ion was used as internal standard to minimize solvent effects on chemical shifts.[12]

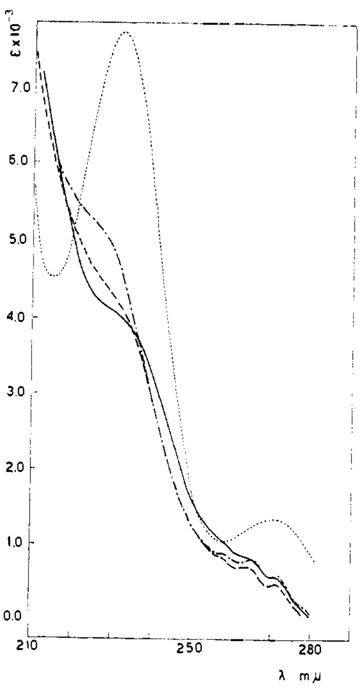

Figure 2. Uv spectra in aqueous perchloric acid of phenyl methyl sulfoxide: —, water; – –, $HClO_4$, 3.36 M ($H_0 = -1.47$); —·—, $HClO_4$, 4.26 M ($H_0 = -1.9$); · · · ·, $HClO_4$, 10.3 M ($H_0 = -6.42$).

By plotting $\Delta\nu$ values against H_0 for $HClO_4$ and H_2SO_4 solutions we obtained sigmoid curves spread over a range of 4–5 H_0 units. An example is reported in Figure 1.

Chemical shifts of free ($\Delta\nu_B$) and protonated ($\Delta\nu_{BH^+}$) bases are collected in Table I, together with the H_0 values at half-protonation. These values are in good agreement with those reported by Haake and Cook.[7]

Interpretation of the uv data is somewhat more complex, since the spectra in water and in concentrated acid are not very different. A typical example is reported in Figure 2.

However, after Davis and Geissman,[13] it is possible to select two wavelengths close to the points of the maximal difference between the extinction coefficients of the un-ionized and ionized forms. Plots of the differences of the optical densities (O.D.) at these two wavelengths *vs.* H_0 are presented in Figure 3 for phenyl methyl sulfoxide in $HClO_4$ and H_2SO_4. The plots shown on Figure 3 are very similar to those obtained by nmr techniques (see Figure 1).

For a series of aryl methyl sulfoxides as well as for diphenyl and *p*-tolyl phenyl sulfoxide, Table II shows the ΔO.D. values for the protonated and free base, together with the H_0 values at half-protonation. These values reasonably agree with those obtained by the nmr technique.

Discussion

The results obtained by the two independent methods are internally consistent. Moreover, by using the two

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[9] E. M. Arnett, *Progr. Phys. Org. Chem.*, **1**, 223 (1963).

[10] J. F. Bunnett and F. P. Olsen, *Can. J. Chem.*, **44**, 1899 (1966).

[11] D. Landini, G. Modena, F. Montanari, G. Scorrano, and F. Taddei, *Boll. Sci. Fac. Chim. Ind. Bologna*, **26**, 325 (1968).

[12] P. Haake, R. D. Cook, and G. H. Hurst, *J. Amer. Chem. Soc.*, **89**, 2650 (1967).

[13] C. T. Davis and T. A. Geissman, *ibid.*, **76**, 3507 (1954).

Table I. Chemical Shifts of Unprotonated ($\Delta\nu_B$) and Protonated ($\Delta\nu_{BH^+}$) Methyl Sulfoxides (R–SO–CH$_3$) in Aqueous Acids and H_0 at Half-Protonation

R	H_2SO_4			HClO$_4$		
	$\Delta\Delta\nu_B$[a]	$\Delta\nu_{BH^+}$[a]	H_0 at half-protonation[b]	$\Delta\nu_B$[a]	$\Delta\nu_{BH^+}$[a]	H_0 at half-protonation[b]
p-CH$_3$O-Ph	+2.5	−25.5	−3.25			
p-CH$_3$-Ph	+3.5	−25.0	−3.72	+3.0	−23.5	−3.27
m-CH$_3$-Ph	+2.8	−25.0	−3.57			
Ph	+2.5	−26.0	−3.62	+1.5	−24.5	−3.39
p-Cl-Ph	+4.5	−26.0	−3.64			
m-Cl-Ph	+2.5	−26.0	−4.16	+2.0	−26.0	−3.98
p-NO$_2$-Ph	−3.5	−30.0	−4.94			
CH$_3$	+8.0	−14.0	−3.02	+9.5	−11.5	−2.48
t-But	+19.0	−2.5	−2.40			

[a] Values of chemical shifts (in cycles per second at 56.4 MHz) are relative to (CH$_3$)$_3$NH$^+$. Positive indicates upfield shifts. Measured at room temperature. [b] From sigmoid graph of $\Delta\nu$ against H_0.

Table II. Differences of Optical Densities (ΔO.D.) at Selected Wavelengths ($\lambda_1 - \lambda_2$, mμ) of Unprotonated and Protonated Sulfoxides (R–SO–R′) in Aqueous Acids and H_0 at Half-Protonation at 25°

R	R′	H_2SO_4				HClO$_4$			
		$\lambda_1 - \lambda_2$	ΔO.D.$_B$	ΔO.D.$_{BH^+}$	H_0[a]	$\lambda_1 - \lambda_2$	ΔO.D.$_B$	ΔO.D.$_{BH^+}$	H_0[a]
CH$_3$	*p*-CH$_3$O-Ph					230 − 256	+0.530	−0.320	−2.75
CH$_3$	*p*-CH$_3$-Ph	223 − 247	+0.660	−1.050	−3.88	225 − 243	+0.250	−0.660	−3.55
CH$_3$	Ph	216 − 234	+0.360	−0.690	−4.21	216 − 234	+0.440	−0.670	−3.99
CH$_3$	*p*-Cl-Ph	224 − 248	+0.580	−1.300	−5.10				
CH$_3$	*m*-Cl-Ph	236 − 261	+0.390	+0.760	−4.83				
CH$_3$	*p*-NO$_2$-Ph	259 − 281	−0.100	+0.800	−5.29	260 − 280	−0.140	+1.080	−5.04
Ph	Ph	231 − 254	−0.800	−0.020	−4.97				
Ph	*p*-CH$_3$-Ph	236 − 258	+0.750	−0.150	−4.21				

[a] H_0 value at half-protonation, from sigmoid graph of ΔO.D. against H_0.

experimental techniques above described, it is now possible to measure the protonation behavior of any dialkyl (nmr) arylalkyl (nmr and uv) and diaryl (uv) sulfoxide.

The complete protonation of sulfoxides is attained in not less than four H_0 units. This indicates that sulfoxides do not behave as Hammett bases and consequently their pK_a cannot be directly evaluated by the simple plots of log [BH$^+$]/[B] *vs.* the H_0 function.[10,14]

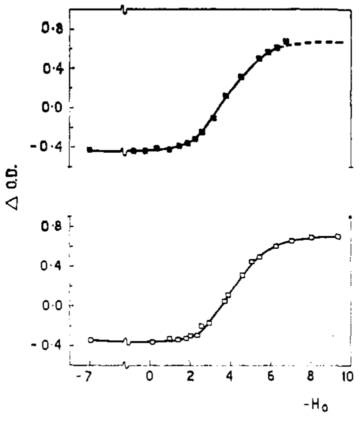

Figure 3. Correlation of ΔO.D. with H_0 for phenyl methyl sulfoxide in aqueous perchloric (■) and sulfuric (□) acids.

Recently Bunnett and Olsen[10] proposed a useful linear free energy relationship concerning protonation equilibria (eq 1; the symbols [BH$^+$] and [B] have been used instead[10] of [SH$^+$] and [S]).

$$\log([BH^+]/[B]) + H_0 = \phi(H_0 + \log[H^+]) + pK_{BH^+} \quad (1)$$

Provided the plot (log [BH$^+$]/[B] + H_0) against (H_0 + log [H$^+$]) is linear, thermodynamic quantities may be evaluated since the intercept of the plot represents the pK_{BH^+} value referred to infinite dilution in water as a standard state. The slope (ϕ) expresses the response of the equilibrium to the changing acid concentration.

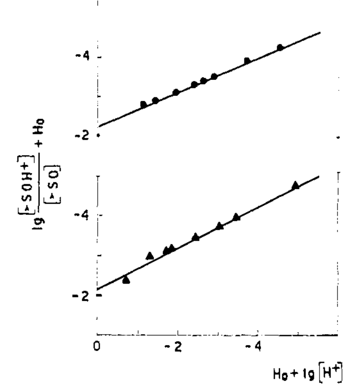

Figure 4. Correlation of (log ([SOH$^+$]/[SO]) + H_0) with (H_0 + log [H$^+$]) for phenyl methyl sulfoxide in aqueous perchloric (●) and sulfuric (▲) acids from nmr data.

By applying eq 1 to our data, linear plots were obtained for all the compounds studied. Typical examples (phenyl methyl sulfoxide in HClO$_4$ and H$_2$SO$_4$) are reported on Figures 4 and 5, and the evaluated pK_a's as well as ϕ values are collected in Table III.[15]

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(14) (a) M. A. Paul and F. A. Long, *Chem. Rev.*, 57, 1 (1957); (b) E. M. Arnett and G. W. Mach, *J. Amer. Chem. Soc.*, 86, 2671 (1964); (c) K. Yates, J. B. Stevens, and A. R. Katritzky, *Can. J. Chem.*, 42, 1957 (1964); (d) K. Yates and R. A. McClelland, *J. Amer. Chem. Soc.*, 89, 2686 (1967); (e) C. C. Greig and C. D. Johnson, *ibid.*, 90, 6453 (1968).

Table III. pK_a Values of Sulfoxides (R–SO–R′) from Uv and Nmr Data Evaluated by Equation 1

		H_2SO_4				$HClO_4$				
		Uv		Nmr		Uv		Nmr		
R	R′	pK_a	ϕ[a]	pK_a	ϕ[a]	pK_a	ϕ[a]	pK_a	ϕ[a]	pK_a av[b]
CH_3	*p*-CH_3O-Ph			−2.08	0.46	−2.02	0.36			−2.05
CH_3	*p*-CH_3-Ph	−2.27	0.51	−2.33	0.45	−2.12	0.49	−2.14	0.45	−2.22
CH_3	*m*-CH_3-Ph			−2.26	0.48					−2.26
CH_3	Ph	−2.37	0.54	−2.18	0.51	−2.25	0.55	−2.27	0.43	−2.27
CH_3	*p*-Cl-Ph	−2.53	0.60	−2.38	0.46					−2.45
CH_3	*m*-Cl-Ph	−2.61	0.58	−2.67	0.46			−2.55	0.46	−2.61
CH_3	*p*-NO_2-Ph	−2.86	0.57	−3.11	0.47	−2.83	0.54			−2.96
CH_3	CH_3			−1.84	0.52			−1.75	0.41	−1.80
CH_3	*t*-Bu			−1.62	0.45					−1.62
Ph	Ph	−2.54	0.59							−2.54
Ph	*p*-CH_3-Ph	−2.39	0.55							−2.39

[a] ϕ is the slope of the plot (log ([BH^+]/[B]) + H_0) *vs.* (H_0 + log H^+); the correlation coefficients from least-squares analysis are better than 0.99. [b] Mean values of the data reported on the table. The reliability of the data is to be considered[10] within ±0.2.

For both the acidic media, the agreement among pK's determined by the two experimental techniques is quite satisfactory (see Table III), since the uncertainty in the pK_a estimates is of ±0.2 unit.[10]

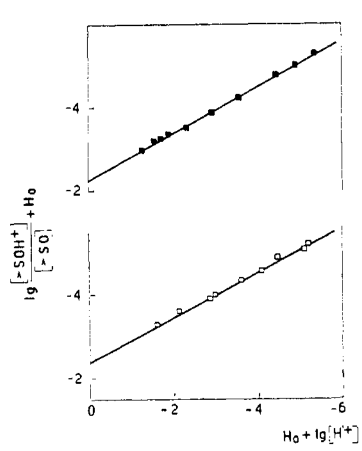

Figure 5. Correlation of (log ([SOH^+]/[SO]) + H_0) with (H_0 + log [H^+]) for phenyl methyl sulfoxide in aqueous perchloric (■) and sulfuric (□) acids from uv data.

The ϕ values (0.4–0.6) lie in a fairly narrow range, suggesting that sulfoxides represent a homogeneous class of compounds as far as their behavior toward acids is concerned;[10] therefore, an acidity function specific for sulfoxides could be defined.

It happens that most of the reported ϕ values of amides (0.42–0.55)[10] are in the same range as those for sulfoxides.

This suggests that amides and sulfoxides should have similar behavior toward acids and hence that the same acidity function should hold for the two classes of compounds. This hypothesis was checked by treating our experimental results for two typical sulfoxides in sulfuric acid with the H_A function proposed by Yates, *et al.*,[14c] for amides.

By plotting the ΔO.D. for Ph-SO-Me (see Table II) and the $\Delta\nu$ for DMSO (see Table I) at the various sulfuric acid concentrations *vs.* the corresponding H_A function values, good sigmoid curves were obtained. The region in which a change in slope occurs is within 2–3 H_A units and the slope of the plot log [BH^+]/[B] against H_A is close to unity (PhSOMe = 0.98; DMSO = 0.95). Such results are sound evidence that sulfoxides follow the H_A function to a good approximation.[16]

The H_A corresponding to half-protonation should give the pK_a values for the sulfoxides above. The following values were obtained: PhSOMe = −2.83; DMSO = −2.16 [compare with the thermodynamic pK_a values of −2.3 (± 0.2) and −1.8 (± 0.2), respectively, evaluated by the Bunnett's l.f.e.r.].

It has been suggested,[10] on the basis of other evidence, that the H_A scale should be shifted about 0.3 H_A unit toward less negative values. Such a shift would bring the half-protonation values on the H_A scale into agreement, within the estimated errors, with the thermodynamic pK_a's.

Structural effects on the basicity of the SO group are not very large. The pK_as of substituted phenyl methyl sulfoxides are well correlated by the Hammett σ ρ relationship; a plot of log K/K_0 *vs.* σ is linear with a ρ = 0.85 (r = 0.997). This is similar to the ρ's found for other reactions of sulfur compounds, which usually are not very far from 1.0.[18–21]

We are able to verify the suggested[5,6] correlation between pK_a of sulfoxides in water and HNP (in millivolts) in acetic anhydride for the series of substituted phenyl methyl sulfoxides (slope = −197.4; r = 0.995). However, the DMSO and Ph_2SO points lie off the straight line more than expected on the basis of experimental errors. This means, perhaps, that different linear correlations hold for different classes of sulfoxides.

The linear correlation found for amines (Streuli:[5] s = −44.32, r = 0.999; Andersen:[6] s = −51.52, r = 0.991) cannot, however, be used for sulfoxides, since the pK_a *vs.* HNP linear relationship for sulfoxides is steeper than that for amines.

Consequently, it appears that the pK_a's of sulfoxides proposed by Streuli and by Andersen (as suggested by the authors themselves) are only proportional to the

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(15) Similar pK_a values could be obtained by applying the equation, based on the proportionality among acidity functions,[14d] proposed by Creig and Johnson.[14e] This is not unexpected since the two treatments of data[10,14e] arise from the same basic idea.

(16) Recently, Zalewski, *et al.*,[17] reported that a number of aromatic and α,β-unsaturated aliphatic aldehydes, ketones, and carboxylic acids in sulfuric acid obey the H_A acidity function, rather than H_0, and again ϕ values (0.47–0.57) similar to those of amides were found. It emphasizes the meaning and usefullness of this parameter in characterizing the protonation behavior of bases.

(17) R. I. Zalewski and G. E. Dunn, *Can. J. Chem.*, 46, 2469 (1968).

(18) R. Curci and G. Modena, *Tetrahedron Lett.*, 1749 (1963); *Gazz. Chim. Ital.*, 94, 1257 (1964).

(19) A. Cerniani and G. Modena, *ibid.*, 89, 843 (1959).

(20) R. Curci and G. Modena, *Tetrahedron Lett.*, 863 (1965).

(21) G. Modena and L. Maioli, *Gazz. Chim. Ital.*, 87, 1306 (1957).

Table IV. pK_a's and Hydrogen Bonding with Phenol in CCl$_4$ of Sulfoxides

	t-BuSOMe	DMSO	PhSOMe	Ph$_2$SO
$\Delta\nu_{OH}{}^a$	393	366	330	305
pK_a	-1.62	-1.80	-2.27	-2.54

^{a} Free. ν_{OH} = 3615 cm^{-1}.

thermodynamic ones. On the same basis the large ρ value (3.84) reported by Andersen might also be rationalized.

Relations between basicity and strength of hydrogen bond with a given hydrogen donor (as measured by the shift of X–H stretching frequencies) have been found for several classes of compounds.[9,22] Such a relation seems to hold also in the case of sulfoxides.

In fact, the pK_a's in water of DMSO, t-BuSOMe, PhSOMe, and Ph$_2$SO are found to correlate well (s = 91.01; r = 0.992) with the $\Delta\nu_{OH}$ (cm^{-1}) of phenol in CCl$_4$[23] due to hydrogen bonding with the sulfoxides above (Table IV).

The present study clearly shows that the protonation behavior of sulfoxides differs considerably from that of typical Hammett bases. This fact caused previous attempts to measure the pK_a's of sulfoxides to fail, since either Hammett primary amine bases or the H_0 function were employed as reference.

We also feel that many studies on acid-catalyzed reactions of sulfoxides[24–28] should be reconsidered on the basis of our findings.

Experimental Section

DMSO, trimethylamine, and sulfuric and perchloric acids were Analar grade commercial products, purified, where necessary, by standard methods.

The sulfoxides were synthetized by oxidation with iodobenzene dichloride[29] of the corresponding sulfides, in turn prepared by standard methods. All sulfoxides were carefully purified by column chromatography and by repeated crystallizations. The physical constants agreed with the best values reported in the literature.

Sulfuric and perchloric acids solutions were prepared by dilution and titrated with standard NaOH. The H_0 and H_A values were obtained by interpolation of published data.[14c,30,31]

The solutions of the sulfoxides (about 0.2 M for nmr spectra and 2×10^{-4} M for uv spectra) were made immediately before running the spectra.

The nmr spectra were recorded on a Varian DP 60 instrument operating at 56.4 MHz using (CH$_3$)$_3$N (about 0.2 M) as internal standard. Calibration was performed by the side-band technique.

The uv spectra were recorded on a Cary 14 and/or a Zeiss M4Q instruments in 1-cm thermostated cells.

The ionization ratio [BH$^+$]/[B] were obtained by the usual relations.[12,14] The least square treatment of data was performed taking points from 5 to 95% protonation.

Acknowledgments. We wish to thank Drs. J. F. Bunnett and J. Steigmann for helpful discussions, the Consiglio Nazionale delle Ricerche (Rome) for financial support, and Mr. E. Mancini of the Istituto di Chimica Organica e Industriale, Laboratorio C.N.R. per lo Studio dei Composti del Carbonio Contenenti Eteroatomi, Bologna, for technical assistance in recording nmr spectra.

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(22) D. Hadzi, Ed., "Hydrogen Bonding," Pergamon Press, New York, N. Y., 1959.

(23) P. Biscarini, G. Galloni, and S. Ghersetti, *Boll. Sci. Fac. Chim. Ind. Bologna*, **21**, 154 (1963).

(24) S. Allenmark, *Acta Chem. Scand.*, **15**, 928 (1961), and other papers in this series.

(25) J. H. Krueger, *Inorg. Chem.*, **5**, 132 (1966).

(26) S. Oae and N. Kunieda, *Bull. Chem. Soc. Japan*, **41**, 696 (1968); S. Oae, M. Yokoyama, and M. Kise, *ibid.*, **41**, 1221 (1968).

(27) D. Landini, F. Montanari, G. Modena, and G. Scorrano, *Chem. Commun.*, 86 (1968).

(28) R. A. Strecker and K. K. Andersen, *J. Org. Chem.*, **33**, 2234 (1968).

(29) G. Barbieri, M. Cinquini, S. Colonna, and F. Montanari, *J. Chem. Soc., C*, 659 (1968).

(30) K. Yates and H. Wai, *J. Amer. Chem. Soc.*, **86**, 5408 (1964).

(31) R. S. Ryabova, I. M. Medvetskaya, and M. I. Vinnik, *Russ. J. Phys. Chem.*, 40, 182 (1966).

The Mechanism of Arylation and Carbomethoxylation of Olefins with Organopalladium Compounds

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Abstract: Phenylation and carbomethoxylation of olefins with "phenyl and carbomethoxylpalladium acetate," prepared *in situ* by the exchange reaction of the corresponding mercury compounds and palladium acetate, have been investigated under conditions where the initially formed products are stable. The reactions yield almost completely "anti-Markovnikov" products except with the least substituted (least hindered) olefins, such as propylene, where up to 30% "Markovnikov" addition may occur depending upon the reaction conditions. Substantial amounts of nonconjugated olefins are generally formed depending upon the substituents present. The reactions are quite stereospecific, yielding products expected from a *cis*-addition of the organopalladium acetate followed by a *cis*-elimination of hydridopalladium acetate. Minor amounts of unexpected olefin products are seen in some reactions, apparently arising from readdition of the eliminated palladium hydride species in the reverse direction followed by re-elimination of a hydride containing a different hydrogen atom.

Arylation, methylation, and carboalkoxylation of olefins with organomercury compounds and palladium salts have been shown to be useful reactions for the synthesis of a wide variety of vinyl-substituted olefinic compounds.[1] Little information was obtained about

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(1) R. F. Heck, *J. Amer. Chem. Soc.*, **90**, 5518 (1968).