Equilibria and Nitration of Sulphonic Acids in Concentrated Sulphuric Acid

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Protonation equilibria of alkane- and arene-sulphonic acids in concentrated aqueous solutions of sulphuric acid have been investigated, and the pK_a values estimated using the M_c activity coefficient function. The reliability of the new values is discussed, since the results are found to disagree with the previous figures obtained by an acidity function procedure.

The equilibrium data have been applied to nitration studies of arenesulphonic acids reacting in an analogous medium. The $k_{2\text{obs}}$ and k_2° rate constants were estimated in connection, respectively, with the stoichiometric (rate = $k_{2\text{obs}}$[Aromatic]$_{\text{st}}$ [HNO_3]$_{\text{st}}$) and with the effective concentration of solutes (rate = k_2° [Aromatic][NO_2^+]).

In the range 40–90 wt% H_2SO_4, the k_2° rates are found to be independent of solvent effects. Above 90 wt% H_2SO_4, a large decrease is observed in the rates of nitration of benzenesulphonic acid compared with that of other substrates, so that the involvement of $PhSO_3^-\cdot NO_2^+$ ion-pair at high acidity is suggested.

Equilibria and nitration of phenyl sulphoxides have also been discussed, and it is suggested that it is the unprotonated species (*i.e.* $PhSO_3^-$,PhSOMe) that undergoes nitration.

The protonation equilibria of alkane- and arene-sulphonic acids as solutes and solvents in concentrated aqueous solutions have been extensively studied,[1–11] but the acid strength of many key compounds appears to be uncertain.[12,13] For instance, discrepancies are observed in the pK_a value of methanesulphonic acid, with a value of *ca.* −2 from Raman studies in aqueous solutions[5,8,11] and a value of *ca.* −6 from NMR studies, using CH_3SO_3H as the solute in concentrated sulphuric acid.[9]

The difference is surprisingly high and it is not clear to what extent it is related to different experimental techniques or to different data handling in calculations. Indeed in the study of indicators (B) undergoing protonation in concentrated acid solutions [equilibrium (1)], one has to obtain, using a correct procedure, a value with a thermodynamic significance. From a practical point of view it requires the evaluation of the activity coefficient term ($\log f_B f_{H^+}/f_{BH^+}$) which appears in the thermodynamic eqn. (2).

$$B + H^+ \rightleftharpoons BH^+ \qquad (1)$$

$$pK_{BH^+} = \log[BH^+]/[B] - \log[H^+] - \log f_B f_{H^+}/f_{BH^+} \qquad (2)$$

This subject has been extensively reviewed[12,14–17] and two approximations are now fundamentally followed for the description of equilibrium (1) in non-ideal solutions: a procedure using the Hammett acidity function[18] (H_x) [eqn. (3)] and another one using the M_c activity coefficient function[19] [eqn. (4)].

$$H_x = -\log a_{H^+} f_B/f_{BH^+};\ pK_{BH^+} = \log[BH^+]/[B] + H_x \qquad (3)$$

$$M_c = -\log f_B f_{H^+}/f_{BH^+}; pK_{BH^+} = \log[BH^+]/[B][H^+] + nM_c \qquad (4)$$

Both procedures have been widely exploited[11,14–21] and opposing conclusions have been drawn, supporting either one as the best available method.[11,12,20–23]

In the present paper the protonation equilibria of a number of sulphonic acids are re-investigated and a reliable estimate of their acid strengths is sought. The results are used in the study of nitration rates[24,25] in order to determine, for aromatic compounds of this class reacting in acid solutions, whether the anion ($PhSO_3^-$) or its uncharged parent acid ($PhSO_3H$) is the species which actually undergoes nitration.[25,26]

For comparison, analogous studies of related compounds are reported. Equilibria[27,28] and rate profiles[29,30] for phenyl sulphoxides were examined, as examples of sulphur compounds which are predominantly protonated ($\text{S=O} \rightleftharpoons \overset{+}{\text{S}} - \text{OH}$) in the nitration medium. Rate profiles for methyl phenyl sulphone[26,31] and dimethylphenylsulphonium methyl sulphate[32] were taken into account, since the free base ($-SO_2Me$) and the cationic species ($-\overset{+}{\text{S}}\text{Me}_2$) are nitration substrates (PhX) whose concentrations are unaffected by the medium acidity. The acidity dependence of the nitration of toluene, whose rate profile is available over a wide acidity range,[33–36] was also considered.

In this study $k_{2\text{obs}}$[25] and k_2°[31,37] rate constants were determined. These are related to the stoichiometric concentration of nitric acid and to the effective concentration of electrophilic species (NO_2^+) by eqns. (5) and (6) respectively. Eqn. (6a), rather than eqn. (6), was used in the study of aromatics with a basic substituent involved in a protonation equilibrium ($PhZ + H^+ \rightleftharpoons PhZH^+$), *e.g.* $ArSO_3H$.

$$\text{rate} = k_{2\text{obs}}[PhX]_{\text{st}}[HNO_3]_{\text{st}} \qquad (5)$$

$$\text{rate} = k_2^{\circ}[PhX][NO_2^+] \qquad (6)$$

$$\text{rate} = k_2^*[PhZ][NO_2^+] \qquad (6a)$$

The concentration of NO_2^+, experimentally available in the range 82–94 wt% H_2SO_4, has been estimated according to Raman,[21] UV[21] and ^{14}N NMR[38] studies of HNO_3 in H_2SO_4 [equilibrium (7)]. Outside this range of measurements the concentration of nitrating species was determined by eqn. (8).

$$HNO_3 + H^+ \rightleftharpoons H_2O + NO_2^+ \qquad (7)$$

$$\log[NO_2^+][H_2O]/[HNO_3][H^+] = pK_{NO_2^+} - n_{NO_2^+} M_c \qquad (8)$$

Table 1 Protonation equilibrium of benzenesulphonic acid[a] in aqueous sulphuric acid by UV spectroscopy at 25 °C: normalized extinction coefficients (ε_N)

wt% H_2SO_4	ε_N (224 nm)	ε_N (274 nm)	wt% H_2SO_4	ε_N (224 nm)	ε_N (274 nm)
20–35	0.00	0.00	81.31		33.86
42.56		1.44	81.35		34.35
49.97		1.43	81.85	45.83	
55.35		3.80	83.35		44.54
55.73	2.59		83.52	45.68	47.42
59.60		4.09	83.69	53.78	
59.61	3.60		85.33	63.30	59.54
59.74		3.62	85.35		52.66
63.80		5.67	85.52	60.60	
64.11	3.15		87.02	66.60	70.20
64.14		5.97	87.32		63.61
69.87	6.25	8.24	87.51	69.03	
69.92		8.76	88.82	78.82	
70.32		5.38	89.18	80.50	72.80
70.38	9.04		89.37	77.93	
72.00	8.85		89.38	79.50	
75.06	13.82	17.82	90.96		83.64
75.16		18.11	90.99		80.82
76.12		17.00	91.22	84.00	
76.40		22.81	93.59	92.70	
77.22		23.30	93.75	91.60	93.80
79.26		29.30	95.53	96.50	
79.61		31.26	98–99.5	100	100
79.81		30.70			

[a] Slope (n) and intercept (pK_a) estimated by eqn. 11 $n = 0.62$, $pK_a = -4.85$. From experimental data of refs. 7, 9 and 10 the estimated pK_a values are: $PhCH_2SO_3H$ (-2.1); CF_3SO_3H (-3.5); p-$MeC_6H_4SO_3H$ (-4.66); m-$MeC_6H_4SO_3H$ (-4.69); p-$BrC_6H_4SO_3H$ (-5.14); p-$SO_3^-C_6H_4SO_3H$ (-5.15); p-$\underset{+}{N}H_3C_6H_4SO_3H$ (-5.41); m-$\underset{+}{N}H_3C_6H_4SO_3H$ (-5.66).

Experimental

Equilibria.—The protonation equilibrium of benzenesulphonic acid in sulphuric acid has already been determined by solubility[1,2] and UV measurements,[7] and the dissociation constant estimated by H_0,H_0^{a} and H_A acidity function methods.[14–16]

Additional UV experimental data are now reported, using a procedure analogous to the one already described[11] and concentrations of aromatic between 10^{-4} and 10^{-5} mol dm^{-3}. Above 6–7 × 10^{-4} mol dm^{-3} a dependence of the molar extinction coefficients (ε) on aromatic concentrations is observed.

The ε values have been measured in the range 200–280 nm (*i.e.* at 200, 205, 220, 222, 224, 252, 260, 263, 270 and 274 nm) and the results at 224 and 274 nm are reported. At these selected wavelengths the same normalized titration curve (ε_N *vs.* sulphuric acid concentration)* is obtained (Table 1). This experimental trend allows us to avoid arbitrary assumptions related to the choice of the wavelength in a case where the effects of the medium on the spectra are observed. However, detectable uncertainties still affect the results (see Table 1) in spite of the accuracy of the measurements. The compound is 50% protonated at 84% H_2SO_4, in agreement with the previous estimation performed by UV measurements at 274 nm.[7]

In Table 1 the pK_a values of a number of alkane- and arenesulphonic acids, estimated by the M_c activity coefficient function, are given. Experimental ionization ratios from the literature have been used, by estimating from the relationship between log I and H_0,H_0^{a} or H_A,[7] or from the available figures.[7,9] Some uncertainty in the calculation is expected but it should not substantially affect the results, as it was tested in the case of benzenesulphonic acid for which both experimental and inferred data can be compared.

In Table 2 the normalized extinction coefficients (ε_N) of phenyl sulphoxides are listed. The measurements were performed in sulphuric acid by UV spectroscopy at the selected wavelengths already discussed,[27] where the spectral shifts due to the solvent appear to be minimal.

Kinetics.—Nitration rates of benzenesulphonic acid and dimethylphenylsulphonium methyl sulphate have been reported.[26,32] In order to minimize random as well as systematic errors, new kinetic runs were performed under the experimental conditions listed in Table 3. Rates k_2° and k_2^{*} were estimated using the experimental procedure reported in refs. 31 and 37.

Results and Discussion

The thermodynamic pK_{HA} value of methanesulphonic acid (HA), related to equilibrium (9) was found to range between -1.2 and -1.92.[5,6,8]

$$HA \rightleftharpoons H^+ + A^- \qquad (9)$$

The constant, described formally by eqn. (10), was practically

$$\log [HA]/[H^+][A^-] = pK_{HA} + \log f_{H^+}f_{A^-}/f_{HA} \qquad (10)$$

determined by extrapolating to infinite dilution in water the activity of solutes obtained in aqueous acid solutions between 0.4 and 4 mol dm^{-3} (*ca.* 4–32 wt% CH_3SO_3H).

A very similar value was found by plotting the concentration of solutes (log $[HA]/[H^+][A^-]$) *versus* the M_c activity coefficient function in CH_3SO_3H.[11] The experimental behaviour shows a linear relationship between 1 and 97 wt% CH_3SO_3H and an intercept whose value strongly supports the validity of the M_c procedure. However, this intercept is related to an apparent ionization constant (pK_a), as can be seen by rewriting eqn. (10) as eqn. (11), where $\log[HA]/[H^+][A^-] = \log (1 - \alpha)/\alpha^2 c$ and pK_a is the intercept (c is the stoichiometric molarity of acid and α the corresponding degree of dissociation determined in aqueous solutions by Raman measurements[11]).

$$\log [HA]/[H^+][A^-] = pK_a - n_a M_c \qquad (11)$$

It was of interest to test, by eqn. (11), the protonation equilibrium of methanesulphonic acid as solute in sulphuric acid. A plot of $[CH_3SO_3H]/[CH_3SO_3^-][H^+]$ *versus* M_c in H_2SO_4 gives a dissociation constant in agreement with the thermodynamic value [Fig. 1(*a*)] but in contrast with the previous one (*ca.* -6) based on the H_0^{a} acidity function.[9] The results, both obtained from the same experimental $[CH_3SO_3H]/[CH_3SO_3^-]$ ratios,[9] point out the rather serious anomalies arising from the application of acidity functions.

Attempts to measure the strength of nitric acid in different solvents by the M_c method again provide satisfactory results. The values derived from the degrees of dissociation of HNO_3 in water[20] and from the $[HNO_3]/[NO_3^-]$ ratios using HNO_3 as solute in sulphuric and perchloric acid[21] are in agreement with the corresponding thermodynamic pK_{HA}.

The results discussed above prompted us to estimate the strength of different sulphonic acids using the M_c procedure. The obtained values are given in Table 1 and the pK_a values plotted against the appropriate σ_I and σ constants of substituents[39] are shown in Fig. 1(*b*) and Fig. 1(*c*).

For aromatic derivatives the influence of substituents on pK_a is not very large (ρ *ca.* 1) and comparable to the effect of

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* ε_N represents the percentage of the substrate present as either its protonated or unprotonated form, as calculated from the measured extinction coefficients at each acid concentration.

Table 2 Protonation equilibria of phenyl sulphoxides in aqueous sulphuric acid by UV spectroscopy at 25 °C: normalized extinction coefficients (ε_N)

Compound	wt% H_2SO_4	ε_N	wt% H_2SO_4	ε_N
p-MeC$_6$H$_4$SOMe[a]	5–10	100	46.09	60.62
	15.25	98.25	47.89	56.27
	20.37	97.05	51.12	43.60
	25.57	90.72	52.82	36.47
	30.50	86.75	53.85	32.50
	35.75	81.22	59.50	15.47
	41.03	72.12	61.25	13.10
	43.34	65.37	71–84	0.00
PhSOMe[b]	5–10	100	53.71	50.68
	14.71	98.20	54.89	46.88
	14.71	98.60	55.04	45.60
	20.07	97.04	57.07	36.88
	20.07	97.40	57.10	37.76
	20.58	97.88	58.93	30.16
	29.74	90.96	60.28	27.52
	35.41	85.28	61.08	23.32
	41.04	78.44	62.35	26.28
	41.18	78.56	63.56	21.80
	42.97	74.24	63.79	22.08
	45.00	70.08	64.79	13.48
	46.89	64.16	67.22	15.28
	50.03	60.00	69.62	5.88
	50.58	57.52	72.28	3.16
	51.92	54.68	73.16	2.08
	52.52	53.72	78–85	0.00
	52.58	50.52		
m-NO$_2$C$_6$H$_4$SOMe[c]	10–30	0.00	61.56	67.80
	35.88	5.07	63.80	79.81
	40.67	8.22	64.45	81.71
	45.80	17.91	67.69	88.85
	49.59	27.92	70.16	93.11
	51.79	36.10	77.93	98.82
	55.18	46.65	78.36	99.46
	56.96	55.11	83–92	100
	59.59	64.02		
p-NO$_2$C$_6$H$_4$SOMe[d]	10–20	0.00	64.30	52.11
	30.38	1.62	66.92	63.25
	35.85	4.46	68.78	70.75
	40.79	7.07	70.08	73.09
	46.35	10.43	71.72	79.31
	51.79	15.06	74.85	91.72
	56.91	24.14	77.93	95.35
	58.36	29.07	82.78	97.94
	61.45	41.76	88.91	100
	63.96	51.33		
p-MeC$_6$H$_4$SOPh[e]	5–25	100	63.56	43.11
	30.50	97.38	66.16	29.93
	35.82	95.83	67.29	26.87
	41.03	94.31	69.52	20.12
	46.09	86.63	70.62	15.21
	51.12	79.28	72.69	12.15
	56.54	65.50	76.76	7.86
	56.87	66.41	78.62	4.49
	61.25	51.09	79.55	2.03
	62.03	48.02	85–91	0.0
PhSOPh[f]	5–15	100	68.75	41.14
	25.72	99.64	70.16	34.69
	41.18	97.85	72.26	27.50
	52.37	86.35	74.27	23.92
	55.07	81.70	77.93	16.02
	57.06	78.83	82.40	9.56
	62.30	62.67	88.26	2.02
	63.77	59.44	94.42	0.58
	65.09	52.27	96–98	0.00
	67.23	43.29		
m-NO$_2$C$_6$H$_4$SOPh[g]	2–20	0.00	69.89	54.58
	30.58	0.62	70.38	59.33
	35.88	1.22	71.48	65.25
	40.68	1.20	72.09	67.60
	41.04	1.20	72.65	71.19
	44.89	2.40	73.05	75.35
	46.30	2.99	73.16	76.53
	50.58	5.35	74.87	80.70
	51.48	7.14	74.88	80.08
	57.10	13.08	76.86	85.42
	61.53	21.37	76.89	87.79
	63.56	27.89	78.46	93.12
	66.75	39.77	81.64	96.09
	67.34	42.14	81.67	96.20
	68.02	46.87	83.12	97.27
	68.89	52.21	88–95	100
p-NO$_2$C$_6$H$_4$SOPh[h]	20–40	0.00	72.34	59.45
	46.85	1.91	74.27	66.39
	51.82	4.62	74.85	70.25
	57.07	10.78	77.93	77.98
	62.43	19.28	78.49	84.95
	63.71	20.83	82.39	88.95
	65.09	28.55	84.87	93.82
	67.26	38.60	87.85	96.40
	68.75	44.39	90.30	99.22
	70.16	50.18	94–97	100

Wavelength employed (nm), n, pK_a [from eqn. (11)], wt% H_2SO_4 at half-protonation: [a] 219, 0.60, −2.29, 49.5; [b] 214, 0.58, −2.45, 53.5; [c] 213, 0.76, − 3.17, 56; [d] 257, 0.61, −3.25, 63.5; [e] 235, 0.59, −2.98, 61.5; [f] 229, 0.52, − 3.09, 66; [g] 248, 0.66, −3.75, 68.5; [h] 265, 0.62, −3.79, 70.

Table 3 Second-order rate coefficients (k_2/dm^3 mol^{-1} s^{-1}) for nitration in aqueous sulphuric acid at 25 °C

Compound	wt% H_2SO_4	log k_{2obs}[a]	wt% H_2SO_4	log k_{2obs}[a]
PhSO$_3$H[b]	76.20	−3.460	89.65	0.655
	79.34	−2.222	90.51	0.621
	81.58	−1.437	93.37	0.218
	83.48	−0.742	94.14	0.002
	85.36	−0.080	94.41	−0.075
	86.95	0.409	96.41	−0.395
	89.14	0.605	97.56	−0.637
	89.17	0.609	98.47	−0.748
PhS(Me)$_2{}^+$CH$_3$SO$_4{}^-$[c]	84.10	−3.897	90.32	−2.543
	85.29	−3.505	90.97	−2.541
	85.44	−3.438	91.48	−2.554
	86.40	−3.144	91.75	−2.563
	87.30	−2.950	92.32	−2.613
	88.24	−2.709	92.73	−2.598
	88.43	−2.733	95.58	−2.702
	89.84	−2.535	95.90	−2.714
	89.98	−2.522	96.56	−2.736

[a] Estimated percentage of standard error 2.5–3%. [b] [Aromatic] = 10^{-4}–10^{-3} mol dm^{-3}; [HNO$_3$] = 10^{-4}–10^{-1} mol dm^{-3}. [c] [Aromatic] = 10^{-4} mol dm^{-3}; [HNO$_3$] = 10^{-2}–10^{-1} mol dm^{-3}.

substituents in the ring on the pK_a values of methyl phenyl (ρ *ca.* 1) and diphenyl sulphoxides (ρ *ca.* 0.9) (Fig. 2).

Also of interest are the linear relationships of pK_a *versus* σ_I and HNP *versus* pK_a (HNP = half-neutralization potential[40]) observed, respectively, for alkane-sulphonic acids and methyl phenyl sulphoxides. They also suggest the new pK_a, as estimated by the M_c procedure, to be reasonable. For instance

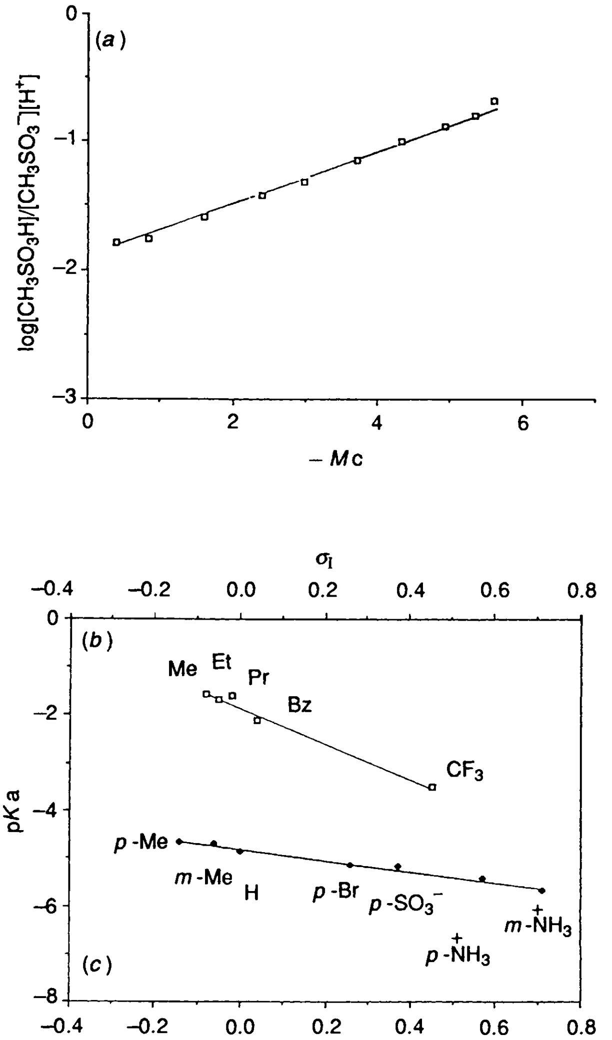

Fig. 1 Equilibria of sulphonic acids in sulphuric acid: (*a*) log $[CH_3SO_3H]/[CH_3SO_3^-][H^+]$ *vs.* M_c. Experimental ratios from ref. 9 by NMR in H_2SO_4. (*b*) Dependence of dissociation constants on σ_I of alkane sulphonic acids (Y-SO_3H), (slope *ca.* 3.80). Y = Me, Et, Pr: Thermodynamic pK_{HA} from refs. 8 and 11 by Raman and NMR in H_2O. Y = Bz, CF_3: pK_a Estimated by eqn. (11). Experimental data from ref. 9 by NMR in H_2SO_4. (*c*) Dependence of dissociation constants on σ of arene sulphonic acids (X-$C_6H_4SO_3H$), (slope *ca.* 1). pK_a estimated by eqn. (11). Experimental data from refs. 7, 9, and 10 and from this work, by NMR and UV in H_2SO_4.

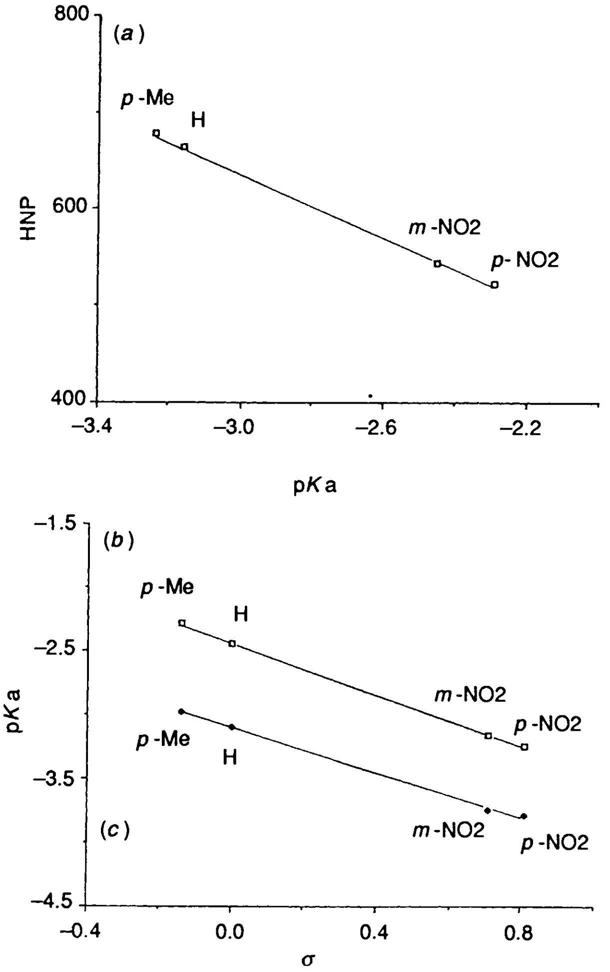

Fig. 2 Equilibria of sulphoxides in sulphuric acid: (*a*) HNP *vs.* pK_a of methyl phenyl sulphoxides (XC_6H_4SOMe). (*b*) pK_a *vs.* σ of methyl phenyl sulphoxides (XC_6H_4SOMe) (slope *ca.* 1). (*c*) pK_a vs. σ of diaryl sulphoxides (XC_6H_4SOPh) (slope *ca.* 0.9). pK_a estimated by eqn. (11). Experimental data from this work, by UV in H_2SO_4. HNP values from ref. 40.

CH_3SO_3H and $PhSO_3H$ exhibit very different pK_a values (−2, −4.85) as expected from their different structure but similar values (−6, −6.65) were found[7,9] by the acidity function procedure.

The aromatic sulphonic acid with one site for removal or addition of a proton, can react with electrophilic species in acidic media *via* the most reactive form ($PhSO_3^-$) or the predominant protonated form depending on the reaction conditions. The nitration of these compounds in sulphuric acid is reported here and the rate profiles obtained from eqn. (5) are shown in Fig. 3 together with the profiles of some related compounds (*i.e.* PhSOMe, $PhSO_2Me$, $Ph\overset{+}{S}Me_2$) undergoing nitration in the same acid solutions.

There is evidence that the dependence of k_{2obs} on the sulphuric acid concentration cannot help in determining the reacting species of the substrates, since ions and neutral species behave similarly.[25,41] For instance, in the range 50–90% H_2SO_4 a large solvent effect is observed on rates; between 80 and 100 wt% a different dependence of rates upon acidity is found below and above 90 wt% H_2SO_4, for all the investigated compounds.[25]

A different picture of aromatic nitration under acidic condition was obtained by taking into account the actual concentrations of reacting species. Indeed, the results in Fig. 4 show that: (*a*) in the range below 90wt% H_2SO_4 the rate profiles obtained by eqns. (6) or (6a) are practically independent of the medium acidity; (*b*) k_2^* of arenesulphonic acids and sulphoxides, related respectively to SO_3^- and SO groups, behaves as k_2° of nitration substrates whose concentrations are unaffected by protonation. This behaviour suggests that essentially unprotonated species undergo nitration.

In Fig. 5 rates of different aromatics are compared. It appears that k_2° (and/or k_2^*) rates are directly related to one another when $-SO_3^-$, $-\overset{+}{N}Me_3$ and −OMe groups, as substituents of analogous compounds ($Ph[CH_2]_nX$), are taken into account. Likewise, rates for monosubstituted *versus* those for *para*-disubstituted $\overset{+}{N}Me_3$, $\overset{+}{N}H_3$ and $\overset{+}{S}Me_2$ derivatives satisfy a linear relationship.

A linear relationship between k_2° values has also been reported[49] for the comparison of analogous compounds, undergoing nitration in different acids (*i.e.* H_2SO_4, $HClO_4$,

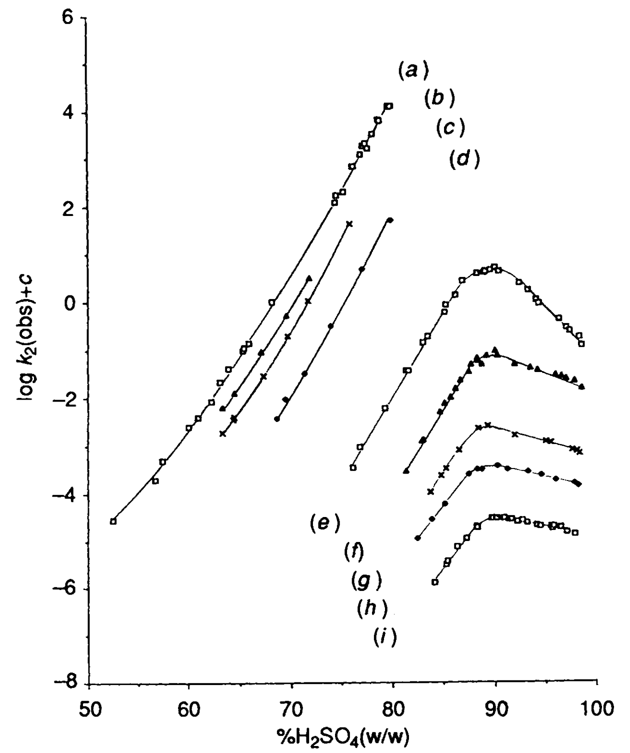

Fig. 3 Rate profiles for nitration in aqueous sulphuric acid at 25 °C. log k_{2obs} vs. wt% H_2SO_4 (*a*) PhMe; (*b*) $Ph[CH_2]_3SO_3H$; (*c*) $Ph[CH_2]_2SO_3H$; (*d*) $PhCH_2SO_3H$; (*e*) $PhSO_3H$; (*f*) $PhSO_2Me$; (*g*) PhSOPh ($C = -1$); (*h*) PhSOMe ($C = -1$); (*i*) $Ph\overset{+}{S}(Me)_2$ ($C = -2$). (Experimental data for (*a*) from refs. 33–36; (*b*), (*c*), (*d*) from ref. 26; (*e*) from ref. 26 and this work; (*f*) from refs. 26 and 31; (*g*) from ref. 29; (*h*) from ref. 30; (*i*) from ref. 32 and this work).

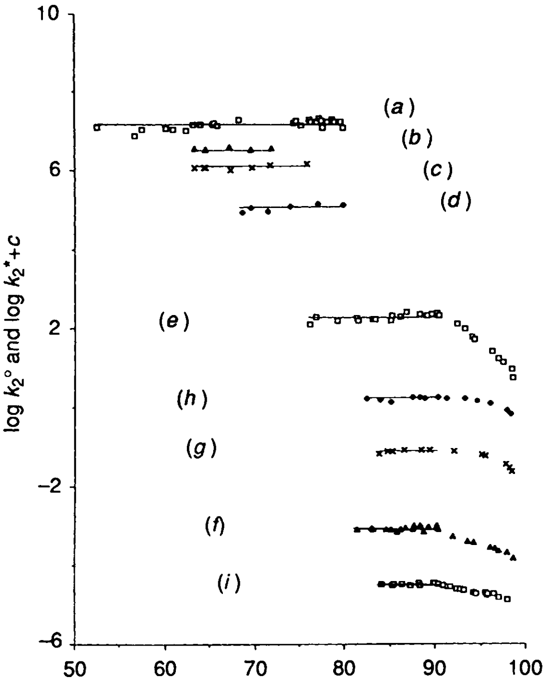

Fig. 4 Rate profiles for nitration in aqueous sulphuric acid at 25 °C. log k_2° vs. wt% H_2SO_4 (*a*) PhMe (*b*) $Ph(CH_2)_3SO_3H$; (*c*) $Ph(CH_2)_2SO_3H$; (*f*) $PhSO_2Me$ ($C = -2$); (*i*) $Ph\overset{+}{S}(Me)_2$ ($C = -2$). log k_2* vs. wt% H_2SO_4. (*d*) $PhCH_2SO_3H$; (*e*) $PhSO_3H$ ($C = 1$); (*g*) PhSOPh ($C = -1$); (*h*) PhSOMe. Experimental nitration rates from refs. as in Fig. 3. Experimental equilibrium data for (*d*) from ref. 9; (*e*), (*g*), (*h*) from this work. Parameters (n, pK_a) estimated by eqn. (11).

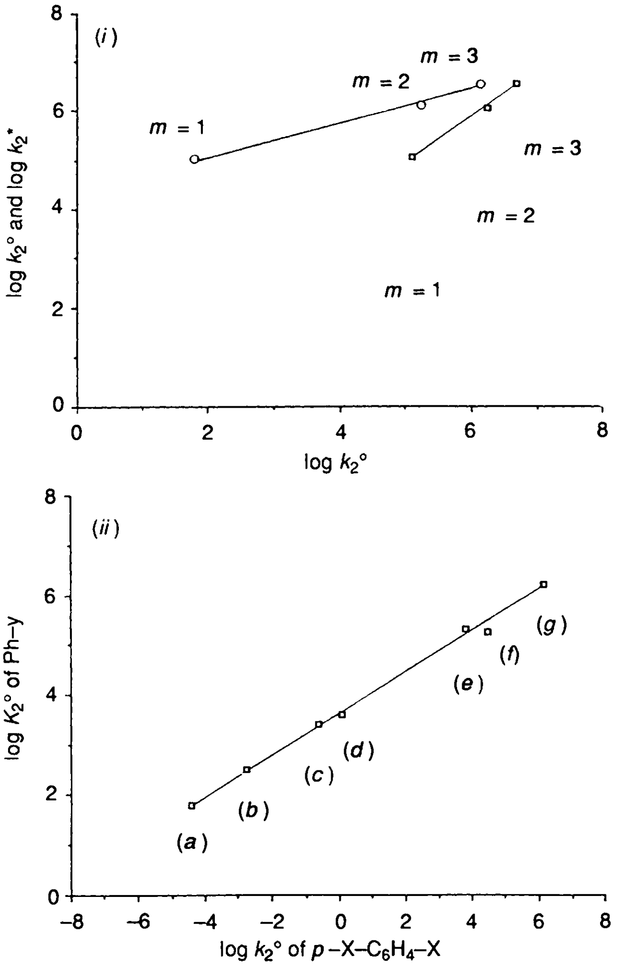

Fig. 5 Nitration of aromatic compounds in aqueous sulphuric acid: (i) (○) log k_2° and log k_2* of $Ph(CH_2)_mSO_3H$ vs. log k_2° of $Ph(CH_2)_m\overset{+}{N}Me_3$. Experimental data from refs. 26, 42 and 43. (□) log k_2° and log k_2* of $Ph(CH_2)_mSO_3H$ vs. log k_2° of $Ph(CH_2)_mOMe$. Experimental data from refs. 26 and 44. (ii) log k_2° of PhY vs. log k_2° of p-XC_6H_4X: (*a*) $Y = X = CH_2\overset{+}{N}Me_3$; (*b*) $Y = X = CH_2\overset{+}{S}Me_2$; (*c*) $Y = X = CH_2\overset{+}{N}H_2Me$; (*d*) $Y = X = CH_2\overset{+}{N}H_3$; (*e*) $Y = X = (CH_2)_2\overset{+}{S}Me_2$; (*f*) $Y = (CH_2)_2\overset{+}{N}Me_3$, $X = [CH_2]_2\overset{+}{N}H_3$; (*g*) $Y = X = (CH_2)_3\overset{+}{N}Me_3$. Experimental data from refs. 42, 43, 45–48.

CF_3SO_3H). This also holds in comparing nitration in aqueous acid media (*i.e.* H_2SO_4) with the gas phase.[49,50]

The large decrease in the rate of nitration of benzenesulphonic acid above 90wt% (Fig. 3), where nitric acid is entirely converted into nitronium ion,[21,38] is worthy of some interest. This does not happen to the same extent for all the other sulphur compounds studied. A very similar trend appears in Fig. 4 where rate profiles corrected for the actual concentrations of NO_2^+ and aromatic [eqn. (6) and (6a)] are shown.

It has been suggested that, at high acidity, interactions between ions,[51] giving $HSO_4^-NO_2^+$ ion pairs, affect the dissociation process of electrophilic species, with a decrease in rate for all substrates. If this is true, additional interactions, *i.e.* $PhSO_3^-NO_2^+$, are to be expected for benzenesulphonic acid, since the reacting species is a base with a negative charge ($PhSO_3^-$).

Also, Raman studies of equilibria in H_2SO_4[52] and CF_3SO_3H[53] (HA) support the involvement of $A^-H_3O^+$ in very concentrated aqueous solutions of the solvents. Similarly, they support the involvement of $CF_3SO_3^-NO_2^+$; $CF_3SO_3^-H_3O^+$ in CF_3SO_3H–H_2O–HNO_3 mixtures, with nitric acid as solute in concentrated acid solutions.[54,55]

It is noteworthy that the correction previously suggested[56] for k_{2obs}, by using the activity coefficients of aromatics, gives results inconsistent with the expected trend of $k_2°$. For instance, the new plots for nitrobenzene and *o*-chloronitrobenze, clearly show, above 90%, that rates increase by a factor of 3–4 for increasing acidity, instead of reaching a constant value.

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Paper 1/01132D
Received 11*th March* 1991
Accepted 10*th June* 1991