Tetrahedron. Vol. 30, pp. 1211 to 1213. Pergamon Press 1974. Printed in Great Britain

SOLUTES IN SULPHURIC ACID—V[a]

EFFECTS OF SUBSTITUENTS ON THE IONIZATION OF BENZENESULPHONIC ACIDS

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(*Received in the UK* 19 *October* 1973; *Accepted for publication November* 1973)

Abstract—The ionization of the three isomeric aniliniumsulphonic acids and *m*-trimethylammoniumbenzenesulphonic acid has been measured by UV techniques. The ionizations are governed by the benzophenone acidity function H_0^*. The ionization of the aniliniumsulphonic acids studied involves the oxygen bonded hydrogen. Substituent effects on the ionization are small ($\rho = 0{\cdot}7 \pm 0{\cdot}1$).

It was recently shown[1] that arenesulphonic acids ionize in aqueous sulphonic acid according to

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

In connection with our studies on the sulphonation of aromatic amines, it was of interest to study the ionization behaviour of arenesulphonic acids containing the strongly electron-withdrawing $-NH_3^+$ and $-NMe_3^+$ substituents.

Half-neutralization potentials of several arenesulphonic acids (including metanilic and sulphanilic acids) in aqueous alcoholic media have been estimated.[2] It was found that the acidities of the sulphonic acids follow the order predicted by the Hammett substituent constants.

The ionization of the aniliniumsulphonic acids in aqueous sulphuric acid was studied by the UV technique.[1] Absorption spectra in aqueous sulphuric acid ≤50 and ≥99·5% H_2SO_4 were taken to represent those of the aniliniumsulphonates and the aniliniumsulphonic acids respectively. The pK_a of the sulphonic acid ionization is defined by[3]

$$\log [BH]/[B^-] = -m \,.\, H_x + pK_a \qquad (2)$$

where BH and B$^-$ stand for $ArSO_3H$ and $ArSO_3^-$ respectively and *m* is the slope of the graph obtained by plotting log [BH]/[B$^-$] *vs* the acidity function H_x. For the acidity function that governs the sulphonic acid ionization *m* should be equal to unity. The [BH]/[B$^-$] ratios were obtained from the graphs of E/cd at an appropriately selected wavelength *vs* the appropriate acidity function. This type of graphs showed that there is a small medium effect on ϵ_{B^-} and no medium effect on ϵ_{BH}. A similar behaviour was observed with the arenesulphonic acids containing a neutral substituent. This is not unexpected, since the sulphonic acid medium effect on the B-band of the anilinium ion is small (Table 1), as was observed with benzene,[4] and it is virtually absent for the trimethylphenylammonium ion (Table 1). In order to obtain optimal accuracy, such wavelengths were selected that 1st the difference in ϵ of the unionized and the ionized forms is large and that 2nd the apparent medium effect on ϵ_{B^-} is minimal.† The selected wavelengths and the corresponding ϵ values for the sulphonic acid form in

Table 1. Spectra of ammonium ions

Compound	% H_2SO_4	λ_{max}, nm[a]			
$C_6H_5NH_3^+$	15·0	243·8 (101)	248·3 (136)	254·0 (166)	260·1 (127)
	99·65	243·1 (106)	247·2 (151)	253·0 (187)	259·2 (140)
$C_6H_5{-}NMe_3^+$ [5]	15·0	247·7 (172)	253·6 (228)	257·7 (225)	264·0 (158)
	80·0	247·6 (175)	253·5 (228)	257·6 (225)	263·9 (160)

[a] The data between brackets are the corresponding molar extinction coefficients expressed in l mol^{-1} cm^{-1}.

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[a] Part IV: *Rec. Trav. Chim.* **91**, 199 (1972).

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† Because of the medium effect on ϵ_{B^-}, the [BH]/[B$^-$] ratio and thus the estimated pK_a will depend somewhat on the wavelength employed. With e.g. metanilic acid the pK_a values for λ = 258, 264, 272 and 273 nm were found to be −7·03, −7·00, −7·04 and −7·09 respectively.

Table 2. Spectra and ionization of ammoniumbenzenesulphonic acids

	100% H_2SO_4 unionized sulphonic acid		15% H_2SO_4 sulphonate ion		pK_a determination				
					selected wavelength	ϵ			
Substituent	λ_{max}	ϵ_{max}	λ_{max}	ϵ_{max}	λ	100% H_2SO_4	15% H_2SO_4	m^a ($\pm$ 0·05)	$-H_0^a$ at half protonation
	B-band								
o-NH_3^+	259 (sh)	780	258 (sh)	360	272·5	830	140	0·94	7·5 ± 0·1
	264·4	1050	263·0	420					
	271·5	930	269·7	365					
m-NH_3^+	259 (sh)	590	258 (sh)	305	273·0	640	130	0·86	7·09 ± 0·05
	264·3	840	263·0	370					
	271·2	760	269·8	340					
p-NH_3^+	259 (sh)	800	258 (sh)	355	274·0	640	50	0·82	7·04 ± 0·05
	264·0	1140	263·5	420					
	271·2	1060	269·2	390					
m-NMe_3^+	258 (sh)	550	258 (sh)	280	274·0	310	50	0·80	7·23 ± 0·05
	264·0	750	262·5	310					
	271·2	710	269·4	250					

[a] $m = d(\log [BH]/[B^-])/d(-H_0^a)$.

100% H_2SO_4 and the sulphonate form in 15% H_2SO_4 are given in Table 2.

On plotting ϵ_λ against the common acidity functions H_0, H_0^a and H_A sigmoid curves were obtained. The graphs of $\log [BH]/[B^-]$ *vs* the acidity functions are linear. As judged from the m values, the most satisfactory correlation is obtained with H_0^a, the correlation with H_A is somewhat less and that with H_0 poor;* with e.g. sulphanilic acid for λ = 274 nm the m values for H_0^a, H_A and H_0 are 0·82, 0·70 and 0·51 respectively. Accordingly the ionization of the aniliumsulphonic acids in concentrated aqueous sulphuric acid involves the oxygen (and not the nitrogen) bonded hydrogen. The similarity in ionization behaviour of these sulphonic acids and m-trimethylammoniumbenzenesulphonic acid further substantiates this conclusion. The pK_a data based on H_0^a are collected in Table 3. The ionization of the nitrogen-bonded hydrogen in e.g. p-aniliniumsulphonate takes place at much lower acidities, its pK_a being 3·23.[12]

The graph of pK_a *vs* σ for the presently and previously[1] studied m- and p-substituted benzenesulphonic acids is linear (Fig 1), the ρ value being 0·7 ± 0·1. The σ value of a charged substituent is known to vary somewhat with the ionic strength of the medium;[13] the points for this type of substituents, however, do fall on the line defined by the neutral substituents. The σ value reported by Kreshkov *et al.* for p-NH_3^+ in the poorly solvating aqueous alcohol (= 0·84)[2] would lead to a strongly deviating point and does apparently not apply to our sulphuric acid system.

Table 3. pK_a of ammoniumbenzenesulphonic acids based on H_0^a

Substituent	$-$pK_a	σ
o-NH_3^+	7·5 ± 0·1	
m-NH_3^+	7·09 ± 0·05	0·64[10]
p-NH_3^+	7·04 ± 0·05	0·485[10]
m-NMe_3^+	7·23 ± 0·05	0·88[11]

The ionization behaviour of protonated phenylsulphamic acid in dilute aqueous sulphuric acid

$$Ar\text{-}NH_2^+\text{-}SO_3^- \rightleftharpoons Ar\text{-}NH\text{-}SO_3^- + H^+ \qquad (3)$$

differs from that of the isomeric aniliniumsulphonic acids in that equilibrium (3) is governed by the H_0 acidity function (m = 0·87).[14] Accordingly the protonation of phenylsulphamic acid occurs at nitrogen and not at oxygen. The pK_a based on H_0 was found to be $-$ 2·03 ± 0·05, a value close to that reported for the p-methoxy derivative.[15]

The pK_a's of the nitrobenzenesulphonic acids defy determination by the UV technique. With o-nitrobenzenesulphonic acid the spectral variation with varying sulphuric acid concentration is substantial,[1] but similar to that of nitrobenzene (in 15% H_2SO_4: λ_{max} = 268·8 nm, ϵ = 7300 whereas in 95·3% H_2SO_4: λ_{max} = 290·0 nm, ϵ = 3490[5]) indicating that the spectral variations of the sulphonic acid ionization are completely overshadowed by the spectral variations of the nitro-moiety, possibly as a result of variations in solvation. The spectral variations of m- and p-nitrobenzenesulphonic acid are both

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* H_0^a,[6] H_A[7,8] and H_0[9] are the benzophenone, the primary amide and primary aniline acidity function, respectively.

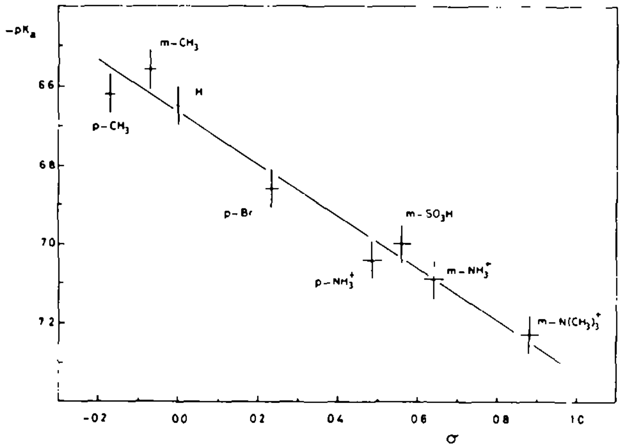

Fig 1. Correlation of $\mathrm{p}K_a$ with σ for arenesulphonic acids.

small as compared with the *o*-isomer (for the 250–280 nm region absorption: $\Delta\lambda_{max} \sim 2$ nm, $\Delta\epsilon_{max} < 4\%$; for the 208 nm absorption of the *meta*-isomer $\Delta\lambda = 0{\cdot}4$ nm, $\Delta\lambda_{max} \leq 4\%$). A similar failure to detect the sulphonic acid ionization by UV spectra was recently reported for the two naphthalene-monosulphonic acids.[16]

EXPERIMENTAL

The UV measurements were made with a Zeiss PMQ-3 and a Cary 14 spectrophotometer.

Sulphanilic acid (Fluka, puriss.) was recrystallized from aqueous alcohol. Orthanilic (Fluka, pract) and metanilic acid (Fluka, tech) were treated with charcoal and recrystallized several times from aqueous alcohol. *m*-Trimethylammoniumbenzenesulphonate was prepared from metanilic acid by methylation and purified by recrystallization from 95% ethanol.[17] The preparation of the potassium *o*-, *m*- and *p*-nitrobenzenesulphonates has been described previously.[1]

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