Basicity of Nitrogen-Sulphur(VI) Compounds. Part 2.[1] Protonation Equilibria of *N*-Arylsulphamates using Ultraviolet and Nuclear Magnetic Resonance Methods

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The equilibrium $ArN(R)SO_3^- + H^+ \rightleftharpoons Ar\overset{+}{N}HRSO_3^-$ was examined using seven arylsulphamates and one mixed alkylarylsulphamate, *i.e.* *N*-methyl-*N*-phenylsulphamate. H_0 Values at half protonation, $(H_0)_{\frac{1}{2}}$, have been calculated, together with Bunnett and Olsen pK_{BH^+} values, from ionization data obtained from u.v. spectra. N.m.r. downfield shifts generally in deuteriosulphuric acid have been used for four of the compounds to obtain protonation data from which $(H_0)_{\frac{1}{2}}$ values have been calculated. The agreement between the $(H_0)_{\frac{1}{2}}$ values obtained by the two methods is generally good. Some recent Russian data agrees well with the Bunnett and Olsen pK_{BH^+} values. *N*-Protonation to give a zwitterion rather than *O*-protonation to give $ArNHSO_3H$ is favoured.

IN recent years there has been much interest in the study of protonation equilibria of compounds containing various sulphur functions. Thus, the protonation equilibria of sulphides,[2,3] sulphones,[4] sulphoxides,[3-7] sulphonic acids,[8-10] sulphonamides,[11,12] and various other sulphur systems [13,14] have been studied.

In Part 1 [1] we reported on the ionization $R\overset{+}{N}H_2SO_3^- \rightleftharpoons RNHSO_3^- + H^+$ for aliphatic and alicyclic sulphamates. These compounds are protonated in the pH range and have pK_{BH^+} values in the range 1—1.9. In the present paper the same ionization is considered for the more weakly basic aromatic and mixed aromatic–aliphatic sulphamates. Their protonation can only be studied in stronger acids and we have used two independent techniques, namely u.v. and ^1H n.m.r. spectroscopy, to obtain ionization data for these compounds.

EXPERIMENTAL

U.v. measurements were made at 25° on a Cary 14 spectrophotometer and n.m.r. measurements were taken on a JEOL MH-100 100 MHz spectrometer at 28°.

Materials.—The amines used were purified either by recrystallization in the case of solids (*p*-toluidine, *p*-anisidine, *m*-anisidine, *p*-chloroaniline, *p*-bromoaniline) or by distillation over zinc powder in the case of liquids (*p*-phenetidine, *p*-ethylaniline). Chloroform, pyridine, chlorosulphonic, acid, ethyl alcohol, sodium and potassium carbonate, and sodium and potassium hydroxide were all used as obtained.

Hydrochloric and sulphuric acids of molarity <5M were prepared from Volucon (M and B) standards. Acids of molarity >5M were made up by dilution of AnalaR (B.D.H.) of Proanalys (M and B) grades hydrochloric and sulphuric acid. Perchloric acid of all molarities was prepared by dilution of AnalaR (H and W) acid. Deuteriosulphuric acid (99.5% D; Ryvan Chem. Co.) was diluted with deuterium oxide (99.1% D; Aldrich and Koch–Light) to prepare a set of twelve acids varying in strength from 0.1 to 7.4M. The strengths of all acids were checked before use by titration with standard base.

The preparation of *N*-phenyl- and of *N*-phenyl-*N*-methyl-sulphamates has been described previously.[15] Other sulphamates were prepared by the method of Audrieth and Sveda,[16] except *N*-*p*-chloro- and *N*-*p*-bromo-phenylsulphamates which were prepared by an adaptation of a method described by Sureau and Obellianne [17] for the preparation of sulphamates containing nitro-substituents in the ring. Briefly this involved the slow addition of chlorosulphonic acid (12.2 ml) to pyridine (50 ml) so that the temperature of the mixture did not rise above 0°. The amine (*p*-chloro-, *p*-bromo-aniline) was added slowly to the mixture followed by a further quantity of pyridine (31 ml). After 15 min the mixture was placed in a bath at 60° for 2 h and then chilled overnight. After neutralization with sodium (potassium) hydroxide solution, excess of pyridine was removed by steam distillation and the residue filtered hot. Crystals of sulphamate salt separated out on cooling and these were recrystallized three times from 95% ethyl alcohol. All the sulphamates used gave satisfactory C, H, and N analyses.

pK_{BH^+} *Determination by U.v. Spectroscopy.*—The absorbance of equivalent amounts of substrate in acids of various molarities was measured at an appropriate wavelength (see Table 1). A dispenser was used to place equal amounts of

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[11] See ref. 4, p. 110.

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[16] L. F. Audrieth and M. Sveda, *J. Org. Chem.*, 1944, **9**, 89.

[17] R. Sureau and P. Obellianne, U.S.P. 2,789,139/1957 (*Chem. Abs.*, 1957, **51**, 155,716).

acid in the cell for each reading and 10 µl of a *ca.* 0.5M solution of substrate was injected into the cell with a microsyringe. A reference cell containing acid of the same strength as that in the reaction cell was used in each case.

TABLE 1

Wavelengths used in the measurement of ionization data for arylsulphamates $XC_6H_4N(R)SO_3^-$ [a]

Sulphamate X	R	λ/nm [c]
H [b]	H	274
H [b]	CH_3	272
4-Br [b]	H	283
4-Cl	H	282.5
4-CH_3	H	278
4-C_2H_5	H	280
3-CH_3O [d]	H	
4-CH_3O	H	284
4-C_2H_5O [b]	H	283

[a] Sodium salts used, unless otherwise stated. [b] Potassium salt. [c] λ_{max} for the compounds in water. At these wavelengths the difference between the absorbance of the unprotonated substrate (in water or very dilute acid) and that of the protonated substrate (in acid, >10M) was greatest and the absorbance of the protonated substrate was very small (ref. 10*a* and A. R. Katritzky, A. J. Waring, and K. Yates, *Tetrahedron*, 1963, **19**, 465). [d] Anomalous spectral shifts on varying the acid strength precluded us from making measurements on this compound.

The absorbance was recorded immediately after the addition of substrate. In some cases in the strongest acids there was some slight hydrolysis of the substrates before the absorbance was recorded. In such cases the measured absorbance was extrapolated back to the time of injection.

Figure 1 shows the changes in the u.v. spectrum of potassium *N*-phenylsulphamate at various acid concentrations. Plots of absorbance against H_0 gave good sigmoidal curves. Figure 2 shows such a plot for potassium *N*-phenylsulphamate. Ionization ratios (*I*) were calculated from equation (1) where ε_B is the absorbance of the unprotonated substrate and ε_{BH^+} that of the protonated substrate.

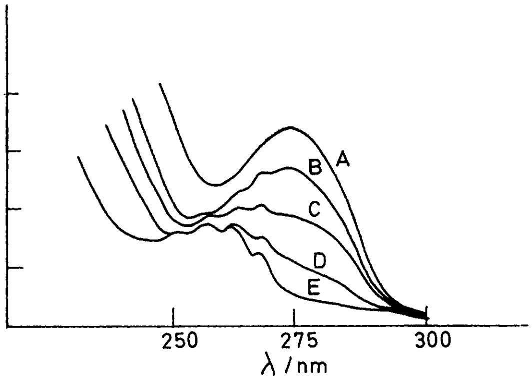


FIGURE 1 U.v. spectrum of *N*-phenylsulphamate in A, 0.1M; B, 4M; C, 5.5M; D, 7M; and E, 10M-HCl

$$I = [BH^+]/[B] = (\varepsilon_B - \varepsilon)/(\varepsilon - \varepsilon_{BH^+}) \quad (1)$$

pK_{BH^+} *Determination by N.m.r. Spectroscopy.*—Measurements were made on *N*-phenyl-, *N*-*p*-tolyl-, and *N*-*p*-anisyl-sulphamates. Poor solubility in acids >1M precluded use of this method with the other arylsulphamates. Deuteriosulphuric acid in deuterium oxide was used for measurements because of interference by water bands (in H_2SO_4), though in the case of *N*-methyl-*N*-phenylsulphamate, measurements were also possible with non-deuteriated acids. In each measurement 1—2 mg of substrate was weighed into an n.m.r. tube and 0.35 ml of acid of the appropriate strength was added, followed by 1—5 µl of internal standard. The tube was closed and inverted until a homogeneous solution was obtained and the n.m.r. spectrum was then immediately recorded. The stronger deuteriated acids were added to the n.m.r. tubes in a dry box. Ionization data were calculated from equation (2) where ΔV_{BH^+} and ΔV_B are the maximum and minimum

$$I = (\Delta V_B - \Delta V)/(\Delta V - \Delta_{BH^+})$$

downfield shifts (see Table 2) observed in strong and dilute acids respectively using trimethylamine (TMA) as internal standard for the *N*-methyl-*N*-phenylsulphamate and a sweep width of 270 Hz and pyrrolidine as internal standard for the other compounds with sweep widths of 1 080 and 540 Hz. Over the range of acids used the observed *J* value for the methyl resonance of TMA was 5.4 ± 0.2 Hz at a sweep width of 270 Hz. At a sweep width of 1 080 the α- and β-proton resonances of pyrrolidine were 129 ± 2 Hz apart over the range of acid strengths used.

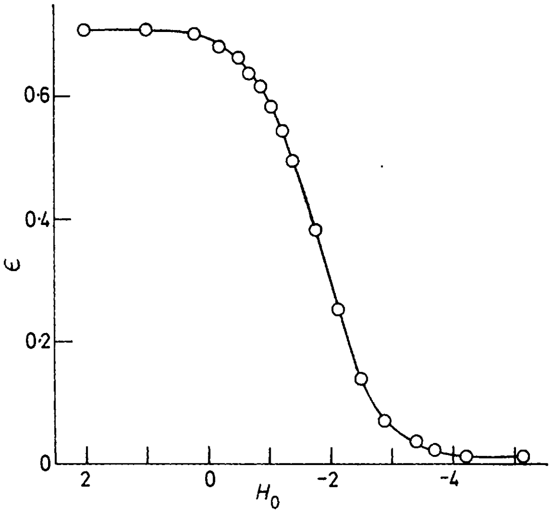


FIGURE 2 Plot of absorbance ε *versus* H_0 for potassium *N*-phenylsulphamate in HCl at 25°

TABLE 2

Chemical shifts of unprotonated (ΔV_B) and protonated (ΔV_{BH^+}) sulphamates $XC_6H_4N(R)SO_3^-$ in various acids [a]

Sulphamate X	R	Acid	ΔV_B/Hz	ΔV_{BH^+}/Hz
H	H	D_2SO_4	521.8	554.2
4-CH_3	H	D_2SO_4	527	551
4-CH_3O	H	D_2SO_4	514	539
H	CH_3	D_2SO_4	26.5	56.5
H	CH_3	H_2SO_4	23.2	57.8
H	CH_3	$HClO_4$	28.0	55.0
H	CH_3	HCl	23.0	52.4

[a] Chemical shifts (at 100 MHz) at 28° from pyrrolidinium ion for the first three compounds and relative to trimethylammonium ion for X = H, R = CH_3. For X = R = H, the downfield shifts from pyrrolidinium to the highest point of the aromatic multiplet were measured; for X = 4-CH_3 and 4-CH_3O, R = H, the downfield shifts from pyrrolidinium to the centre of the AA′BB′ multiplet were measured; for X = H, R = CH_3 the downfield shifts from trimethylammonium of the NMe group were measured.

RESULTS AND DISCUSSION

We decided to use both the u.v. and the n.m.r. methods[18] for measuring the basicity of the *N*-arylsulphamates since we expected that they would be readily amenable to these methods. Of the nine compounds synthesised it proved possible to determine ionization data for eight by following the u.v. spectral changes on protonation. The n.m.r. method while offering a valuable alternative was more restricted due principally to the poor solubility of the sulphamates in the stronger acids and occasional overlapping of aromatic peaks by water bands arising from small amounts of water present in the deuteriated acids. U.v. results are in Table 3 and n.m.r. results in Table 4.

TABLE 3

Basicity constants of *N*-(*p*-substituted phenyl) sulphamates $XC_6H_4N(R)SO_3^-$ determined at 25° by the u.v. method.

Sulphamate X	R	Acid	$-(H_0)_{\frac{1}{2}}$ [a,b]	% w/w Acid at $C_{BH^+} = C_B$	d $\log_{10}I/d(-H_0)$ [c]	r [d]	$-pK_{BH^+}$ [e]	% w/w Acid at pK_{BH^+}	ϕ	r [d]
H	H	HCl	1.79	17.0	0.89	0.999 (9)	1.59	15.4	0.203	0.980 (9)
H	H	$HClO_4$	1.95	35.0	0.78	0.998 (10)	1.50	28.5	0.330	0.969 (10)
4-Cl	H	$HClO_4$	2.52	41.5	0.80	0.995 (10)	2.09	36.5	0.242	0.930 (10)
4-Br	H	$HClO_4$	2.54	41.8	0.70	0.994 (10)	1.89	34.0	0.335	0.957 (10)
4-CH_3	H	$HClO_4$	1.51	28.5	0.82	0.995 (10)	1.20	24.0	0.339	0.969 (10)
4-C_2H_5	H	$HClO_4$	1.58	29.7	0.82	0.998 (10)	1.33	26.0	0.240	0.970 (10)
4-CH_3O	H	$HClO_4$	1.61	30.0	0.78	0.997 (10)	1.22	24.3	0.360	0.990 (10)
4-C_2H_5O	H	$HClO_4$	1.54	29.0	0.75	0.998 (10)	1.21	24.2	0.323	0.982 (10)
H	CH_3	$HClO_4$	0.58	14.0	1.10	0.996 (6)				
H	CH_3 [f]	$HClO_4$	0.65	15.5	1.37	0.994 (6)				
H	CH_3	HCl	0.92	9.2	1.09	0.999 (6)	0.99	9.8	0.130	0.940 (6)
H	CH_3 [g]	HCl	0.55	6.0	0.98	0.998 (6)				
H	CH_3 [f]	HCl	0.93	9.2	1.17	0.999 (6)				

[a] Calculated from equation (3). [b] H_0 Values were taken from ref. 23 ch. 2, pp. 39 and 43 and H_A values from K. Yates and J. C. Riordan, *Canad. J. Chem.*, 1965, **43**, 2328 and K. Yates, H. Wai, G. Welch, and R. A. McClelland, *J. Amer. Chem. Soc.*, 1973, **95**, 418. [c] *I.e.* the slopes (m) of plots of $\log_{10}I$ *versus* $-H_0$ or $-H_A$. [d] The figures in parentheses are the number of points taken. [e] Calculated from equation (4). [f] Using H_A. [g] Runs at 40°.

The m values in Table 3 show clearly that H_0 does not describe the protonation behaviour properly *i.e.* m is generally $\neq 1.0$. Neither does H_A, the amide acidity function, describe the protonation (see runs, with footnote *f* in Table 3). These findings corroborate the results of Cerfontain *et al.*,[11b] who obtained an m value of 0.87 from a plot of $\log_{10}I$ *versus* $-H_0$ for *N*-phenylsulphamic acid and found that a plot of $\log_{10}I$ *versus* $-H_A$ had a slope of 1.23. Their pK_a value measured in sulphuric acid for phenylsulphamate was -2.03 ± 0.05 (based on H_0). This value is reasonably near to the values in Table 3 for this compound. Further, Belyaev and Kotlyar[19] have obtained a pK_a of -1.62 ± 0.2 for *N*-*p*-methoxyphenylsulphamic acid in perchloric acid and an m value of 0.80 can be calculated from their data. These values are the same as those in Table 3. In earlier work[20] we have also tried using the tertiary amine acidity function, H_0''' to correlate the protonation of *N*-1-naphthylsulphamate but the m value obtained (0.55) was lower than that obtained with H_0.

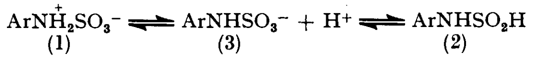
TABLE 4

Basicity constants of *N*-(*p*-substituted phenyl) sulphamates $XC_6H_4N(R)SO_3^-$ determined at 28° by the n.m.r. method

Sulphamate X	R	Acid	$d(\log_{10}I)/d(-D_0$ or $-H_0)$ [b]	$-(D_0)_{\frac{1}{2}}$ [c]	$-(H_0)_{\frac{1}{2}}$ [d,e]	r
H	H	D_2SO_4 [a]	0.86	1.64	(2.21)	0.983 (6)
4-CH_3	H	D_2SO_4	0.94	1.11	(1.68)	0.992 (7)
4-CH_3O	H	D_2SO_4	0.80	1.14	(1.71)	0.984 (7)
H	CH_3	D_2SO_4	1.23	0.53		0.992 (6)
H	CH_3	H_2SO_4	0.91		1.10	0.996 (7)
H	CH_3	$HClO_4$	1.0		0.86	0.996 (9)
H	CH_3	HCl	1.13		0.84	0.997 (7)

[a] For deuteriosulphuric acid, $D_0 = H_0$ in the range 0.6—12M.[24] Values of D_0 for acidities <0.6M were taken from ref. 24. [b] For the first four runs D_0 was used in the plot; for the remaining three runs H_0 was used. [c] Calculated from equations (2) and (5). [d] Calculated from equations (2) and (4). [e] The values in parentheses were calculated by subtracting 0.57 from the $(D_0)_{\frac{1}{2}}$ values. [f] The figures in parentheses are the number of points taken.

Though m is generally $\neq 1.0$ when H_0 is used, we prefer to use this acidity function since protonation is probably occurring on nitrogen to give the zwitterion (1) rather than on oxygen to give the neutral species (2) (Scheme 1).



$$\underset{(1)}{Ar\overset{+}{N}H_2SO_3^-} \rightleftharpoons \underset{(3)}{ArNHSO_3^-} + H^+ \rightleftharpoons \underset{(2)}{ArNHSO_2H}$$

SCHEME 1

The $(H_0)_{\frac{1}{2}}$ values in Table 3 have been calculated using equation (1) and the equation for the situation at half-protonation, $[BH^+] = [B]$ and then $m(H_0)_{\frac{1}{2}} = pK_{BH^+}$. Therefore, if the intercept of equation (3) is calculated and divided by the slope (m), $(H_0)_{\frac{1}{2}}$ values are obtained.

$$\log_{10}([BH^+]/[B]) \text{ or } \log_{10}I = -mH_0 + pK_{BH^+} \qquad (3)$$

$$(\log I + H_0) = \phi(H_0 + \log H^+) + pK_{BH^+} \qquad (4)$$

Table 3 also gives values of pK_{BH^+} calculated by applying the Bunnett and Olsen method[21] [equation (4)]. Plots of $(\log I + H_0)$ against $(H_0 + \log H^+)$ are found to be generally linear and extrapolation to the intercept at $(H_0 + \log H^+) = 0$ gives pK_{BH^+}. This method appears to be generally valid, whether H_0 is

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[21] J. F. Bunnett and F. P. Olsen, *Canad. J. Chem.*, 1966, **44**, 1899.

followed or not. The slopes of these plots (ϕ) measures the response of the equilibrium to changing acid concentration. A positive ϕ value implies that log I increases less rapidly than $-H_0$ and so corresponds to an m value <1 in equation (3).

When the values of $(H_0)_{\frac{1}{2}}$, calculated from equation (3) are compared with the $\mathrm{p}K_{\mathrm{BH}^+}$ values calculated by the Bunnett and Olsen method using equation (4) it is seen that there are differences of 0.2—0.6 units between the estimates of basicity. Differences of this magnitude between basicity constants calculated by the two methods have been widely observed.[21,22] The explanation is thought to be that the estimation of the intercept ($\mathrm{p}K_{\mathrm{BH}^+}$) from equation (4) requires an extrapolation of the graph to infinite dilution in water. This extrapolation is longer the weaker the base being studied. The extrapolation assumes that equation (3) is linear down to infinite dilution in water and that the slope, ϕ, is constant down to this point, neither of which assumptions may be true.[23] Barnett and O'Connor [22] have clearly shown that the weaker the base the greater is the discrepancy between $(H_0)_{\frac{1}{2}}$ values from equation (3) and $\mathrm{p}K_{\mathrm{BH}^+}$ values from equation (4). Discrepancies as large as 6.0pK_a units have been found.[2b] Generally, equation (3) gives the more negative values.

Table 4 contains data obtained by the n.m.r. method.

$$\log_{10} I = -mD_0 + \mathrm{p}K_{\mathrm{BD}^+} \qquad (5)$$

$(D_0)_{\frac{1}{2}}$ Values were calculated from equations (2) and (5) where $[\mathrm{BD}^+] = [\mathrm{B}]$ so that (5) reduces to $m(D_0)_{\frac{1}{2}} = \mathrm{p}K_{\mathrm{BD}^+}$.

Generally it has been found that substrates behave as stronger bases in deuteriated than in non-deuteriated acids,[24-26] and $\mathrm{p}K_{\mathrm{BD}^+} > \mathrm{p}K_{\mathrm{BH}^+}$ by 0.2—0.6 units depending on the type of base involved. In order to compare the basicity constants obtained by the two methods (u.v. and n.m.r.) it is necessary to first convert the $(D_0)_{\frac{1}{2}}$ values obtained in deuteriated acids to $(H_0)_{\frac{1}{2}}$ values. Fortunately for one of the sulphamates used, *N*-methyl-*N*-phenylsulphamate, the n.m.r. chemical shifts could be followed in both non-deuteriated and deuteriated media and thus subtraction of the value obtained in H_2SO_4 from the value obtained in D_2SO_4 gives a $\Delta\mathrm{p}K$ value of 0.57, *i.e.* $-0.53 - (-1.10)$. Addition of this value to the first three $-(D_0)_{\frac{1}{2}}$ values in Table 4 converts these to $-(H_0)_{\frac{1}{2}}$ values. In Table 5 a direct comparison of basicity constants obtained by the two methods is made. The agreement between the values seems to be reasonable except for *N*-methyl-*N*-phenylsulphamate measured in perchloric acid. The u.v. value of -0.58 is clearly too high and in fact seems to be anomalous even in Table 3 where values of -0.92 and -0.93 were obtained for this compound in hydrochloric acid.

When this work had been completed we became aware of further work by the Russian group [27] in which they also measured pK_a values for the equilibrium (1) $\rightleftharpoons$ (3) (see Scheme 1) and from an analysis of their kinetic data they calculated pK_a values for the second equilibrium (1) $\rightleftharpoons$ (4) (Scheme 2).

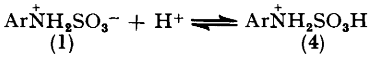
TABLE 5

Comparison of pK_a values of sulphamates $XC_6H_4N(R)SO_3^-$ determined from u.v. and n.m.r. data

Sulphamate		U.v.		N.m.r.	
X	R	Acid	$-\mathrm{p}K_a$[a]	Acid	$-\mathrm{p}K$[b]
H	H	$HClO_4$	1.95	D_2SO_4	2.21
H	H	HCl	1.79		
4-CH_3	H	$HClO_4$	1.51	D_2SO_4	1.68
4-CH_3O	H	$HClO_4$	1.61	D_2SO_4	1.71
H	CH_3	$HClO_4$	0.58	$HClO_4$	0.86
H	CH_3	HCl	0.92	HCl	0.84
				H_2SO_4	1.10

[a] $(H_0)_{\frac{1}{2}}$ Values taken from Table 3. [b] $(H_0)_{\frac{1}{2}}$ Values taken from Table 4.

They defined the most appropriate acidity function to describe the protonation occurring in (1) $\rightleftharpoons$ (3) as $H_s' = H_0 - 2 \log a_{\mathrm{H_2O}}$ and they calculated $\mathrm{p}K_{(1),(3)}$ values for compounds with Ar = 4-$CH_3OC_6H_4$ (-1.21 ± 0.05), 4-$CH_3C_6H_4$ (-1.35 ± 0.05), 3-$CH_3C_6H_4$- (-1.51 ± 0.05), Ph (-1.63 ± 0.05), and 3-ClC_6H_4 (-2.27 ± 0.05). In addition from their plot of $\mathrm{p}K_{(1),(3)}$ *versus* Hammett σ values, they calculated $\mathrm{p}K_{(1),(3)}$ values for compounds with Ar = 3-$CH_3OC_6H_4$ (-1.83) and 4-ClC_6H_4 (-2.02). These are near to our Bunnett–Olsen values (see Table 3) and this suggests that the values which we have obtained using equation (4) are nearest to being true thermodynamic values. Not surprisingly the second equilibrium (1) $\rightleftharpoons$ (4), which involves *O*-protonation is described by H_A with $\mathrm{p}K_{(1),(4)}$ values from -2.67 (3-Cl) to -2.04 (4-CH_3O). In work on the rearrangement of phenylsulphamic acid to aniliniumsulphonic acid Cerfontain and Maarsen [28] discuss the importance of the various phenylsulphamate species (1)—(4) and their equilibria in concentrated sulphuric acid. The reacting and the majority substrate species were identified as (2) and (1) respectively. The identification of (2) as the reactive species in sulphonation contrasts with the view that in solvolysis studies it is the zwitterion (1) which is the reactive intermediate.[27,29-31]



$$\underset{(1)}{\mathrm{Ar}\overset{+}{\mathrm{N}}\mathrm{H_2SO_3^-}} + \mathrm{H^+} \rightleftharpoons \underset{(4)}{\mathrm{Ar}\overset{+}{\mathrm{N}}\mathrm{H_2SO_3H}}$$

SCHEME 2

Site of Protonation.—In this study we consider that the equilibrium under study is (2) $\rightleftharpoons$ (1) and not (2) $\rightleftharpoons$ (3). *A priori* one would favour *N*-protonation since

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there is considerable evidence that the zwitterionic form of sulphamic acid, $\overset{+}{N}H_3SO_3^-$, is important in solution.[32,33] Also, u.v. and n.m.r. studies of the basicity and site of protonation of aliphatic and aromatic sulphonamides have been interpreted in favour of nitrogen protonation at the sulphonamide group.[12,34]

The fact that H_0 is the most appropriate acidity function suggests that protonation occurs on nitrogen.[10b] Circumstantial evidence in support of this includes the facts that the Hammett ρ value obtainable from our Bunnett and Olsen data (Table 3) is -1.65 (r 0.969; no. of points 7) and that obtainable from the Russians' data [27] is -1.64 (no. of points 5). Those values, while not being close to that for the protonation of aniline (-2.77 [35]) or to the value predicted (-2.7 [29,36]) from data on the acid-catalysed hydrolysis of arylsulphamates, nevertheless point to N-protonation since values much closer to -0.7 would be expected if O-protonation was occurring.* The ρ value for the $(H_0)_{\frac{1}{2}}$ data in Table 3 is -2.11 (r 0.972; no of points 7).

* The ρ value for the ionization of benzenesulphonic acids is $+0.7$.[10a,b]

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