Solutes in Sulphuric Acid. Part VI.[1] A Nuclear Magnetic Resonance Study of Organic Sulphonic Acids and ^{1}H Nuclear Magnetic Resonance Standards; pK_{BH} Determination of Sulphonic Acids

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The behaviour of some alkane- and arene-sulphonic acids in sulphuric acid as solvent has been investigated. In aqueous sulphuric acid the sulphonic acids ionize: $ArSO_3H \rightleftharpoons ArSO_3^- + H^+$. The ionization follows the H_0^{a} acidity function and half-ionization is observed at $-5{\cdot}8 > H_0^{a} > -6{\cdot}8$. In fuming sulphuric acid the sulphonic acids exhibit both protonation and sulphur trioxide complexation with formation of $RSO_3H_2^+$ and RS_2O_6H respectively. The chemical shifts of some ^{1}H n.m.r. standards for the sulphuric acid system are reported. The preferred standards are the $(CH_3)_4N^+$ ion as internal standard, and neat liquid tetramethylsilane as external standard.

RECENTLY we have reported pK_{BH} values for the ionization (1) of benzenesulphonic acid and a number of monosubstituted derivatives in concentrated aqueous sulphuric acid which were determined by the u.v.

$$ArSO_3H \rightleftharpoons ArSO_3^- + H^+ \qquad (1)$$

method.[1,2] The use of this method seems to be restricted to aromatic sulphonic acids and further seems to require an isolated B band, as *e.g.* the nitrobenzene- and the naphthalene-sulphonic acids defy determination of the ionization constant by this method.[1,3]

An n.m.r. technique has recently been used successfully for the study of protonation equilibria.[4] We have applied this technique to study the ionization of some alkane- and arene-sulphonic acids. In connection with this and our sulphonation studies, we further report on the use of internal and external ^{1}H n.m.r. standards for the sulphuric acid system.

RESULTS AND DISCUSSION

Sulphonic Acids.—The chemical shifts of the various types of proton of an alkanesulphonic acid relative to tetramethylammonium ion as internal standard have been determined as a function of the concentration of the aqueous sulphuric acid solvent for a number of linear alkane-1-sulphonic acids and phenylmethanesulphonic acid.† The chemical shifts of the protons of the higher linear alkanesulphonic acids, *e.g.* $C_8H_{17}SO_3H$, could not be determined in 20—90% H_2SO_4 because of low solubility and micelle formation.

When the chemical shifts of the protons near the sulpho-group are plotted against acidity sigmoidal curves are obtained. Typical curves for the H_0^{a} acidity function are shown in Figure 1A and B. Similar curves were obtained by plotting the difference of the chemical shifts of these protons and of another more remote proton (see later) against acidity (Figure 1B). The other protons then constitute an intramolecular n.m.r. standard.

The n.m.r. spectrum in aqueous $\geqslant 95\%$ H_2SO_4 was taken to represent the spectrum of the un-ionized sulphonic acid (with the exception of CF_3SO_3H, *vide infra*) and the spectrum in aqueous $\leqslant 30\%$ H_2SO_4 that of the sulphonate anion. The chemical shifts for the ionized and un-ionized forms are collected in Table 1. For the alkane-1-sulphonic acids, $CH_3[CH_2]_nSO_3H$, the difference in chemical shift between the terminal methyl

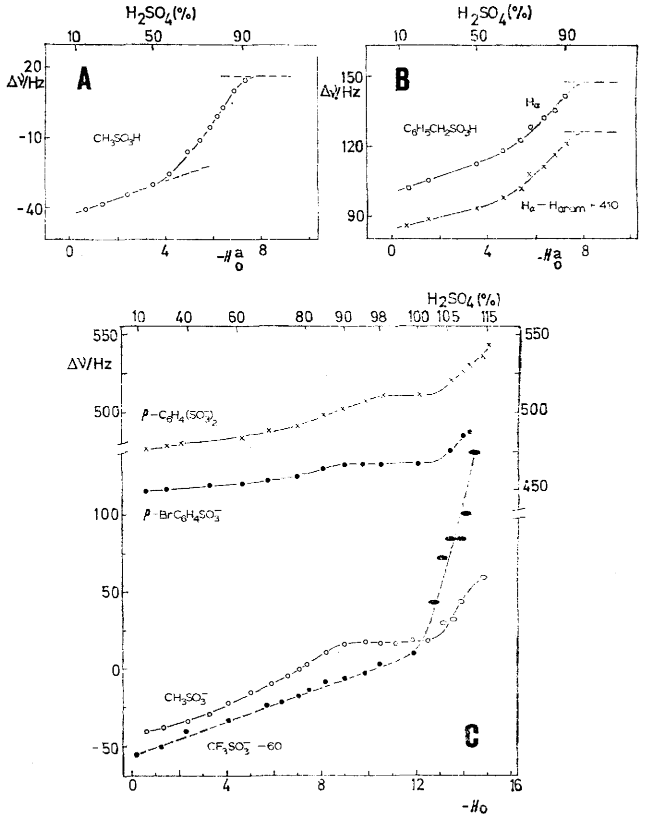

FIGURE 1 Variation of *chemical* shift relative to internal $(CH_3)_4N^+$ with acidity. For CF_3SO_3H the ^{19}F *resonance* shift relative to external CF_3CO_2H is plotted.

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† Phenylmethanesulphonic acid is sulphonated slowly in $>98\%$ H_2SO_4.[5]

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of the sulphonic acid species (in 98·4% H_2SO_4) and that of the sulphonate anion species (in D_2O) decreases with increasing alkyl chain length, $\Delta\Delta\nu$ for n 0, 1, 2, 3, 7, and 9 being 56·4, 33·2, 19·3, 16·6, 11·9, and 9·5 Hz respectively

The pK_{BH} of reaction (1) is defined by equation (2),

$$\log(|BH|/|B^-|) = -H_0^a + pK_{BH} \qquad (2)$$

where BH = RSO_3H. It can be shown that for a given sulphuric acid concentration $|BH|/|B^-| = (\Delta\nu - \Delta\nu_{B^-})/(\Delta\nu_{BH} - \Delta\nu)$ where $\Delta\nu$ is the observed chemical shift of a given non-exchanging proton at that acid concentration.[4] There is a substantial medium effect on $\Delta\nu_{B^-}$ (Figure 1) and no such effect on $\Delta\nu_{BH}$ (for *e.g.* methane- and phenylmethane-sulphonic acid $\Delta\nu_{\alpha\text{-}H}$ is constant at 93—100% H_2SO_4 with values of 16 ± 1 and 147 ± 1 Hz respectively). For the calculation of the $|BH|/|B^-|$ ratio the assumption was made that the medium effect on $\Delta\nu_{B^-}$ remains linear with the acidity function and that $\Delta\nu_{BH}$ remains constant for the extrapolations involved. For the monosulphonic acids, the graphs of $\log|BH|/|B^-|$ against the common acidity functions H_0,[6] H_0^a,[7] and H_A [8] are linear. As judged from the slopes of these graphs the correlations with H_0^a (Table 1) and H_A are much better than the correlation with H_0: the slope is significantly smaller for H_0 than for H_0^a and H_A, which are about the same and closer to the required value of unity.[4] This result is similar to that obtained with the u.v. technique.[1,2] The ionization is thus governed by H_0^a or H_A. This is not surprising since these acidity functions were determined using indicators which, like the sulphonates, are protonated on oxygen.

TABLE 1

Chemical shifts of the sulphonic acid and sulphonate species, and pK_{BH} values

	Chemical shifts (Hz) [a]								pK_{BH} [b]			
	Un-ionized sulphonic acid in 98% H_2SO_4				Sulphonate anion in 30% H_2SO_4				N.m.r.[c]			
Substrate	H_α	H_β	H_ω	H_{arom}	H_α	H_β	H_ω	H_{arom}	A	B	C	U.v.[2]
CH_3SO_3H	16(s)				−37(s)				6·0 ± 0·3 (0·7 ± 0·2)	6·2 ± 0·2		
$CH_3CH_2SO_3H$	41(q)	−153(t)			−11(q)	−180(t)			5·8 ± 0·3 (0·8 ± 0·1)	5·8 ± 0·2	6·4 ± 0·4	
$CH_3[CH_2]_2SO_3H$	24(t)	−119(m)	−202(t)		−25(t)	−145(m)	−218(t)		6·2 ± 0·3 (0·8 ± 0·1)	6·3 ± 0·2	6·2 ± 0·2	
$CH_3[CH_2]_3SO_3H$	35(t)		−209(t)									
$CH_3[CH_2]_7SO_3H$	29(t)		−220(t)									
$CH_3[CH_2]_9SO_3H$	30(t)		−221(t)		−31(t) [d]		−228(t) [d]					
$C_6H_5CH_2SO_3H$	147(s)			431(s)	106(s)			438(s)	6·5 ± 0·2 (0·7 ± 0·1)	6·7 ± 0·2	6·5 ± 0·2	
p-$BrC_6H_4SO_3H$				451(s)				467(s)	6·6 ± 0·2 (1·0 ± 0·1)	6·7 ± 0·2		6·86 ± 0·05
p-$C_6H_4(SO_3H)_2$				511(s)				478(s) [e]		6·8 ± 0·3		
m-$C_6H_4(SO_3H)_2$												7·0 ± 0·2

[a] Relative to $(CH_3)_4M^+$ as internal standard; the data in parentheses refer to the observed multiplicity of the signal. [b] Based on the H_0^a acidity function. [c] A: determined from the graphs of log (|BH|/|B⁻|) against H_0^a; the data in parentheses give the slopes $d[\log(|BK|/|B^-|)]/d(-H_0^a)$. B and C: estimated from the inflection points of the graphs of $\Delta\nu_{\alpha\text{-}H}$ or $\Delta\nu_{ar\text{-}H}$ against H_0^a and $(\Delta\nu_{\alpha\text{-}H} - \Delta\nu_X)$ against H_0^a respectively. [d] In 15% H_2SO_4. [e] Disulphonate anion.

The acidity of the alkanesulphonic acids is somewhat less than those of phenylmethane- and *p*-bromobenzenesulphonic acid (Table 1), as also observed for the corresponding carboxylic acids.[9]

The behaviour of methane-, *p*-bromobenzene-, and benzene-1,4-disulphonic acid has also been studied in *fuming* sulphuric acid. At high sulphuric acid concentrations sulphonation of *p*-bromobenzenesulphonic acid is observed, as is apparent from the growing ABX absorption pattern in the n.m.r. spectrum due to the formation of 4-bromobenzene-1,3-disulphonic acid.[10] This sulphonation becomes so rapid as to render the chemical shift determination of the parent substrate impossible at acid concentrations >109% H_2SO_4. Benzene-1,4-disulphonic acid exhibits a singlet n.m.r. absorption over the whole sulphuric acid range (0—118% H_2SO_4). Unexpectedly *p*-bromobenzenesulphonic acid behaves similarly, illustrating the magnetic equivalence of the four aromatic protons over the whole sulphuric acid range (0—109% H_2SO_4). With methanesulphonic acid only one singlet absorption is observed over the whole sulphuric acid range, illustrating that *C*-sulphonation [11] does not occur. The absence of *C*-sulphonation was further verified by quenching experiments.

Above 100% H_2SO_4, the chemical shifts of the carbon-bonded protons of each of the three sulphonic acids increase strongly with increasing sulphuric acid concentration (Figure 1C). This may be explained *a priori* in terms of protonation of the sulphonic acid (3), in terms of complex formation with sulphur trioxide with formation of pyrosulphonic acid (4), or in terms of anhydride formation (5), provided these reactions are

$$RSO_3H + H^+ \rightleftharpoons RSO_3H_2^+ \qquad (3)$$

$$RSO_3H + SO_3 \rightleftharpoons RS_2O_6H \qquad (4)$$

$$RSO_3H + RS_2O_6H \rightleftharpoons (RSO_2)_2O + H_2SO_4 \qquad (5)$$

fast on the n.m.r. time scale. Evidence in favour of this requirement has been advanced.[12] The anhydride formation is unlikely in view of the low solute concentration employed (0·16mM). Further, with methanesulphonic anhydride as solute in fuming sulphuric acid, only one ^1H singlet absorption is observed at exactly

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the same chemical shift as that observed for methanesulphonic acid as solute. This is most easily explained in terms of a very rapid conversion of the anhydride into sulphonic and pyrosulphonic acid (5). These two considerations seem to rule out the third explanation.

For methanesulphonic acid the difference in chemical shift for 100 and 115% H_2SO_4 (43 Hz) is in between that expected for protonation (100 ± 5 Hz[13]) and for pyrosulphonic acid formation (21 Hz[12]). This may imply either that there is only 43% protonation, or that both protonation and pyrosulphonic acid formation occur. The possibility of partial protonation seems unlikely, since the actual increase in acidity (2·5 units in H_0) would lead to at least 75% protonation. Recently evidence for the conversion of arenesulphonic acids in fuming sulphuric acid into their conjugate acids and/or their pyrosulphonic acids has also been obtained from the variation in the sulphonation isomer distributions of some of these acids.[14]

The apparent ^{19}F resonance shift of trifluoromethanesulphonate in sulphuric acid as solvent increases gradually from 0 to 100% H_2SO_4 (about linearly with Hammett's acidity function) and more steeply above 100% H_2SO_4 (Figure 1C). A detailed explanation must be deferred in view of the absence of accurate data on the volume magnetic susceptibility for acid concentrations >90% H_2SO_4.* It seems obvious, however, that the large increase in the resonance shift at acid concentrations >100% H_2SO_4 is due to a chemical process. Trifluoromethanesulphonic acid is an extremely strong acid,[17] much stronger than methanesulphonic acid.[18] Accordingly the variation in the resonance shift at acid concentrations <100% H_2SO_4 is ascribed to solvent effects on the $CF_3SO_3^-$ ion, and the much larger variation at acid concentrations >100% H_2SO_4 to protonation and/or sulphur trioxide complex formation of the $CF_3SO_3^-$ anion.

^1H *N.m.r. Standards for the Sulphuric Acid System.*—TMS (Tetramethylsilane) and DSS (sodium 4,4-dimethyl-4-silapentane-1-sulphonate) cannot be used as ^1H n.m.r. standards in sulphuric acid solution because of decomposition with formation of methane and disiloxane, as is evident from the growing n.m.r. absorptions at δ 0·25 and 0·56 respectively.[19] The $(CH_3)_4N^+$ [20] and $(CH_3)_3HN^+$ [21] ions have been used as internal references. The dependence of the chemical shifts of these internal standards relative to external liquid TMS, or TTP (sodium 2-trimethylsilyltetradeuteriopropionate) in D_2O on the sulphuric acid concentration is shown in Figure 2A. Both the $(CH_3)_4N^+$ and $(CH_3)_3HN^+$ ions are stable over the acid range studied. The observed variation of the $(CH_3)_4N^+$ ion up to 100% H_2SO_4 is equal to the variation in the sulphuric acid bulk volume magnetic susceptibility (Figure 2B) which is given by $2\pi(\chi_{standard} - \chi)/3$ [22] where χ and $\chi_{standard}$ stand for the volume magnetic susceptibilities of the sulphuric acid solution[15,16] and the external reference[22] respectively. The $(CH_3)_3HN^+$ ion is a less satisfactory standard than $(CH_3)_4N^+$ as it exhibits a doublet methyl hydrogen absorption and a larger variation in the chemical shift in aqueous sulphuric acid. This variation is ascribed to a change in hydrogen bonding of the nitrogen-bonded

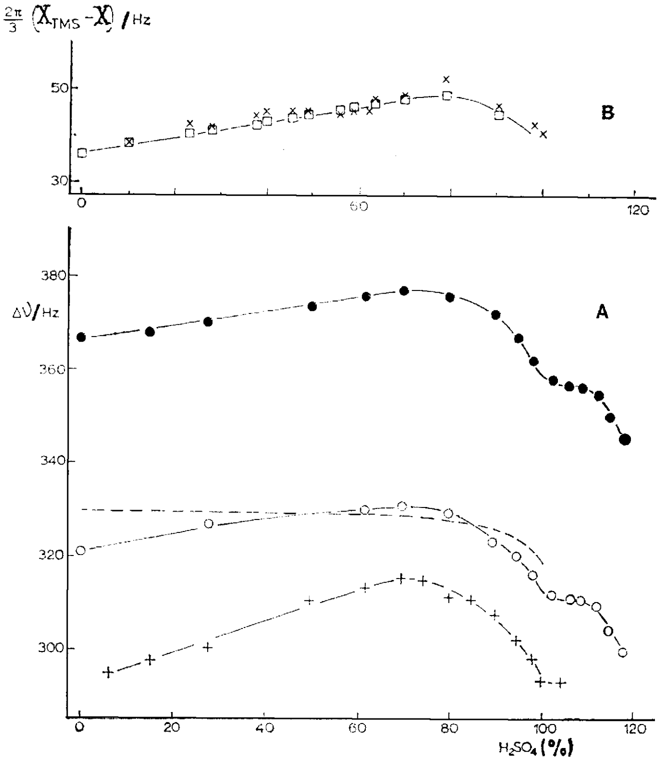

FIGURE 2 A, Variation in the *resonance* shift of the $(CH_3)_4N^+$ and $(CH_3)_3HN^+$ ions relative to external TTP and TMS with the sulphuric acid concentration: + $(CH_3)_3HN^+$ (0·6M) relative to external TTP (200 mg) in D_2O (1 ml); ○ $(CH_3)_4N^+$ (0·06M) relative to external TTP (200 mg) in D_2O (1 ml); ● $(CH_3)_4N^+$ (0·06M) relative to external neat liquid TMS. B, Shift difference to convert *resonance* shift (relative to external liquid TMS) to *chemical* shift (relative to TTP in D_2O). The dotted line in A gives the *chemical* shift of $(CH_3)_4N^+$ relative to external liquid TMS

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* The data of Pacault[15] which cover the range 0—100% H_2SO_4 exhibit a larger scatter than those of Cini[16] which only cover the range 0—90% H_2SO_4.

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hydrogen of the cation to the different solvent entities (*cf.* ref. 23).

TABLE 2

^{1}H Resonance shifts of sulphuric acid

Medium		$\Delta\nu$(Hz) relative to	
H_2SO_4 (%)	'Free' SO_3 (%)	Liquid $TMS_{external}$	$(CH_3)_4N^+_{internal}$
0		520·2	153·5
14·8		609·5	
27·7		700	329·6
39·2		771·3	
50·0		853·8	
61·9		939·0	561·6
69·9		1027·5	651·0
78·0		1102·9	
79·8			747·5
84·1		1154·0	
87·6		1170·7	
90·2		1178·3	805·9
93·4		1178·2	
94·9		1172	805·2
95·4		1167·3	
98·2		1144	782·0
98·4		1142·8	
100·1	0·4	1116·5	
102·3	10·2	1119	761·7
105·5	24·4	1120·9	
108·8	39·1	1109	750·9
112·3	54·7	1083	728·9
118·1	80·4	1040	696·2

The use of liquid TMS in a coaxially sealed off capillary is simpler than the addition to the sulphuric acid solution of an accurately known small amount of (hygroscopic) tetramethylammonium chloride, or the addition of gaseous trimethylamine.

An alternative n.m.r. standard for the sulphuric acid solutions is the hydrogen acid absorption. This reference has, however, the disadvantage that the resonance shift of the acid peak is strongly dependent on the sulphuric acid concentration (Table 2) and, at a given sulphuric acid concentration, will vary with addition of solutes. The observed variation in the resonance shift with the sulphuric acid concentration agrees with that reported by Gillespie,[24] but the present data cover a larger acid range. The correction for the variation in the volume magnetic susceptibility (Figure 2B) is almost negligible compared to the variation in the resonance shift up to 100% H_2SO_4. If the variation in the resonance shift of $(CH_3)_4N^+$ (Figure 2A) is a measure of the change in the solvent susceptibility, then it is also small for the acid range >100% H_2SO_4.

Some chemical and resonance shift differences which are of use by application of internal and external references respectively for water as solvent are collected in Table 3.

EXPERIMENTAL

The synthesis of phenylmethanesulphonic acid has been described.[4] DSS was prepared according to ref. 25. The other sulphonates, or sulphonic acids were commercial products. The sulphonic acids were purified by distillation if they contained >2% of water. Methanesulphonic anhydride was prepared as described by Owen and Whitelaw.[26] Tetramethylammonium chloride (B.D.H.) was dried in vacuum over P_2O_5.

All ^{1}H n.m.r. measurements of the substrates in sulphuric acid solution were made with a Varian HA 100 spectrometer at a sample temperature of 31° using neat liquid TMS (sealed capillary) as an external standard, or tetramethylammonium chloride (0·060M) as an internal standard. The concentration dependence of the methyl hydrogen absorption of $(CH_3)_4N^+$ and $(CH_3)_3HN^+$ is small, <2 Hz for variation in solute concentration from 0·060 to 0M.

The ^{19}F n.m.r. measurements of $(CF_3SO_3)_2Ba$ in the sulphuric acid solutions were made with a Varian HR 60 spectrometer at 56·4 MHz using trifluoroacetic acid as external reference (*cf.* ref. 27). The solute concentrations were ⩽0·16M. The concentration dependence of the chemical shift at 0·050—0·520M was negligible.

TABLE 3

^{1}H Resonance shift differences

			$\Delta\Delta\nu$(Hz)		
Solute	Solvent	External standard	$\lim(\Delta\nu_{solute} - \Delta\nu_{H_2O})_{\lvert solute \rvert \to 0}$	$\Delta\nu_{ext. st.} - \Delta\nu_{H_2O}$	$\Delta\nu_{solute} - \Delta\nu_{ext. st.}$
TMS	H_2O		−484		
TMS	D_2O [a]		−481 [b]		
DSS	D_2O [a]		−472 [b,c]		
TTP	H_2O		−475		
TTP	D_2O [a]		−473 [b]		
$(CH_3)_4N^+Cl^-$	H_2O	TMS (sealed) [d]	−153 [e]		367
	H_2O	TMS (sealed) [d]		−520	
	D_2O [a,b]	TMS (sealed) [d]		−518	
	H_2O	TMS (open) [d]		−522	
	H_2O	TTP in D_2O [a,f]		−474	

[a] D_2O contained ~0·3% HDO. [b] Relative to the HDO absorption. [c] For a concentration DSS (7 mg)–D_2O (1 ml). [d] TMS (sealed) and TMS (open) stand for neat liquid TMS in a sealed off and an open coaxial cell respectively. [e] For a concentration $(CH_3)_4N^+Cl^-$ (7 mg)–H_2O (1 ml). [f] For a concentration TTP (200 mg)–D_2O (1 ml).

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