Protonation of Alkyl Aryl Sulphides in Antimony Pentafluoride–Fluorosulphonic Acid Solution

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The mode of protonation of several mono- and di-alkyl-substituted alkyl aryl sulphides in SbF_5–FSO_3H solution was studied by low temperature n.m.r. spectroscopy. Protonation on sulphur was observed for all substrates, as revealed by ^1H and ^{13}C n.m.r. measurements. The measured chemical shifts of carbon atoms at various positions in the ions were compared with charge densities evaluated by the MINDO/3 procedure.

PROTONATION of aliphatic sulphides in SbF_5–FSO_3H–SO_2 solution has been extensively examined by Olah and his co-workers.[1] Protonation on sulphur was established at −60 °C by ^1H n.m.r. spectroscopy. Studies of protonation of aromatic sulphides in strong acids are surprisingly lacking. An exception is provided by recently reported work on the protonation of perfluorophenyl methyl sulphide in several strong acids.[2] As in the case of alkyl sulphides, protonation on sulphur was found by ^1H n.m.r. measurements.

In order to obtain further insight into the behaviour of aromatic sulphides in superacid media, we have performed both ^1H and ^{13}C n.m.r. studies of unsubstituted thioanisole and several of its derivatives in SbF_5–FSO_3H solution. Here, we report results on the protonation of mono- and di-alkyl derivatives.

In view of the recent theoretical interest in the electronic structures of organic sulphur compounds,[3] we also carried out MINDO/3 calculations [4] of the charge density redistribution upon protonation for some of the studied thioanisoles.

RESULTS AND DISCUSSION

Thioanisole and a number of its mono- and di-alkyl derivatives were protonated in 11.5 mol % SbF_5–FSO_3H solution at −80 °C. In addition, the protonation of *p*-methylthiophenetole was also performed under the same experimental conditions. The ^1H n.m.r. spectra of the resulting mixtures were recorded at −60 °C. Some of the characteristic ions were also examined by ^{13}C n.m.r. spectroscopy. Assignments of the ^{13}C resonances were made on the basis of their multiplicities in the off resonance ^1H-decoupled ^{13}C n.m.r. spectra, and comparison with the ^{13}C n.m.r. chemical shifts of the related positions in similar phenylonium ions.[5] The resonances which could not be assigned by using these criteria were assigned on a tentative basis and their assignments are designated as interchangable. Typical spectra are shown in Figures 1 and 2, respectively.

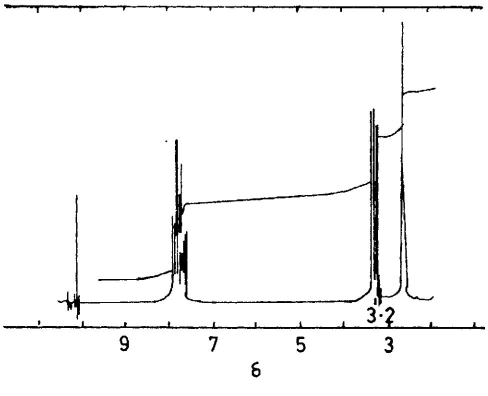

FIGURE 1 The ^1H n.m.r. spectrum of *p*-methylthioanisole in 11.5 mol % SbF_5—FSO_3H at −60 °C

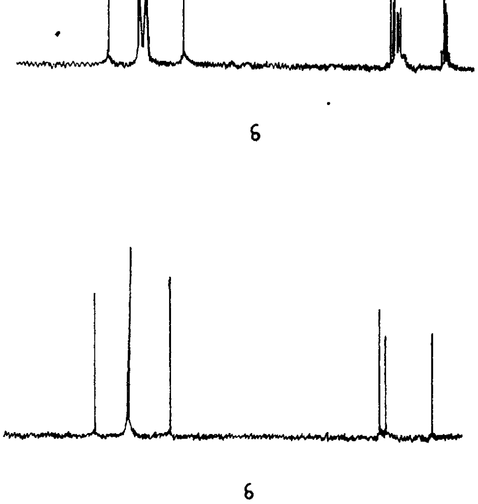

FIGURE 2 The ^{13}C n.m.r. spectra of *p*-methylthioanisole in 11.5 mol % SbF_5–FSO_3H at −55 °C. The lower portion is the proton decoupled spectrum, and the upper is the off-resonance ^1H-decoupled spectrum

The measured n.m.r. parameters indicate that all investigated bases are protonated exclusively at the sulphur atom. The ^1H and ^{13}C n.m.r. data of the examined ions are summarized in Tables 1 and 2, respectively.

^1H N.m.r. Spectral Properties.—The ^1H n.m.r. spectra of solutes are characterized by a doublet at *ca.* δ 3.2, assigned to the methylthio-group and markedly deshielded multiplet for the ring protons centred at *ca.* δ 7.5. No substantial change in the methylthio proton chemical shift is evident, with exception of ion (5), for which the shielding of *ca.* 0.1 p.p.m. relative to other sulphonium ions was observed.

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TABLE 1

^{1}H N.m.r. data for protonated sulphides (1)—(9) in 11.5 mol % SbF_5–FSO_3H at −60 °C

Ion	Substituent in thioanisole	Chemical shifts and multiplicities [a]				
		SCH_3	CH_3	Ring protons	CH_2	CH
(1)		3.22 (d)		7.74—8.02 (m)		
(2)	2-CH_3	3.18 (d)	2.70 (s)	7.52—7.88 (m)		
(3)	4-CH_3	3.16 (d)	2.50 (s)	7.69 (m) [b]		
(4)	4-$CH(CH_3)_2$	3.24 (d)	1.42 (d)	7.78 (m) [b]		3.24 (s)
(5)	2,6-$(CH_3)_2$	3.08 (d)	2.70 (s)	7.38—7.80 (m)		
(6)	2,4-$(CH_3)_2$	3.16 (d)	2.52 (s) 2.67 (s)	7.46—7.78 (m)		
(7)	3,4-$(CH_3)_2$	3.20 (d)	2.46 (s)	7.46—7.74 (m)		
(8)	2,5-$(CH_3)_2$	3.16 (d)	2.53 (s)	7.52—7.62 (m)		
(9)	4-Methylthiophenetole [a]		1.54 (t) 2.58 (s)	7.63 (m) [b]	4.26 (q)	

[a] ^{1}H N.m.r. chemical shifts are referred to $(CH_3)_4N^+$ as internal standard in p.p.m., the chemical shift of $(CH_3)_4N^+$ was taken as 3.20 p.p.m. relative to $(CH_3)_4Si$. Multiplicities are given in parentheses: s = singlet, d = doublet, t = triplet, q = quintet, s = septet, m = multiplet. The SH^+ signal coincides with those of the aromatic protons. [b] Centre of multiplet.

The signal for the proton on the sulphur atom has not been observed as a separate signal. However, on the basis of integral ratios and multiplicities of other signals in the recorded spectra, it was concluded that this resonance is hidden beneath the aromatic ring protons.

The protonated sulphides showed no appreciable cleavage up to −30 °C. At this and higher temperatures considerable decomposition of the ions was observed. No attempt to analyse so formed products was performed. The change of the size of alkylthio group, as well as the alkyl chain in the *para*-ring position, did not affect, neither the mode of protonation, nor the stability of the formed ions.

^{13}C *N.m.r. Spectral Properties.*—The ^{13}C n.m.r. spectra of protonated sulphides show typical changes of the ^{13}C n.m.r. chemical shifts for benzene derivatives upon protonation on the substituent.[5-7] The carbon atom which is most affected by protonation is the one bearing the methylthio group. Its shift moves upfield by *ca.* 20 p.p.m. The *ortho*-, *meta*-, and *para*-ring positions move considerably downfield, the *meta*-position changing to a substantially less extent. This finding indicates an increase in positive charge at each of these positions, the effect being particularly pronounced at the *para*- and *ortho*-sites.

Chemical shifts for the C(1) ring carbon atom in the protonated bases were practically unaffected by *ortho*-methyl substitution, while an enhanced upfield shift was observed upon *para*-methyl substitution. Both effects can be rationalized on the basis of the additivity parameters for the methyl group.[8]

Olah has recently reported ^{13}C chemical shifts for the ring carbon atoms of dimethylphenylsulphonium ion, obtained by methylation of thioanisole with CH_3F–SbF_5 in SO_2ClF.[5] The measured ^{13}C n.m.r. spectra of protonated thioanisole in SbF_5–FSO_3H superacid resembles the spectral characteristics of dimethylphenylsulphonium ion, except for the *ipso*-position, presumably due to the different structural and electronic characteristics of the sulphonium pole.

Charge Density Redistribution.—The previous studies on protonated benzene derivatives have shown that these molecules can be successfully treated theoretically as isolated species at the *ab initio* [9] and semiempirical [5,6] levels of sophistication. Considerable attention in several studies has also been given to the relationship between the ^{13}C n.m.r. shifts and charge redistribution induced by protonation.[5,6,10] Generally, calculated variations in charge densities were found to be in good qualitative agreement with the measured ^{13}C chemical shift differences for a number of benzenium [6] as well as phenylonium [5,6] ions.

In order to examine the extent to which the change in charge distribution influences the ^{13}C chemical shifts in protonated sulphides we performed MINDO/3 calculations on thioanisole and its *ortho*- and *para*-methyl derivatives protonated at the sulphur atom. During the computations geometries were fully optimized for all compounds considered.[11] The calculated charge densities for ring carbon atoms and sulphur are summarized in Table 3, together with the changes in the ^{13}C chemical shifts for the same positions caused by protonation.

The MINDO/3 method predicts charge distribution for the neutral bases in accord with the measured carbon

TABLE 2

^{13}C N.m.r. data for protonated sulphides (1)—(3), (5), and (6) in 11.5% mol % SbF_5–FSO_3H at −55 °C

Protonated sulphide	Chemical shifts and multiplicities [a]								
	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	SCH_3	*o*-CH_3	*p*-CH_3
(1)	117.6 (s)	132.0 (d) *	131.7 (d) *	135.2 (d)	131.7 (d) †	132.0 (d) †	23.1 (q)		
(2)	117.7 (s)	141.3 (s)	132.9 (d)	135.1 (d)	129.7 (d)	132.5 (d)	22.6 (q)	18.8 (q)	
(3)	113.8 (s)	132.2 (d) *	132.0 (d) *	147.1 (s)	132.0 (d) †	132.2 (d) †	23.3 (q)		20.6 (q)
(5)	117.7 (s)	141.0 (s)	130.8 (d)	134.8 (d)	130.8 (d)	141.0 (s)	20.8 (q)	19.4 (q)	
(6)	113.6 (s)	141.6 (s)	132.3 (d)	146.0 (s)	129.6 (d)	132.1 (d)	23.3 (q)	18.9 (q)	19.2 (q)

[a] ^{13}C N.m.r. shifts are referred to $(CH_3)_4Si$ as external standard. Multiplicities are given in parentheses: s = singlet, d = doublet, q = quartet. Resonances within a spectrum which are labelled with * or † have interchangeable assignments.

chemical shifts. An increase of positive charge upon protonation is observed for all ring positions except for the *ipso*-ring carbon atom. The highest increment of positive charge occurs at the *para*-ring position and the smallest at the *meta*-position, what is compatible with the measured ^{13}C chemical shift changes. The overall agreement between MINDO/3 results and experimental data is satisfactory, indicating that changes in the measured ^{13}C shifts can be fairly well interpreted in terms of the charge density variation in the carbon skeleton for the system under investigation. The largest disagreement between the magnitude of the charge density change and $\Delta\delta$ ^{13}C is found for the *ipso*-carbons, as observed also in several previous studies of related species.[5,6]

TABLE 3

MINDO/3 Charge densities and ^{13}C chemical shift differences for sulphides and protonated sulphides

Molecule or ion	Charge densities (e) and $\Delta\delta$ ^{13}C (p.p.m.) [a]						
	C(1)	C(2)	C(3)	(C4)	C(5)	(C5)	C(6)
$C_6H_5SCH_3$	0.180	−0.058	0.035	−0.020	0.031	−0.046	−0.218
$C_6H_5\overset{+}{S}(H)CH_3$	0.136	−0.010	0.046	0.032	0.047	−0.017	0.071
$\Delta\delta$ ^{13}C	−21.0	4.9	3.2	10.2	3.2	4.9	
$2\text{-}CH_3C_6H_4SCH_3$	0.162	−0.030	0.021	−0.019	0.034	−0.055	−0.206
$2\text{-}CH_3C_6H_4S(H)CH_3$	0.122	0.021	0.027	0.034	0.045	−0.016	0.064
$\Delta\delta$ ^{13}C	−20.1	5.3	3.0	10.3	4.3	5.9	
$4\text{-}CH_3C_6H_4SCH_3$	0.175	−0.058	0.027	−0.009	0.024	−0.045	−0.207
$4\text{-}CH_3C_6H_4S(H)CH_3$	0.125	−0.002	0.020	0.070	0.022	−0.002	0.079
$\Delta\delta$ ^{13}C	−21.3	4.2	2.6	12.2	2.6	4.2	

[a] $\Delta\delta$ ^{13}C designates shift difference from unprotonated parent. A negative sign means an upfield shift on protonation.

EXPERIMENTAL

The sulphides were prepared by *S*-alkylation of the corresponding thiophenols with alkyl sulphate in base.[12] Thiophenols were commercially available (thiophenol and *p*-methylthiophenol), or synthesized by standard methods, either from related anilines,[13] or by reduction of corresponding sulphonyl chlorides.[14] All compounds were purified by vacuum distillation prior to the protonation study.

Fluorosulphonic acid (Fluka) and antimony pentafluoride (Merck) were purged with dry nitrogen for several hours and distilled *in vacuo* before use.[15] Solutions for n.m.r. measurements were prepared by low temperature dissolution of base in an excess of superacid under nitrogen.[15] After the n.m.r. studies, solutions were quenched as previously described.[15] The starting sulphides were recovered quantitatively in all cases (as indicated by g.l.c., i.r., and n.m.r. studies) showing that no side-reaction took place.

A JEOL PS-100 spectrometer equipped with a variable temperature probe was used for recording ^1H n.m.r. spectra. ^{13}C N.m.r. spectra were obtained in the Fourier transform mode with a JEOL JNM FX-100 spectrometer.

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