Basicity of Nitrogen–Sulphur(VI) Compounds. Part 3.[1] Protonation Equilibria of Sulphamates using Potentiometric and ^{13}C Nuclear Magnetic Resonance Methods

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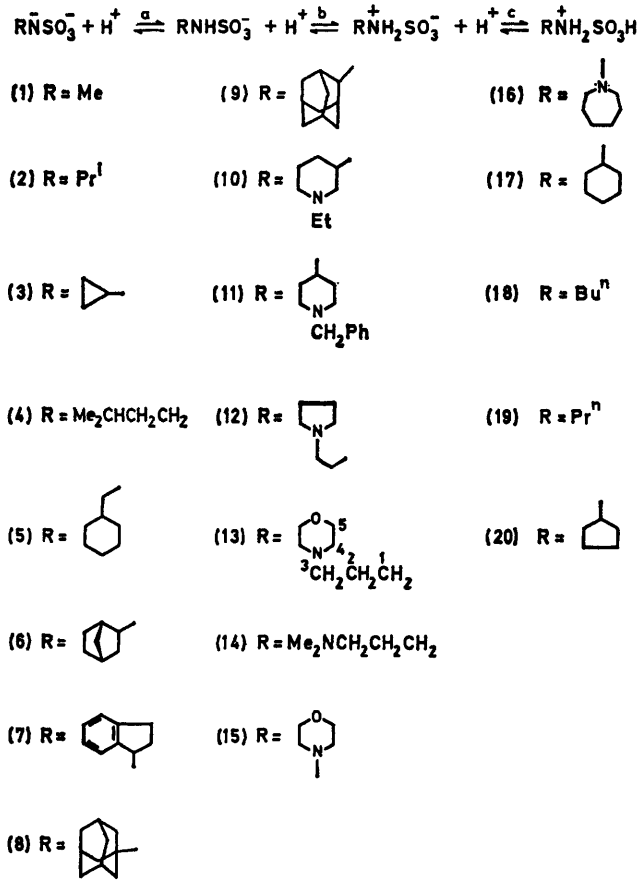
Potentiometric and ^{13}C n.m.r. methods have been used to study the sulphamate equilibria in Scheme 1. pK_a Values for step b have been determined for 19 sulphamates including seven hetero-sulphamates which contain an additional nitrogen atom. The determination of pK_1 (for the hetero-nitrogen atom) and pK_2 (for the sulphamate nitrogen atom) required the use of a computer program in a few instances where the basicities of the two nitrogens were close (overlapping pK_a values). pK_a Values (*ca.* 12) for step a have been determined for five compounds. Step c has been studied in H_2SO_4 and the pK_a values (−1.2 to −1.74 from th e Bunnett and Olsen equation) have been determined for three compounds.

In previous papers[1,2] we examined the equilibrium represented as b in Scheme 1 for some aliphatic, alicyclic, alkylaryl-, and aryl-sulphamates. In this paper pK_a values for equilibrium b have been determined for 19 additional sulphamates including seven hetero-sulpham-

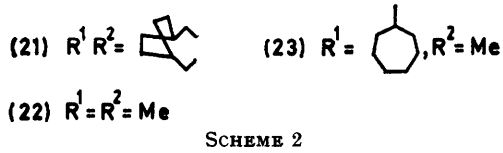


Scheme 1

ates containing an extra nitrogen site. For some of the hetero-sulphamates the calculation of pK_2 (for the sulphamate nitrogen atom) and pK_1 (for the hetero-nitrogen atom) has been possible by the use of standard equations[3] since the basicities of the two nitrogens are separated by at least six pK units. Three hetero-sulphamates had pK_1 and pK_2 overlapping and a computer program was used to calculate the pK_a values.[4]

The equilibrium a has been examined for some alkyl and alicyclic sulphamates and equilibrium c for some alkyl- and hetero-sulphamates.

Potentiometric and ^{13}C n.m.r. methods have been used to determine ionization data.



Scheme 2

EXPERIMENTAL

Materials.—Sulphamic acid (B.D.H.; analytical grade), cyclohexylsulphamic acid (Fluka), and sodium cyclohexylsulphamate (Fluka) were used as obtained. Sodium sulphamate was prepared from the free acid using standard sodium hydroxide. The material obtained gave a satisfactory N, H, and S analysis. Other sulphamates were synthesised as their sodium salts (unless otherwise stated in the Tables) either by the method of Audrieth and Sveda[5] or by that of Boyland *et al.*[6] by sulphamation of the appropriate commercially available amines. Yields varied from 2 to 30% (based on the amines used). *N*-Methylcycloheptylamine was prepared in 56% yield from cycloheptylamine and dimethyl sulphate[7] and the amine was subsequently sulphamated.

All the sulphamates prepared gave a satisfactory (±0.5%) C, H, and N analysis except sodium 3-dimethylaminopropylsulphamate. I.r. spectra of all the sulphamates prepared were recorded as Nujol mulls on a Perkin-Elmer 377 spectrophotometer. All the sulphamates gave characteristic bands[8,9] at 3 400—3 190 (NH), 1 240—1 210 (asym-SO_3), 1 203—1 170 (sym-SO_3), 1 072—1 040 (sym-SO_3), and 730—660 cm^{-1} (NS). All the sulphamates gave a positive ' sulphamate ' test.[10]

Hydrochloric and sulphuric acid and sodium hydroxide solutions were prepared from Volucon (M and B) standards. Deuteriated sulphuric acid (99% D) (Ryvan Chem. Co.) and

deuterium oxide (Prochem) were used as obtained. Buffered solutions for pH 4, 7, and 9.2 were prepared from buffer tablets (B.D.H.).

Potentiometric Measurements.—A Pye-Unicam model 290 MK 2 pH meter standardized with a 1% (w/w) aqueous solution of sulphamic acid (pH 1.18 [11]) and buffers of pH 4.0, 7.0, and 9.2 were used. The following procedures were used for potentiometric titrations.

Method A.[12] The following procedure was typical. Compound (2) (0.0805 g) was dissolved in distilled water (47.5 ml) * in a 100 ml. titration flask which was placed in a water-bath maintained at 25 °C.† A magnetic stirring pellet and a glass electrode were placed in the flask. After recording the initial pH, 0.1M-HCl (5 ml) ‡ was added in 0.5 ml portions from a 10 ml microburette. After each addition of titrant the stirrer was started for *ca.* 20 s, then stopped and the pH was recorded. The concentration of (2) was such that at half-neutralization it corresponds to a 0.01M solution. In the calculation of the pK_a values allowance was made for varying hydrogen ion concentrations. A correction for the dilution of the substrate was also applied.

Method B. This was analogous to Method A except that an amount of the appropriate compound was dissolved in distilled water (23.75 ml) such that at half-neutralization the concentration of the sulphamate solution was 0.01M. In the titration 0.1M-HCl (2.5 ml) was added in 0.25 ml portions.

Method C. In this method a quantity of the compound was dissolved in distilled water (45 ml) such that at half-neutralization the concentration of the sulphamate solution was 0.01M. 0.1M-HCl (10 ml) was added in 0.2 ml portions for the titration.

Method D. A quantity of the compound was dissolved in distilled water (22.5 ml) such that at half-neutralization the concentration of the sulphamate was 0.01M. 0.1M-HCl (5 ml) was added in 0.25 ml portions but, for compounds (14) and (15), the portions added were 0.2 ml and then near the equivalence point 0.1 ml portions were added.

Method E. This was similar to method A except that 0.1M-NaOH was used as titrant. In a typical procedure, compound (17) (0.101 g) was dissolved in distilled water (47.5 ml) such that at half-neutralization the concentration of sulphamate was 0.01M. 0.1M-NaOH (5 ml) was added in 0.2 ml portions. Compound (4) (0.0473 g) was dissolved in distilled water (22.5 ml) and titrated with 0.1M-NaOH (2.5 ml) in 0.25 ml portions. In this method corrections were made in the calculation for varying hydroxide ion concentration and for dilution of the substrate.

Other corrections. Some sulphamates contained water of hydration and in such cases allowance was made for this when weighing out the compound. Occluded water of hydration is a common problem with sulphamates even after thorough drying.[13] In the few instances where barium (rather than sodium) sulphamates were used allowance was made for the fact that two sulphamate anions are released in solution from each molecule of salt.

^{13}C N.m.r. Measurements.—^{13}C Spectra were measured on a JEOL JNM FX 60 spectrometer in 10 mm tubes at 28 °C at 15 MHz with proton decoupling. Chemical shifts (Hz) were determined using D_2O (internal lock). Resolution, pulse width, and pulse repetition were 0.3 Hz, 13 μs, and 1.0 s respectively.

Determination of pK_a in the pH Region.—The following represents the conditions of a typical run. Compound (4) (50 mg) was dissolved in 1.3M-HCl (3 ml) and D_2O (0.4 ml) was added. The initial pH and the chemical shifts of the five carbon atoms were measured. The addition of small volumes of sodium hydroxide (4M, 1M, and 0.5M) changed the pH and the chemical shifts. After each addition of base the pH was redetermined, a portion of the solution was withdrawn (and later returned) and added to the n.m.r. tube, and the chemical shifts measured. In order to determine the shifts more rapidly an additional amount (*ca.* 50 mg) of compound (4) was added to the more dilute acid media.

Determination of pK_a in Strong Acid Media.—The following represents the conditions of a typical run. Compound (17) (20—40 mg, depending on solubility) was dissolved in a series of sulphuric acid solutions from 1.5 to 17.8M (1.6 ml), each solution containing D_2O (0.4 ml), giving a series of H_2SO_4 solutions from 1.2 to 14.2M. Two additional measurements were made by (i) dissolving the compound in 17.8M-H_2SO_4 (1.6 ml)–D_2O (0.2 ml) and (ii) in 17.8M-H_2SO_4 (1.6 ml)–17.8M-D_2SO_4 (0.4 ml). The chemical shifts of the four different carbon atoms of compounds (17) and (18) were determined in each of the solutions using C-4 as an intramolecular standard. For compound (13) the chemical shifts were determined for all the different carbon atoms.

* 1 l = 10^{-3} m³.
† °C = K − 273.15.
‡ 1M = 10^3 mol m^{-3}.

RESULTS AND DISCUSSION

Equilibrium b.—In Table 1 pK_a values are given for equilibrium b for 12 sulphamates including three sulphamates of secondary amines. Both potentiometric (methods A and B) and ^{13}C methods were used to determine ionization data.

TABLE 1

pK_a Values at 25 °C for sulphamates $RNHSO_3^-$ and $R^1R^2NSO_3^-$ in equilibrium b

Compound	Method	pK_a	Spread [a] (±)	n [b]
(1) [c]	A	1.50	0.06	9
(2)	A	1.55	0.06	7
(3)	A	1.70	0.02	8
(4)	A	1.86	0.04	10
(4)	^{13}C	1.46	0.05	4 [d]
(5)	A	2.11	0.05	8
(6)	A	2.03	0.04	8
(6)	^{13}C	1.34	0.04	4 [d]
(7)	B	1.29	0.16	8
(8)	A	2.23	0.03	8
(9)	A	1.58	0.09	7
(21)	B	2.29	0.07	7
(22) [e]	A	2.35	0.02	9
(23)	A	2.26	0.04	8
(23)	^{13}C	1.83	0.05	6 [d]

[a] The scatter or spread was calculated as described in ref. 3, ch. 1. [b] n = No. of pK_a values averaged to obtain the value given; generally the first and the last values were omitted. [c] 0.02M–(0.133 g)–sulphamate used in 47.5 ml. [d] n = No. of ways in which the pK_a was calculated from the chemical shift data in the upper part of Table 4; the value given is the average of these values. [e] Barium salt.

In the calculations based on the potentiometric measurements the pK_a values were calculated at each pH from equation (1) where $\alpha = ([Na^+] + [H^+] + [Cl])/[Na^+]$. The spread or scatter [3] and the number

$$pK_a = pH + \log(1 - \alpha)/\alpha \qquad (1)$$

of pK_a values determined in each set are given in Table 1. A pK_a of 1.13 ± 0.04 was determined for sodium

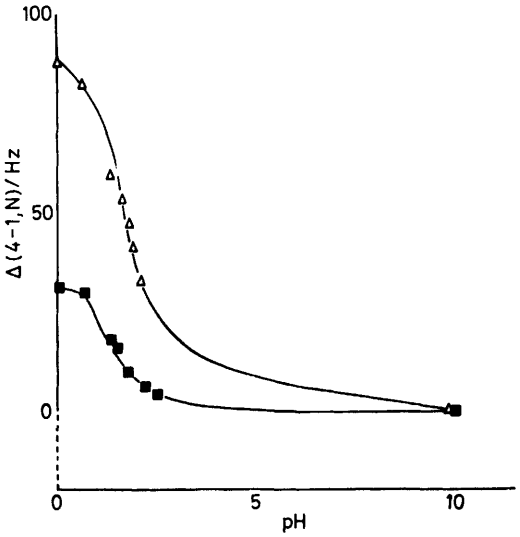
sulphamate in a trial run using a 0.1M solution (at 50 ml dilution) of the salt. This value is in good agreement with the potentiometrically determined value of Hargreaves [14] (1.19).

The advantages of ^{13}C over ^{1}H n.m.r. and the methodology involved has been discussed previously.[2] In the upper part of Table 4 chemical shift differences (in Hz) for the carbon atoms of compounds (4), (6), and (24) are given. The shifts at pH *ca.* 0 and at *ca.* 10 were taken to represent the protonated (BH^+) and unprotonated (B) forms respectively. Chemical shifts were measured at about seven intermediate pH values. For compound (4), the chemical shift difference between C-3 and -4 (C-4 and -5 are equivalent) varies only slightly over the whole range of pH and thus these carbons were used as intramolecular standards. The pK_a could then be calculated in four ways utilising the differences $\Delta(4 - 1)$, $\Delta(4 - 2)$, $\Delta(3 - 2)$, and $\Delta(3 - 1)$ and using equation (2)

$$pK_a = \log(\Delta\delta - \Delta\delta_B)/(\Delta\delta_{BH^+} - \Delta\delta) + pH \quad (2)$$

where $\Delta\delta_{BH^+}$ is the appropriate chemical shift difference at pH *ca.* 0 and $\Delta\delta_B$ the chemical shift difference for the same pair of carbon atoms at pH *ca.* 10. For compound (6) the assignments (other than that for C-1) may not be correct. However, the chemical shifts (upfield and downfield) of the various carbons could be readily followed with the steady deprotonation as base was added. Since the chemical shift differences, $\Delta(4 - 3)$ and $\Delta(6 - 3)$, were small over the range of the study the following four shift differences were used to calculate pK_a values: $\Delta(4 - 1)$, $\Delta(2 - 1)$, $\Delta(6 - 1)$, and $\Delta(3 - 1)$ for compound (6). For compound (23) $\Delta(4 - 3)$ was small and pK_a values were calculated using the remaining six shift differences shown for (23) in Table 4. The spreads for the three pK_a values measured by ^{13}C n.m.r. in Table 1 are quite small thus showing that the pK_a values calculated from the various shift differences for each compound are close. Good sigmoidal plots of $\Delta\delta$ *versus* pH were obtained in all cases. Two examples are shown in the Figure.

Some features are worthy of note in Table 1. First, the facts that the sulphamates of secondary amines, *e.g.* (21)—(23), are, as expected, somewhat more basic than those of primary amines, *e.g.* (1) and (2). Though with successive substitution some of the latter sulphamates become more basic, *e.g.* in the series (1), (2), (3), (5), and (8). The reduced basicity of (9) compared with (8) is of interest and could perhaps have been predicted if one could compare the pK_a values of compound (2) and t-



Variation of chemical shift difference with pH for compound (4), $\Delta(4 - 1)$(■) and for compound (23), $\Delta(4 - N)$(Δ). The symbol 'N' is used for the chemical shift of the methyl group attached to nitrogen in (4)

butylsulphamate [regarding the latter compounds as vaguely approximate models for (9) and (8), respectively,] a supposition supported by the virtual identity of the pK_a values of (9) and (2). Second, the pK_a values measured by ^{13}C n.m.r. are 0.4—0.6 pK_a units lower than those measured by the potentiometric method. A somewhat similar lowering of the pK_a was observed earlier when comparing pK_a values measured by ^{13}C n.m.r. and by the potentiometric method (*ca.* 0.4), by a conductimetric method (*ca.* 0.3), and by ^{1}H n.m.r. (*ca.* 0.1).[2] These differences in the pK_a values obtained by different methods are most likely due to medium effects. The conditions under which, for example, the ^{13}C and potentiometric measurements were made, are quite different (see Experimental section).

The compounds in Table 2 have hetero-nitrogen (pK_1) and sulphamate nitrogen (pK_2) sites. In the case of

TABLE 2

pK_1 [a] and pK_2 [b] values at 25 °C for sulphamates $RNHSO_3^-$ in equilibrium b

Compound	Method	pK_1	Spread (±) [c]	Method of calc.	n [d]	pK_2	Spread (±) [c]	Method of calc.	n [d]
(10)	D	9.10	0.05	Equation (1)	6	1.55	0.08	Equation (3)	7
		9.15	0.04	Computer	6	1.68	0.14	Computer	7
(11)	D	8.47	0.11	Equation (1)	7	1.60	0.05	Equation (3)	7
		8.53	0.12	Computer	7	1.71	0.11	Computer	7
(12)	D	9.38	0.05	Equation (1)	6	1.36	0.18	Equation (3)	7
		9.44	0.07	Computer	6	1.49	0.22	Computer	7
(13)	D	7.36	0.04	Equation (1)	7	1.74	0.05	Equation (3)	8
		7.41	0.04	Computer	7	1.80	0.10	Computer	8
(14)	D	1.16	0.15	Computer	12	1.96	0.08	Computer	12
(15)	D	1.90	0.10	Computer	13	1.33	0.08	Computer	12
(16)	C	4.55	0.01	Computer	20	1.05	0.14	Computer	17

[a] pK_1 = the pK of the 'non-sulphamate' nitrogen. [b] pK_2 = the pK for the sulphamate nitrogen. [c,d] See footnotes *a*,*b* respectively in Table 1.

compounds (10)—(13) where the basicity of the hetero-nitrogen is at least six times greater than that of the sulphamate nitrogen equation (1) could be used to calculate pK_1 and equation (3) was used to calculate pK_2.[4] pK_1 and pK_2 were also calculated for these

$$pK_2 = \log([Cl^-] - [Na^+] - [H^+])/(2[Na^+] - [Cl^-] + [H^+]) + pH - \frac{1.5345I^{\frac{1}{2}}}{1 + 1.6I^{\frac{1}{2}}} \quad (3)$$

$$I = 2[Cl^-] - [Na^+] - [H^+]$$

compounds utilising a computer program designed for the separation of overlapping pK_a values. The program gave values of pK_1 and pK_2 in good agreement with those calculated from equations (1) and (3). A test run was carried out with succinic acid using available data[4] with the following results: pK_1 4.134 and pK_2 5.551 compared with values of 4.200 and 5.634, respectively, given by Albert and Sergeant. The program was used to calculate the overlapping pK_1 and pK_2 values for compounds (14)—(16). The values obtained are given in Table 2. Compound (14) may have its sulphamate nitrogen pK_a somewhat similar to the pK_a of compound (4) (1.86, potentiometrically). On this basis we feel that for (14), pK_1 is 1.16 and pK_2 1.96. Taking the related compounds (15) and (16) together, for (16) 4.55 is assigned to pK_1, being too basic to be a sulphamate nitrogen, and pK_2 is then 1.05. For compound (15) the two pK_a values (1.33 and 1.90) given by the computer indicate that the two sites in this compound are of very similar basicities. To assign pK_1 and pK_2 we noted that the pK_a values of morpholine [a model for (15)] (pK_a 8.33[15]) and piperidine [a model for (16)] (pK_a 11.12[15]) differed by 2.79 pK_a units and that a value (2.65) close to this difference is obtained if one substracts 1.90 from 4.55 whereas subtraction of 1.33 from 4.55 gives 3.22. We therefore felt that for compound (15), pK_1 is 1.90 and pK_2 1.33.

Equilibrium a.—Table 3 contains pK_a values for equilibrium a, *i.e.* the removal of a proton from sulphamate anions. While there are a number of reports[16] of dimetallic salts of sulphamic acid, NHM'SO_3M, formed in the reaction $NH_2SO_3M + M'$(liq. NH_3) ⟶ NHM'SO_3M with M' = M and M' ≠ M there are no reports of studies of the acidity of the sulphamate nitrogen in $RNHSO_3^-$. The sulphamate nitrogen is several pK_a units more basic than the analogous sulphonamide nitrogen in benzenesulphonamides $XC_6H_4SO_2NH_2$ (pK_a 9—10.5[17]) and in benzenesulphonanilides $ArSO_2NHAr$ (pK_a 6.2—9[17]). This larger basicity can be rationalized in terms of the electrostatic repulsion created in the sulphamate dianion by the proximity of the two negative charges.

TABLE 3

pK_a Values at 25 °C for sulphamates $RNHSO_3^-$ in equilibrium a

Compound	pK_a [c]	Spread (±) [b]	n [c]
(4)	12.09	0.06	16
(17)	12.15	0.04	18
(18) [d]	12.53	0.05	17
(19)	11.89	0.03	11
(20)	12.09	0.10	11

[a] Using Method E. [b,c] See footnotes *a,b* respectively in Table 1. [c] Barium salt.

The pK_a values were calculated from equation (4) where $[B^-] = [R\bar{N}SO_3^-]$ and $[B] = [RNHSO_3^-]$.

$$pK_a = pH + \log([B] + [B^-] + [OH^-])/([B^-] - [OH^-]) \quad (4)$$

Equilibrium c.—Ionization data were calculated from equation (5) where $\Delta\nu_{BH_2^+}$ and $\Delta\nu_{BH^+}$ are the chemical shift differences of the diprotonated sulphamates $RN\dot{H}_2SO_3H$ and the zwitterionic sulphamate, $RN\dot{H}_2SO_3^-$, respectively. The shifts at 17.8M- and 1.2M-H_2SO_4 were taken to represent the diprotonated and zwitterionic forms respectively.

$$I = (\Delta\nu_{BH^+} - \Delta\nu)/(\Delta\nu - \Delta\nu_{BH_2^+}) \quad (5)$$

The pK_a for compound (17) was determined from the chemical shift difference Δ(3 — 1). The signals due to C-3 and -4 partially overlap in very strong acid. Δ(3 — 2) varies only slightly over the range of acidities involved so that C-2 could also be used as an intramolecular standard. For compound (18) pK_a was determined using Δ(4 — 1). C-3 or -2 also appear to be suitable intramolecular standards. For compound (13), the signals due to C-2, -3, -4', and -5' were assigned by comparison with *N*-ethylmorpholine.[18] The assignments are supported by the fact that the chemical shift difference $\Delta(\nu_{BH^+} - \nu_B)$ for Δ(2 — 1) were of the same sign and magnitude as those for compound (18). The $pK_{BH_2^+}$ value for the sulphamate oxygen was determined from Δ(2 — 1) as it was desired to minimize interference due to simultaneous protonation of the morpholine oxygen. Δ(4 — 2) was used to calculate a pK_a value for the morpholine oxygen as this shift gave the largest and most regular pattern of change with varying acidity. An uncertainty existed as to which acidity corresponds to $\Delta\nu_B$. The chemical shift differences were seen by inspection to be tapering off near 1.96M-H_2SO_4 but between this acidity and 1.5M-H_2SO_4 a relatively large change took place. This we attribute to the commencement of deprotonation of the sulphamate nitrogen of (13) which may be expected to begin to lose its proton at *ca.* 1.5M-H_2SO_4. Accordingly, we have taken the chemical shift differences at 1.96M-H_2SO_4 to represent $\Delta\nu_B$.

Plots of $\log_{10}I$ *versus* $-H_0$ [equation (6)] gave slopes *m* much lower than unity. The first column in Table 5 gives the values obtained as d $\log_{10}I$/d($-H_0$). These values show clearly that H_0 is not followed. The $(H_0)_{\frac{1}{2}}$ values have been calculated using equation (6), when $[BH^+] = [BH_2^+]$, *i.e.* the situation at half-protonation. Then, $-m(H_0)_{\frac{1}{2}} = pK_{BH_2^+}$ and if the intercept of equation (6) is obtained and divided by the slope (*m*), $(H_0)_{\frac{1}{2}}$ values are obtained. $-m(H_0)_{\frac{1}{2}}$ Values are also given. When

$$\log_{10}I = -mH_0 + pK_{BH_2^+} \quad (6)$$

TABLE 4

^{13}C Chemical shift differences (Hz) for unprotonated ($\Delta\nu_B$), protonated ($\Delta\nu_{BH^+}$), and diprotonated ($\Delta\nu_{BH_2^+}$) sulphamates

	Δ(4 − 1)		Δ(4 − 2)		Δ(4 − 3)		Δ(3 − 2)		Δ(3 − 1)	
Compound	$\Delta\nu_B$	$\Delta\nu_{BH^+}$	$\Delta\nu_B$	$\Delta\nu_{BH^+}$	$\Delta\nu_B$	$\Delta\nu_{BH^+}$	$\Delta\nu_B$	$\Delta\nu_{BH^+}$	$\Delta\nu_B$	$\Delta\nu_{BH^+}$
(4)	302.7	334.0	240.2	193.3	50.78	56.64	189.5	136.7	252.0	277.3
(6)	271.5	332.0	54.69	52.73	24.44	7.813	46.88	28.30	263.7	308.6
(23)	60.55	109.4	89.84	68.36	37.11	39.06	50.78	29.30	21.48	70.31

	$\Delta\nu_{BH^+}$	$\Delta\nu_{BH_2^+}$	$\Delta\nu_{BH^+}$	$\Delta\nu_{BH_2^+}$	$\Delta\nu_{BH^+}$	$\Delta\nu_{BH_2^+}$	$\Delta\nu_{BH^+}$	$\Delta\nu_{BH_2^+}$	$\Delta\nu_{BH^+}$	$\Delta\nu_{BH_2^+}$
(17)							87.89	91.80	502.0	550.8
(18)	488.3	525.4	226.6	228.3	97.66	99.66				
(13)	332.0	324.2	644.5	664.1	142.6	148.4	501.9	515.7	189.5	175.8

	Δ(4 − N) [a]		Δ(3 − N) [a]		Δ(2 − 1)		Δ(7 − 1)		Δ(6 − 1)		Δ(5 − 1)		Δ(6 − 3)	
	$\Delta\nu_B$	$\Delta\nu_{BH^+}$	$\Delta\nu_B$	$\Delta\nu_{BH^+}$	$\Delta\nu_{B+}$	$\Delta\nu_{BH^+}$	$\Delta\nu_B$	$\Delta\nu_{BH^+}$	$\Delta\nu_B$	$\Delta\nu_{BH^+}$	$\Delta\nu_B$	$\Delta\nu_{BH^+}$	$\Delta\nu_B$	$\Delta\nu_{BH^+}$
(6)					279.3	216.8	515.6	550.8	388.7	439.5	283.2	361.3	125.0	130.9
(23)	523.4	611.3	484.4	572.2										

			$\Delta\nu_{BH^+}$	$\Delta\nu_{BH_2^+}$	$\Delta\nu_{BH^+}$	$\Delta\nu_{BH_2^+}$
(17)			414.1	459.0		
(13)			312.5	339.8	154.3	140.6

[a] The symbol ' N ' is used for the chemical shift of the methyl group attached to nitrogen in (4).

the benzophenone acidity function (H_0^a) was used the points gave a slightly better fit to a straight line but the m values were still *ca.* 0.25. If H_A was used instead of H_0 in equation (6), the slopes (m) were *ca.* 0.5. The most suitable function appears to be the alcohol acidity function, H_{ROH}.[19] The slopes (m) of plots of $\log_{10}I$ *versus* $-H_{ROH}$ are closer to unity than in the case of the other functions. The $pK_{BH_2^+}$ values obtained with this function are given in Table 5. These values are also in values for compound (17) of −1.79 (n_B 1.30) and −1.67 (m^* 0.19) respectively.

From the chemical shift differences for compound (13) the pK_a for its morpholine oxygen can also be calculated. Using H_0, the slope of $\log_{10} I$ *versus* $-H_0$ is 0.20 and the pK_a value estimated from this is −1.0. Using H_{ROH}, a slope of 0.72 with a pK_a of −1.25 is obtained. This latter value is in reasonable agreement with the Bunnett and Olsen value from equation (7), −1.45. For satur-

TABLE 5

pK_a Values at 28 °C measured in H_2SO_4 for sulphamates $R\overset{+}{N}H_2SO_3^-$ in equilibrium c

Compound	$\frac{d \log_{10}I}{d(-H_0)}$ [a]	$-(H_0)_{\frac{1}{2}}$ [b]	$-m(H_0)_{\frac{1}{2}}$	r [c]	$\frac{d \log_{10}I}{d(-H_x)}$ [d]	$-pK_{BH_2^+}$	r [c]	$-pK_{BH_2^+}$ [e]	ϕ	r [c]
(17)	0.26	4.9	1.14	0.997 (14)	0.87	1.40	0.994 (12)	1.68	0.85	0.987 (14)
(18)	0.24	5.0	1.20	0.990 (9)	0.99	1.75	0.960 (8)	1.74	0.88	0.987 (10)
(13)	0.19	3.2	0.60	0.981 (6)	0.75	0.90	0.994 (6)	1.20	0.87	0.987 (6)
(13) [f]	0.20	5.0	1.00	0.995 (6)	0.72	1.25	0.996 (6)	1.45	0.88	0.966 (6)

[a] *I.e.* the slopes (m) of plots of $\log_{10}I$ *versus* $-H_0$. H_0 Values were taken from C. H. Rochester, ' Acidity Functions,' Academic Press, New York, 1970, ch. 2, pp. 39 and 43. [b] Calculated from equation (6). [c] The figures in parentheses are the number of points taken. [d] *I.e.* the slopes (m) of plots of $\log_{10} I$ *versus* H_{ROH} for compounds (13), (17), and (18). H_{ROH} Values were taken from ref. 19. [e] Calculated from equation (7). [f] Protonation on the morpholine oxygen.

quite reasonable agreement with the values calculated from the Bunnett and Olsen equation (7).

$$\log_{10}I + H_0 = \phi(H_0 + \log[H^+]) + pK_{BH_2^+} \quad (7)$$

There is one report in the literature on the study of equilibrium c for a series of *meta*- and *para*-substituted phenylsulphamates.[20] From the analysis of kinetic data for the acid-catalysed hydrolysis of these compounds, the Russian group have calculated $pK_{BH_2^+}$ values for six phenylsulphamates. The values obtained vary from −2.67(3-Cl) to −2.04 (4-CH_3O) and H_A appears to be followed quite well. In equilibrium b arylsulphamates are more weakly basic than aliphatic and alicyclic sulphamates [1] and not surprisingly this is also the case (though to a lesser extent) in equilibrium c.

Marziano [21] and Cox–Yates [22] plots gave $pK_{BH_2^+}$ ated cyclic ethers values somewhat more negative than this (*ca.* −2 to −2.8) have been reported [23] or can be calculated.[24] The ϕ values in Table 5 are, however, in the area typical for oxygen centres.[25]

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