Acid–Base Behavior of Alkyl Sulfur and Oxygen Bases

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Abstract: The acid–base equilibria in sulfuric acid solutions of simple dialkyl ethers have been evaluated by a nmr technique and compared with results obtained on corresponding sulfides. The pK_{BH^+} values are *ca.* 4 units more positive for ethers than for sulfides. The reasons of different solvation requirements of weak bases are briefly discussed and related to differences in Bunnett and Olsen ϕ values. The ϕ values for ethers (*ca.* +0.8) are much greater than for sulfides (*ca.* −0.3). This makes the ionization ratio of sulfides greater than that of ethers at higher acidities, which is related with the order of basicity observed in the gas phase ($R_2S > R_2O$). Estimation of the basicity of methyl mercaptan and methyl disulfide suggests the basicity scale $R_2S > R_2S_2 \simeq RSH$, whereas methanol is found more basic than dimethyl ether.

It is not rare that different and sometimes conflicting ideas on the properties of simple compounds are accepted among chemists working in different fields. For example, ethers are considered to be more basic than sulfides in dilute aqueous solutions on the basis of differences in the properties, *e.g.*, solubility, of the two classes of compounds[1,2] and some data on pK values of these substrates.[3–7] On the other hand, gas-phase studies indicate the opposite order of basicity since sulfur compounds have lower ionization potentials than oxygen compounds and, indeed, it has been recently shown that the gas phase proton affinity of dimethyl sulfide[8] is 11 kcal/mol higher than that of dimethyl ether.[8,9]

It may seem obvious that these differences stem from the different phase chosen for measurements and from the different solvation requirements of the species involved in the acid–base equilibria. However, an exact knowledge of these equilibria for ethers and sulfides in dilute aqueous solution is preliminary to any discussion.

The basicity of aliphatic ethers has attracted in recent years much interest, and several attempts have been made to determine their basicity constants. Severe experimental problems were encountered, and widely different pK_{BH^+} values have been evaluated by using techniques such as distribution between solvents,[3] titration in nonaqueous solvents,[5] and nuclear magnetic resonance.[4,6]

We have extensively used a nmr technique to evaluate ionization ratios ($I = [BH^+]/[B]$, where $[BH^+]$ and $[B]$ represent the concentration of protonated and free base, respectively) of such weak bases as sulfoxides,[10] phosphine oxides,[11] phosphinates,[11] and sulfides.[7] We have shown that this technique gives results as good as those obtained with other spectroscopic analysis, such as ultraviolet[10] and circular dichroism,[12] where much lower concentrations of base are required. During these studies it became apparent to us that some of the discrepancies found in the earlier basicity measurements could be accounted for by considering that each class of weak bases requires its own acidity function and that, therefore, to correlate ionization ratios with H_0 could lead to misleading results. In light of the results obtained with the corresponding sulfur compounds,[7] we felt a detailed nmr study of the acid–base equilibria of several oxygenated bases (dialkyl ethers and methanol) would also be worthwhile.

Results

The nmr technique employed involves measurement as a function of the acidity of the medium, of the chemical shift of hydrogens linked to the carbon α to the basic center, relative to that of the trimethylammonium ion as internal standard ($\Delta\nu = \nu - \nu_{ref}$, in Hz, at 90 MHz). The $(CH_3)_3NH^+$ ion is taken as reference in order to minimize solvent effects.[10,13]

We followed the methyl chemical shift in methyl alkyl ethers (MeOR; **1a**, R = Me; **1b**, R = Et; **1c**, R = *i*-Pr; **1d**, R = *t*-Bu), methanol (**2**), methyl mercaptan (**3**), and dimethyl disulfide (**4**). The methylene proton resonance was monitored for the diethyl ether (**5**).

The evaluation of the ionization ratios requires the knowledge of the chemical shifts of the free ($\Delta\nu_B$) and protonated ($\Delta\nu_{BH^+}$) base.

$$I = (\Delta\nu_B - \Delta\nu)/(\Delta\nu - \Delta\nu_{BH^+}) \qquad (1)$$

Compounds **3** and **4** undergo a fast decomposition in concentrated acid solution and their $\Delta\nu_{BH^+}$ are unaccessible. The $\Delta\nu_B$ values (**3**, $\Delta\nu_B$ = 77.6; **4**, $\Delta\nu_B$ = 42.0) do not change up to an acid concentration of *ca.* 70% H_2SO_4. At this point, a decrease in $\Delta\nu$ values is accompanied by a fast reaction of decomposition.

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[2] H. Perst, "Oxonium Ions in Organic Chemistry," Academic Press, New York, N. Y. 1971.

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[4] J. T. Edward, J. B. Leane, and I. C. Wang, *Can. J. Chem.*, **40**, 1521 (1962).

[5] J. T. Edward, *Chem. Ind. (London)*, 489 (1963).

[6] D. G. Lee and R. Cameron, *Can. J. Chem.*, **50**, 445 (1972).

[7] P. Bonvicini, A. Levi, V. Lucchini, and G. Scorrano, *J. Chem. Soc., Perkin Trans. 2*, 2267 (1972).

[8] J. L. Beauchamp, Ph.D. Thesis, Harvard University, Cambridge, Mass., 1968.

[9] M. A. Haney and J. L. Franklin, *J. Phys. Chem.*, **73**, 4328 (1969).

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[11] R. Curci, A. Levi, V. Lucchini, and G. Scorrano, *J. Chem. Soc., Perkin Trans. 2*, 531 (1973).

[12] U. Quintily and G. Scorrano, *Chem. Commun.*, 260 (1971); P. Bonvicini, A. Levi, and G. Scorrano, *Gazz. Chim. Ital.*, 102, 621 (1972).

[13] P. Haake and G. Hurst, *J. Amer. Chem. Soc.*, **88**, 2544 (1966); P. Haake, R. D. Cook, and G. H. Hurst, *ibid.*, **89**, 2650 (1967).

Therefore, only a very rough estimate of the basicity of **3** and **4** could be inferred by the observation that they begin to be protonated at acidity values higher than $H_0 = -6.0$.

Compound **1d** also decomposes in acid solutions. The protonation equilibrium has been followed up to 8.7 *M* H_2SO_4. At this acid concentration we estimate the ether to be only *ca.* 20% protonated (see below).

The other substrates were stable enough to allow nmr measurements even in the more concentrated acids (see Experimental Section). However, the plots of $\Delta\nu$ values against $-H_0$ showed that in no case $\Delta\nu_{BH^+}$ values (plateau at high acidity) were experimentally accessible.

We tried at first to measure $\Delta\nu_{BH^+}$ values by using media more acid than 100% H_2SO_4, such as FSO_3H or H_2SO_4 containing free SO_3. However, in experiments with methyl isopropyl sulfide, for which a clean evaluation of $\Delta\nu_{BH^+}$ has been made,[7] different values were obtained for concentrated H_2SO_4, for FSO_3H, and for H_2SO_4–SO_3, suggesting that strong solvent effects, not accounted for by our reference, were involved.

The unreliability of such results forced us to compute $\Delta\nu_{BH^+}$ values for compounds **1a–c**, **2**, and **5** by using a modification of the method used by Lee and Cameron[14] for measuring the pK_{BH^+} of ethanol. The calculation was made on the basis of the Bunnett and Olsen equation[15] (eq 2) by feeding into the computer the experimental $\Delta\nu_B$, $\Delta\nu$, log [H+], and H_0 values. $\Delta\nu_{BH^+}$, ϕ, and pK_{BH^+} were then varied for each experimental point (17–22 for each compound) until the best fit with eq 2 was found (see the Experimental Section for details). The method was checked with the methyl isopropyl sulfide by using values up to 90% protonation; the computed $\Delta\nu_{BH^+}$ is 13.6 to be compared with the experimental[7] 13.2 values. The chemical shifts of the unprotonated and protonated forms of compounds **1–5** are collected in Table I. Figure 1 illustrates the experimental points and the curve, calculated on the basis of eq 2 and the $\Delta\nu_B$ and $\Delta\nu_{BH^+}$ values collected in Table I for the protonation equilibrium of methyl isopropyl ether.

$$\log I + H_0 = \phi(H_0 + \log [H^+]) + pK_{BH^+} \qquad (2)$$

Table I. Chemical Shifts of Unprotonated ($\Delta\nu_B$) and Protonated ($\Delta\nu_{BH^+}$) Bases in Aqueous Sulfuric Acid[a]

Compd	$\Delta\nu_B$	$\Delta\nu_{BH^+}$[b]
MeOMe	−39.7	−134.5
MeOEt	−40.6	−118.2
MeO-*i*-Pr	−37.6	−109.2
MeO-*t*-Bu	−29.5	*c*
EtOEt	−60.7	−152.4
MeOH	−41.5	−113.6
MeSH	77.6	*c, d*
MeSSMe	42.0	*c, d*

[a] Values of chemical shifts (in Hz at 90 MHz) are relative to $(CH_3)_3NH^+$ measured at 25 ± 1°. Positive values indicate upfield shifts. [b] Evaluated as described in text from computer analysis of data at lower acidities than required for complete protonation. [c] The fast decomposition of these compounds prevents any evaluation of the chemical shift of the protonated bases. [d] Protonation starts of H_2SO_4 *ca.* 70%, H_0 = *ca.* −6.

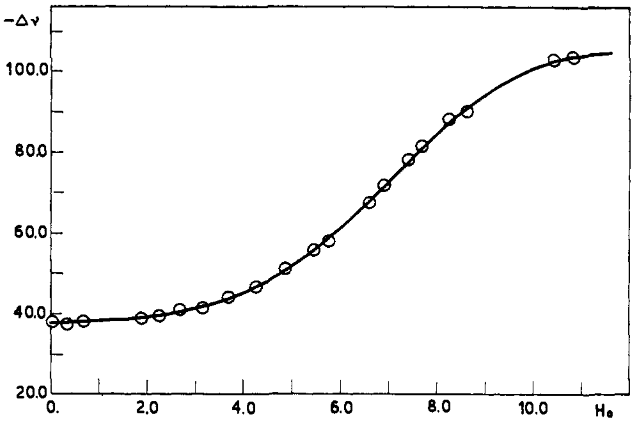


Figure 1. Calculated curve and experimental points for the protonation equilibrium of methyl isopropyl ether.

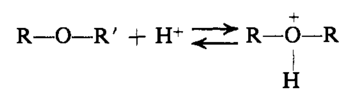
The ionization ratios can then be easily evaluated (eq 1). The pK_{BH^+} and ϕ values, collected in Table II, are calculated from eq 2 taking into account only *I* values between 5 and 95% protonation.

Table II. Acid–Base Equilibria of Dialkyl Ethers (R–O–R′) and Methanol[a]

R	R′	pK_{BH^+}[b]	ϕ[b]	$(H_0)_{1/2}$[c]	*m*[c]
Me	Me	−2.52	0.82	−8.58	0.22
Me	Et	−2.60	0.77	−7.60	0.27
Me	i-Pr	−2.60	0.75	−7.09	0.30
Et	Et	−2.42	0.77	−7.05	0.27
Me	H	−1.98	0.85	−6.89	0.22

[a] In aqueous sulfuric acid at 25°. [b] Evaluated as slope (ϕ) and intercept (pK_{BH^+}) from least-squares analysis of log $I + H_0$ *vs.* H_0 + log [H+] plots; correlation coefficients better than 0.99. [c] Evaluated from least-squares analysis of log *I* *vs.* $-H_0$ plots; *m* are slopes and $(H_0)_{1/2}$ the values for log *I* = 0.

The need to compute $\Delta\nu_{BH^+}$ values does not allow us to discuss as real the small differences in ϕ values, although they are in the right direction. Variations in the slope parameter cause somewhat large errors in the pK_{BH^+} values which are obtained by a long extrapolation of log $I + H_0$ values to H_0 = log [H+]. We estimate the uncertainty in pK_{BH^+} values to be ±0.2 pK_{BH^+} unit.[15] As a consequence and because of the small structural variations in the ethers examined, changes of pK_{BH^+} values are not suitable for evaluating the polar effects on equilibrium 3. We therefore considered a quantity more sensitive to variation in *I* values such as the H_0 values at half-protonation $(H_0)_{1/2}$ which could be obtained from a least-squares analysis of protonation data according to eq 4.



$$\text{R—O—R}' + \text{H}^+ \rightleftharpoons \text{R—}\overset{+}{\underset{\text{H}}{\text{O}}}\text{—R}' \qquad (3)$$

$$\log I = mH_0 + pK \qquad (4)$$

Variations in the slope *m* would, in this case, slightly affect the $(H_0)_{1/2}$ values. They are collected in Table II, together with *m* values. A plot of $(H_0)_{1/2}$ *vs.* Taft's σ^* gives a straight line with slope = 7.56 (r = 0.99). This slope times the mean *m* value (0.265,

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(14) D. J. Lee and R. Cameron, *J. Amer. Chem. Soc.*, **93**, 4724 (1971).

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

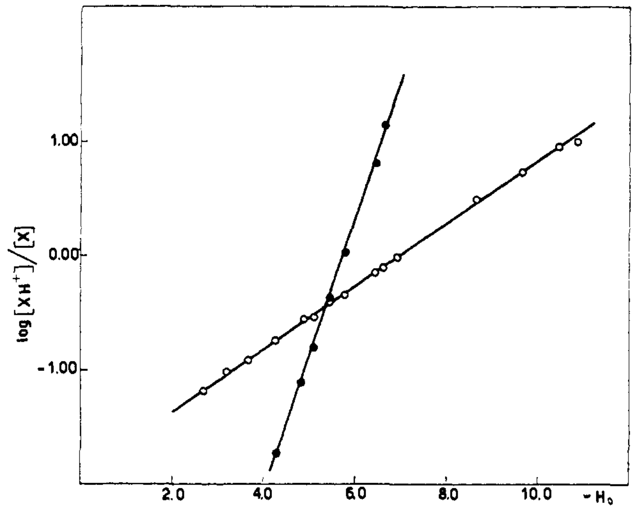

Figure 2. Plots of log [XH$^+$]/[X] values *vs.* $-H_0$ for dimethyl ether (○) and dimethyl sulfide (●) in aqueous sulfuric acid.

Table II) gives a ρ^* of $+2.0$ for the equilibrium 3. The use of the mean m values implies the assumption that the ethers compared follow the same acidity function and that the scattering in m values is largely due to experimental errors.

The $\Delta\nu_{BH^+}$ value for compound **1d** cannot be calculated, due to the small range of protonation experimentally accessible. However, on the basis of the $\Delta\nu_{BH^+}$ values obtained for the ethers **1a–c** ,we estimated a $\Delta\nu_{BH^+}$ value of -98.5 for methyl *tert*-butyl ether (see Experimental Section). This leads to the estimation of an $(H_0)_{1/2}$ value of -5.5 for this compound. These estimations are not reported in Tables I and II since they may be affected by large errors. By taking into account the estimated $(H_0)_{1/2}$ for compound **1d**, a slightly different ρ^* value (+2.5) is obtained.

Discussion

In the Bunnett and Olsen treatment,[15] the ϕ parameter expresses the response of the equilibrium to changing acid concentration. A negative ϕ value means that the log I increases more rapidly than does $-H_0$, whereas a positive ϕ value means that it increases less rapidly.[15]

Ethers have very high positive ϕ values (+0.75 to +0.82), whereas the ϕ values for sulfides are negative (−0.26 to −0.29).[7] As a consequence, when changes in log I values are compared for dimethyl ether and sulfide as a function of the acid concentration (see Figure 2), the steep straight line for the sulfides crosses the line for the ethers at H_2SO_4 *ca.* 67%. Below this point the per cent of protonated ether is greater than that of sulfide, whereas the reverse is true at higher concentration. When the water content of the solution is small, and hence the solvation ability for cations is small, the order of basicity defined by the proton affinity in the gas phase is observed. In dilute acid solution, however, the ethers are stronger bases.

Reversal in the basicity order from gas to liquid phase due to solvation effects has been observed in other cases.[16]

The difference in solvation requirement is not a peculiar property of ethers and sulfides. It is now clear that each class of bases has its own acidity function, ϕ value, and, therefore, solvent effect on the acid–base equilibria. Indeed, it is possible to classify some of the known acidity functions in order of decreasing ϕ value: H_{ROH} (alcohols),[14] H_{ROR} (ethers), H_A (amides,[17] sulfoxides,[10] and phosphine oxides[11,12]), H_0 (primary nitroanilines),[18] H_{RSR} (sulfides),[7] H_0''' (tertiary anilines),[19] H_I (indoles),[20] and H_R (triaryl carbinols–triaryl carbonium ions).[21]

To discuss in more detail the results presented above, the meaning of the ϕ parameter has to be more closely considered. The validity of the Bunnett and Olsen equation[15] (eq 2) may be verified independently. As shown by these authors,[15] eq 2 may be expressed in terms of activity coefficients[22] and simply transformed in eq 5. The term in parentheses on the

$$\log f_{BH^+}f_X/f_Bf_{XH^+} = \phi(\log f_{BH^+}/f_Bf_{H^+}) \qquad (5)$$

right-hand side is, by definition of H_0[18], equal to H_0 + log [H$^+$]. The term on the left-hand side may be evaluated for H_2SO_4 solutions, up to 70% concentration, from data of activity coefficients reported in the literature.[23,24] By plotting the appropriate values, fairly good linear correlations (correlation coefficients better than 0.98) are obtained for different classes of bases and the slopes found (ϕ) are in agreement with ϕ values evaluated through eq 2 (see Table III).

Table III. ϕ Values from Activity Coefficients (eq 5) and from Ionization Ratios (eq 2) for Four Acidity Functions in Sulfuric Acid[a]

Acidity function	ϕ values	
	Equation 5[b]	Equation 2[c]
H_A	0.38 (±0.03)	0.42 to 0.55
H_0'''	−0.47 (±0.04)	−0.33 to −0.48
H_I	−0.61 (±0.03)	−0.26 to −0.46 and −0.67 to −0.85
H_R	−1.11 (±0.09)	−1.02 to −1.59

[a] From 0 to 70%. [b] Values in parentheses are standard deviations as evaluated from least-squares analysis; activity coefficient values have been taken from ref 24. [c] From ref 15.

A further insight into eq 2 (and 5) may be obtained by rearranging eq 5 into eq 6. The latter can be in-

$$\log f_{XH^+}/f_Xf_{H^+} = (1 - \phi)\log f_{BH^+}/f_Bf_{H^+} \qquad (6)$$

dependently obtained by expressing in terms of activity coefficients the relationship H_X + log [H$^+$] =

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[16] J. I. Brauman, J. M. Riveros, and L. K. Blair, *J. Amer. Chem. Soc.*, **93**, 3914 (1971); E. M. Arnett, F. M. Jones, III, M. Taegepera, W. G. Henderson, J. L. Beauchamp, D. Holtz, and R. W. Taft, *ibid.*, **94**, 4724 (1972).

[17] K. Yates, J. R. Stevens, and A. R. Katritzky, *Can. J. Chem.*, **42**, 1957 (1964).

[18] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill, New York, N. Y., 1970; M. J. Jorgenson and D. R. Hartter, *J. Amer. Chem. Soc.*, **85**, 878 (1963).

[19] E. M. Arnett and G. W. Mach, *J. Amer. Chem. Soc.*, **86**, 2671 (1964).

[20] R. L. Hinman and J. Lang, *J. Amer. Chem. Soc.*, **86**, 3796 (1964).

[21] N. C. Deno, J. J. Jaruzelski, and A. Schriesheim, *J. Amer. Chem. Soc.*, **77**, 3044 (1955).

[22] The activity coefficients f are referred, as usual,[15] to dilute aqueous solution as standard state. From here onward B stands for a reference Hammett base and X for a general neutral base.

[23] R. H. Boyd in "Solute-Solvent Interactions," J. F. Coetzee and C. D. Ritchie, Ed., Marcel Dekker, New York, N. Y., 1969.

[24] (a) L. M. Sweeting and K. Yates, *Can. J. Chem.*, **44**, 2395 (1966); (b) K. Yates, H. Way, G. Welch, and R. A. McClelland, *J. Amer. Chem. Soc.*, **95**, 418 (1973); (c) K. Yates and R. A. McClelland, *Progr. Phys. Org. Chem.*, in press.

$(1 - \phi)(H_0 + \log [H^+])$, which is another way[18] to formulate the Bunnett and Olsen equation.

In turn, eq 6 can be reformulated as eq 7 and 7′

$$\log f_{H^+} - \log f_{XH^+}/f_X = (1 - \phi) \times (\log f_{H^+} - \log f_{BH^+}/f_B) \quad (7)$$

$$\log f_{H^+} - \log f_{XH^+}/f_X = (1 - \phi)(-H_0 - \log [H^+]) \quad (7')$$

which separate homogeneous activity coefficient terms.

In aqueous solutions, in particular, f_{H^+} may be taken as equal to $f_{H_3O^+}/f_{H_2O}$ and eq 7 is directly related to the equilibrium 8.

$$XH^+ + H_2O \rightleftharpoons X + H_3O^+ \quad (8)$$

Equation 7, therefore, correlates the free energy changes for transferring the equilibrium 8, from dilute solution in water to an acid solution, with the free energy changes for transferring the similar equilibrium involving a reference base B.

Inspection of eq 7 allows a further insight into the meaning of the ϕ values. Naively, we see that when X = B, say it is an Hammett base, ϕ is equal to zero. Positive values of ϕ will be observed when the change with acid concentration of the ratio f_{XH^+}/f_X approaches the change of f_{H^+} (or better of $f_{H_3O^+}/f_{H_2O}$). A mathematical consequence is that for X = H_2O, ϕ must be equal to unity. It is gratifying that the experimental ϕ values found for methanol (+0.85) and dialkyl ethers (ϕ = +0.82 to +0.77), bases as similar to water as possible, approach the limiting value of +1.0. Negative ϕ values will be observed when the change with acid concentration of f_{XH^+}/f_X is smaller than that of f_{BH^+}/f_B.

The arguments are based on the assumption that the differences on the two sides of eq 7 are both positive, which is equivalent to say that the activity coefficient of the proton (or the ratio $f_{H_3O^+}/f_{H_2O}$) suffers the greatest change with acid concentration and that the activity coefficient of the conjugate acid suffers a greater change than that of the base. Both assumptions seem to be justified on intuitive grounds and on the basis of the f values so far measured.[23,24]

A further consequence is that a small change of f_{XH^+}/f_X with acid concentration means also that variations of f_{XH^+} and of f_X values are of comparable amount. The limiting value for the above ratio is unity, for a theoretical case of the conjugate acid so similar to the base that the solvation interactions are not modified by the addition to the base of a proton. This can be approached when the positive charge is distributed and buried within a large molecule, making the electric field around the conjugate acid very weak. The large negative ϕ values observed for bases following the $H_{R'}$ acidity function substantiate these argumentations.[21]

It may be pointed out that in principle eq 6 is not limited to aqueous solutions and may hold for every other acid solutions and even in the absence of any solvent, *i.e.*, in gas phase. However, there are not enough data for checking the generality of this equation.

The factor[25] which appears to be the more important in increasing solvation requirements (ϕ values) is the density of charge. It will be more localized when the size, and polarizability, of the atom which bonds to the proton is small. Therefore, one would expect[24] that oxonium ions would require more solvation than ammonium or carbonium ions, as is found to be the case. Furthermore, as a consequence of more localized charge density, the hydrogen bonds with the water molecules will be stronger, thus enhancing the efficiency of stabilization through solvation.

Other things being equal, the effectiveness of charge dispersal will increase with the number of hydrogens linked to the protonation site, because of hydrogen bonding to the solvent. This has been found in the ammonium ions series.[18,19]

Following the above argument, it is clear that protonated ethers should be much more sensitive to solvation than are protonated sulfides,[7] as is indeed found.

The polar effects on the protonation equilibria (ethers, ρ^* *ca.* +2.0; sulfides, ρ^* +0.86[7]) are also in line with the above suggestion that the small and less polarizable oxygen atom requires more assistance by the substituent as it does by the solvent than the sulfur atom in order to delocalize the positive charge acquired upon protonation.

In the comparison of alcohols and ethers, simple polar considerations and ionization potentials[26] would lead one to expect ethers to be the more basic.

The results reported by Lee and Cameron[14] and our own clearly indicate that the reverse is experimentally found for pK_{BH^+} measurements in water. This can be rationalized in terms of the above discussion, as arising from the greater solvation of alcohols than ethers. They have an extra hydrogen available for hydrogen bonding to water molecules. Indeed the ϕ values for alcohols (0.85) are somewhat greater than for ethers (0.75–0.82) and smaller than for water (1.0). Once again, the difference in slope parameters (ϕ), albeit small, makes the alcohols more basic in water, although less basic in gas phase.[26]

A similar comparison in the sulfur series (R_2S, RSH, and R_2S_2) would have been interesting. However, mercaptans and disulfides are cleaved by acids before any degree of protonation could be detected. Although this obviously prevents any evaluation of the pK_{BH^+} of the substrates, we may safely assume that sulfides are more basic than both mercaptans and disulfides, since their decompositions begin at acid concentrations where sulfides are substantially protonated. This is not surprising since in the sulfur derivatives the solvation requirements are small and therefore an extra hydrogen (R_2S *vs.* RSH) would not be expected to change the basicity scale in water significantly from that suggested by the ionization potentials.

Experimental Section

The pmr spectra were taken on a Bruker HFX-10 spectrometer at 90 MHz. Sulfuric acid solutions were made up by dilution of AnalaR acid and titrated with standard NaOH. The H_0 values were obtained by interpolation of published data.[27]

Commercial products and those synthesized by standard methods

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(25) The variation of activity coefficients with acid concentration and how this reflects on the behavior of the acidity functions is discussed in detail in a recent review.[24c]

(26) J. L. Beauchamp, *Annu. Rev. Phys. Chem.*, 22, 527 (1971).

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

were carefully purified by fractional distillation at normal pressure. Boiling points (uncorrected) and pmr data (CCl_4, TMS) are reported below for the ethers synthesized: **1b**, bp 7° (lit.[28] bp 6.6°, cor); δ 3.33 (CH_2CH_3, q, J_{HCH} = 7.0 Hz), 3.23 (CH_3, s), 1.13 (CH_2-CH_3, t); **1c**, bp 31° (lit.[29] bp 31° (752 mm)); δ 3.36 ($CH(CH_3)_2$, septet, J_{HCH} = 6.1 Hz), 3.20 (CH_3, s), 1.09 ($CH(CH_3)_2$, d); **1d**, bp 53–54° (lit.[30] bp 55–56° (769 mm)); δ 3.10 (CH_3, s), 1.12 (C-$(CH_3)_3$, s).

pK_{BH^+} Measurements. Solutions of bases (*ca.* 0.05 *M*) were made in sulfuric acid solution (0.5–18.6 *M*) containing Me_3NH^+ (0.05 *M*) as reference.

Care was taken to make the solutions just before measurements since decomposition of some substrates was observed on standing in acid solution. In particular, compounds **3** and **4** suffer decomposition before any degree of protonation could be observed. No detailed analysis of the products deriving from such reaction has been so far accomplished. Attempts to slow down this decomposition by working under nitrogen or with carefully degassed solutions were unsuccessful. Therefore, only $\Delta\nu_B$ values are reported for these substrates. Methyl *tert*-butyl ether (**1d**) also decomposes very fast. By running the spectra within 45 sec after mixing with acids we measured $\Delta\nu$ values up to 8.7 *M* H_2SO_4.

With the other compounds the decomposition is much slower and therefore measurements were made up to 18.6 *M* H_2SO_4. However, $\Delta\nu_{BH^+}$ values had to be computed, since even at this acid concentration protonation was not complete.

The computation was made on the basis of eq 2, by expressing $\Delta\nu$ as a function of $\Delta\nu_B$, H_0, log [H^+], $\Delta\nu_{BH^+}$, ϕ, and pK_{BH^+}. The last three terms were varied by 1% increments until the best fit between calculated and experimental $\Delta\nu$ values was found through the least-squares analysis reported by Sillen.[31] This treatment cannot be used for **1d** because of the small range of protonation experimentally observable.

By plotting $\Delta\nu_{BH^+}$ for **1a–c** *vs.* Taft's σ^*, we obtained a curve from which a value of −98.5 has been extrapolated for **1d**.

Data were treated as before.[10]

Acknowledgment. We are indebted to Professor K. Yates for informing us of the work cited in ref 24 prior to publication.

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[28] V. N. Ipatieff and R. L. Burwell, Jr., *J. Amer. Chem. Soc.*, **63**, 969 (1941).

[29] P. G. Stevens and S. A. V. Deans, *Can. J. Res., Sect. B*, **17**, 290 (1939).

[30] L. C. Bateman, E. D. Hughes, and C. K. Ingold, *J. Chem. Soc.*, 881 (1938).

[31] L. G. Sillen, *Acta Chem. Scand.*, **18**, 1085 (1964), and previous papers.

Bond Scission in Sulfur Compounds. VIII.[1] Reaction of Aryl Chlorosulfates with Anionic Nucleophiles

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Abstract: Reaction of phenyl chlorosulfate, and of *p*-nitrophenyl chlorosulfate, with some anionic nucleophiles is found to give rise to phenol, and *p*-nitrophenol, quantitatively. Kinetic data for the reactions have been obtained in 1% aqueous ethanol (acetate buffers). The observed reactivity order is $S_2O_3^{2-} > CN^- > I^- > SO_3^{2-} \gg Br^-, Cl^-, F^-, AcO^-$. Several possible mechanisms are considered but the one involving nucleophilic displacement at chlorine is strongly favored. On that basis, the results show the halogen center to be a "soft" electrophilic site toward nucleophilic attack. Discussion of activation parameters is also given.

The occurrence of three electrophilic centers in chlorosulfates, carbon, sulfur, and chlorine, renders the $ROSO_2Cl$ substrates of considerable interest since nucleophiles may potentially react at one or several of these centers.[2] It will be recalled that studies from our laboratory have shown that, typically, alkyl chlorosulfates undergo attack at carbon (OSO_2Cl^- leaving group),[3a] while attack at sulfur (Cl^- leaving group) is only a minor process.[3b] Evidence for a possible fragmentation process, $R\cdots OSO_2\cdots Cl$, has also been presented.[3c] On the other hand, we found no evidence of displacement at chlorine in reaction of alkyl chlorosulfates with common nucleophilic reagents.

Aryl chlorosulfates were chosen for further investigation since with these substrates nucleophilic displacement at aromatic carbon should be unlikely,[4] thus increasing the likelihood that attack at the sulfur or chlorine site would become a possibility. It was found in fact that phenyl chlorosulfate reacts with methoxide ion in methanol concurrently through S–O and S–Cl bond scission, that is by attack at sulfur with comparable aryloxy and chlorine leaving group tendencies.[5a] *p*-Nitrophenyl chlorosulfate reacts by the same modes, though the S–O scission process becomes more important in accord with the greater leaving group ability of *p*-nitrophenoxide ion.[5b] Thus chlorine as an electrophilic site still remained elusive.

It seemed possible that significant change in the nucleophilic reagent could induce a change in mechanism of reaction in the aryl chlorosulfates series. Hence a study was initiated of phenyl chlorosulfate and of *p*-nitrophenyl chlorosulfate with a variety of nucleophiles, characterized by varied polarizability, with the view that differentiation between the sulfur and chlorine centers might become feasible; the results of this study are now

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