The Acid–Base Behaviour of Sulphides

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The protonation equilibria of alkyl methyl sulphides have been studied in sulphuric acid solutions. Their $-H_0$ values at half protonation lie in the range $-5{\cdot}4$ to $-5{\cdot}7$ and their pK_{BH^+} values, as determined with the aid of the Bunnett and Olsen equation, in the range $-6{\cdot}7$ to $-6{\cdot}9$. Steric effects are not important even for the t-butyl derivative and the polar effects are small ($\rho^* = 0{\cdot}86 \pm 0{\cdot}09$). The solvation requirements of the protonated sulphides are small as evidenced by the negative ϕ values obtained ($-0{\cdot}26$ to $-0{\cdot}29$).

THE behaviour in acids of sulphides and related bivalent sulphur compounds is of interest on theoretical[1,2] as well as on practical[3] grounds, acid treatment of hydrocarbons being a possible means for removing sulphur compounds from petroleum products.[3]

The available information is scanty. In an extended tabulation of pK_{BH^+} of weak organic bases, Arnett[1] reported values of $-5{\cdot}10$ and $-4{\cdot}52$ for thiacyclopentane, obtained *via* spectroscopic and partition methods respectively,[4] as well as values of $-5{\cdot}3$, $-6{\cdot}15$, and $-6{\cdot}7$ for Me_2S, Et_2S_2, and MeSH, respectively, obtained probably with the solvent extraction technique developed in Arnett's laboratory. Moreover, no information is available as to the kind of acidity function necessary to describe the protonation equilibria behaviour of sulphides in concentrated acids.

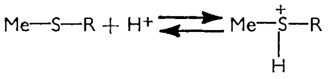
The reliability of the results obtained with the solvent extraction technique seems to depend on the degree of specific interactions between the substrate and the extracting solvent. At least in the case of alcohols,[5] the basicity values determined *via* this technique were found widely different from those obtained *via* Raman[6] and n.m.r.[7] spectroscopy.

We have used the n.m.r. technique, based on measurements of the chemical shift of hydrogen atoms linked to carbons α to the basic centre as a function of the acid concentration, to evaluate pK_{BH^+} of several oxygenated sulphur[8,9] and phosphorus[9] derivatives. Provided the solvent effect is minimized by using a suitable internal standard, the results were within experimental error of those obtained by u.v.[8] or c.d.[10] measurements.

In this paper we report the results of ^1H n.m.r. measurements on some dialkyl sulphides in aqueous sulphuric acid.

RESULTS

The protonation equilibrium (1) of some dialkyl sulphides was studied by measuring the ^1H n.m.r. chemical shifts of α-methyl groups in aqueous sulphuric acid solutions at 25 ± 1 °C. The trimethylammonium ion was used as internal reference.[8-11] By plotting Δν values ($\nu_{Me} - \nu_{ref}$/



$$\mathrm{Me{-}S{-}R + H^{+} \rightleftharpoons Me{-}\underset{\displaystyle H}{\overset{+}{S}}{-}R} \qquad (1)$$

(1) R = Me (2) R = Et
(3) R = Pr^i (4) R = Bu^t

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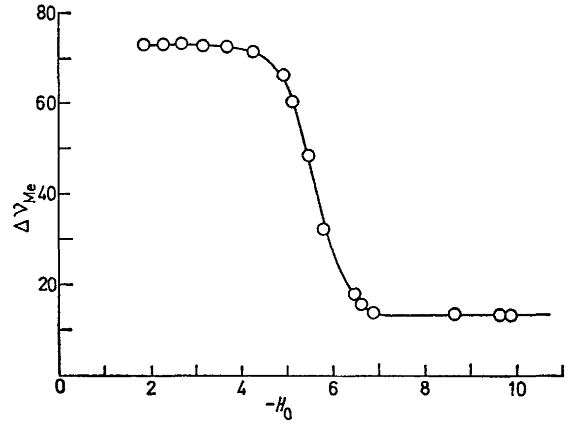
Hz) against the acidity function $-H_0$ we obtained good sigmoid curves. An example is reported in the Figure. From these curves we evaluated $\Delta\nu$ values for free ($\Delta\nu_B$) and protonated ($\Delta\nu_{BH^+}$) bases and hence the ionization ratio I [equation (2)]. Good straight lines were obtained

$$I = [R_2S^+H]/[R_2S] = (\Delta\nu_B - \Delta\nu)/(\Delta\nu - \Delta\nu_{BH^+}) \quad (2)$$

by plotting log I against H_0 (correlation coefficients better than 0·99): the slopes, however, are higher than unity (see Table). This indicates that sulphides are not Hammett bases: therefore only the values of H_0 at half protonation could be obtained by the said plot.



Correlation of $\Delta\nu_{Me}$ with H_0 for isopropyl methyl sulphide in aqueous sulphuric acid

Similar results have been obtained, though with a lesser degree of accuracy, by monitoring the β-methyl groups of methyl isopropyl (3) and methyl t-butyl (4) sulphides. The $\Delta\nu_B$, $\Delta\nu_{BH^+}$, and $-H_0$ values at half protonation obtained in this way are: (3): 150·2, 120·2, and −5·61; (4): 145, 115, and −5·44, respectively. As expected from the interposition of an extra atom, the effect of the protonation on chemical shifts is much less on the β- than on the α-methyl group. This allows a less accurate evaluation of the ionization ratio and therefore only values from α-methyl groups are used in the following calculations.

Acid–base behaviour of alkyl methyl sulphides (RSMe) [a]

R	$\Delta\nu_B$ [b] Hz	$\Delta\nu_{BH^+}$ [b] Hz	Slope [c]	$-H_0$ [c]	pK_{BH^+} [d]	ϕ [d]
Me	71·5	7·2	1·24	5·73	−6·95 (±0·12)	−0·26 (±0·03)
Et	71·7	10·6	1·25	5·61	−6·85 (±0·19)	−0·27 (±0·04)
Pr^i	72·7	13·2	1·25	5·57	−6·81 (±0·13)	−0·27 (±0·03)
Bu^t	75·0	14·5	1·27	5·40	−6·68 (±0·15)	−0·29 (±0·03)

[a] In sulphuric acid at 25 °C. [b] $\Delta\nu_B$ and $\Delta\nu_{BH^+}$ are the chemical shifts of CH_3 protons for the free base and conjugate acid, respectively, as measured in respect to Me_3NH^+. [c] From a plot of log I against $-H_0$ we obtained the reported values for slope and $-H_0$ at half protonation. [d] Obtained from a plot of log $I + H_0$ against $H_0 +$ log[H$^+$] [see equation (2)]: pK_{BH^+} is the intercept and ϕ the slope, values in parentheses are standard deviations.

The thermodynamic pK_{BH^+} values have been obtained by using the Bunnett and Olsen [12] equation (3). The

$$\log I + H_0 = \phi(H_0 + \log[H^+]) + pK_{BH^+} \quad (3)$$

pK_{BH^+} and ϕ values evaluated from the straight lines obtained by plotting log $I + H_0$ against $H_0 +$ log [H$^+$] are collected in the Table together with the other data.

A plot of pK_{BH^+} values as a function of Taft's σ* constants [13] gives a reasonable good straight line (correlation coefficient 0·988) with $\rho^* = 0{\cdot}86 \pm 0{\cdot}09$.

DISCUSSION

The definition of an acid–base equilibrium requires the knowledge of two important quantities, *i.e.*, the thermodynamic pK_{BH^+} of the base and the kind of response of the ionization ratio ($I = [BH^+]/[B]$) on changing the acidity of the medium.[14–16]

The use of the Bunnett and Olsen equation [12] allows the evaluation, through plots of (log $I + H_0$) against ($H_0 +$ log [H$^+$]), of pK_{BH^+} as intercept for $H_0 = -\log[H^+]$, and of ϕ values (slopes) which are a measure of the response of the equilibrium to changing acid concentration. The negative ϕ values obtained (−0·26 to −0·29) indicate that log I increases more rapidly than $-H_0$, as the acid concentration increases. Indeed the plot of log I against $-H_0$ is linear with slopes of 1·24—1·27.

This can be accounted for in terms of less solvation requirements by the protonated sulphide, as compared with anilinium ions, both because of a lesser number of sites for hydrogen bonding and of a greater ability of the larger sulphur atom to disperse a positive charge as compared with the nitrogen atom.

The pK_{BH^+} values are in the range −6·95 to −6·68. They are linearly correlated with Taft's σ* values. This shows the absence of steric effects even in the case of the methyl t-butyl sulphide. The ρ* value is not far from unity (0·86).

Several reactions of bivalent sulphur derivatives have been studied and their polar and steric requirement investigated. A careful scrutiny of the literature reveals that steric effects have been observed only when the attacking group is comparatively large. For instance steric retardations are found in the rate of oxidation of sulphides with bromine,[17] but not with

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hydrogen peroxide;[18] in the addition of alkanesulphenyl chlorides to hex-1-yne[19] but not in the hydrolysis of the same compounds.[20] The finding that the protonation of dialkyl sulphides is not affected by the size of the alkyl group is in agreement with the above hypothesis.

The small ρ^* value found shows slight participation of the alkyl group in stabilizing the positive charge on the conjugate acid of the sulphide. Small polar effects have often been reported both for electrophilic[21] and nucleophilic[22] attacks at bivalent sulphur derivatives.

However, the oxidation of aryl methyl sulphides by bromine in methanol–water, which involves the formation of a bromosulphonium ion, has ρ −3·2.[17] This suggests that further studies are needed to clarify the problem of polar effects in reactions of bivalent sulphur derivatives and, in particular, to evaluate the magnitude of substituent effects in the protonation of alkyl aryl sulphides.

For comparison, it may be recalled that the other class of sulphur derivative for which acid–base measurements have been carried out, sulphoxides (R_2SO), give ϕ values in the range 0·4—0·6 and pK_{BH^+} values *ca.* 5 orders of magnitude more positive: Me_2SO has pK_{BH^+} −1·80.[8]

EXPERIMENTAL

Materials and Solvents.—All b.p.s are uncorrected. The ^1H n.m.r. spectra were taken in CCl_4, with tetramethylsilane as internal standard, on a Bruker HFX-10 spectrometer at 90 MHz. Sulphuric 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.[23]

Sulphides.—The commercial product (Me_2S) and those synthesized by standard methods were carefully purified by fractional distillation at normal pressure. Dimethyl sulphide (1): b.p. 37—38 °C, δ 2·05; ethyl methyl sulphide (2): b.p. 64—66 °C (lit.,[24] 66·65°), δ 2·03 (CH_3, s), 2·44 (CH_3CH_2, q, J_{HCH} 7·2 Hz), and 1·24 (CH_3CH_2, t); isopropyl methyl sulphide (3): b.p. 84—86 °C (lit.,[25] 82—84°), δ 2·01 (CH_3, s), 2·73 [$CH(CH_3)_2$, septet, J_{HCH} 6·7 Hz], and 1·23 [$CH(CH_3)_2$, d]; methyl t-butyl sulphide (4): b.p. 98—100 °C (lit.,[26] 99°), δ 1·98 (CH_3, s) and 1·27 [$C(CH_3)_3$, s].

pK_{BH^+} Measurements.—Solution of sulphides (*ca.* 0·05M) were made in sulphuric acid solution (3·9—17·9M) containing Me_3N (0·05M) as reference. Chemical shifts were measured on a Bruker HFX-10 spectrometer at 90 MHz.

Care was taken to make the solutions just before measurements since, in some cases, decomposition of the substrate was observed on standing in acid solutions. This decomposition is quite fast with methyl t-butyl sulphide for which measurements were made within 30 s after mixing with acids.

Data were treated as before.[8]

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