Thermodynamic Nitration Rates of Aromatic Compounds. Part 3. Nitration of Aromatic Compounds in Concentrated Aqueous Trifluoromethanesulphonic Acid

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The kinetics of nitration of mesitylene, toluene, benzene, bromobenzene and methyl phenyl sulphone, reacting as free bases in the range 50–100 wt% CF_3SO_3H are reported. The rates, related both to the stoichiometric concentration of nitric acid (rate = $k_{2obs}[Ar][HNO_3]$) and to the effective concentration of electrophilic species (rate = $k_2°[Ar][NO_2^+]$) have been determined. Compared with k_{2obs}, which exhibits a large solvent effect, the true nitration rates ($k_2°$) were found to be almost independent of medium acidity and, for a given compound, rather similar in different acids. The $k_2°$ values were also found to be linearly related to the rate constants for nitration in the gas phase.

The rates of reaction for methyl phenyl sulphone in 80–100 wt% acid were found to be lower in CF_3SO_3H than in H_2SO_4 by a factor of 8. A similar rate profile is observed, however, with an increase up to 90% acid and a decrease between 90 and 100%. The dependence of the rate profiles upon acidity and temperature in very concentrated acid solutions is discussed.

Nitric acid in aqueous trifluoromethanesulphonic acid (TFMSA) appears to be a good nitrating system for aromatic compounds because of its high yield and selectivity,[1–3] but the subject has not to date been exhaustively investigated. In the present paper the nitration of aromatic compounds in TFMSA is studied, and we report on the rate profiles for some key compounds reacting as free bases, namely mesitylene, toluene, benzene and bromobenzene in the range <90 wt% CF_3SO_3H, and methyl phenyl sulphone in the range 80–100 wt% CF_3SO_3H.

As in other acidic media, second-order kinetics were found to hold, and rate coefficients related to stoichiometric concentrations of reagents by eqn. (1) were determined. Plots of the

$$\text{rate} = k_{2obs}[Ar]_{st}[HNO_3]_{st} \qquad (1)$$

observed rate constant (k_{2obs}) *versus* medium composition allow a comparison with the kinetics of nitration of other compounds, as described in the literature.[4–7]

Besides the conventional description of the reaction by k_{2obs}, the estimation of the different species involved in the kinetic process seems to be a good starting point for a sound comparison of nitration in different media. Accordingly, we have investigated the dissociation of CF_3SO_3H–H_2O mixtures [equilibrium (2)] between 1–100 wt% CF_3SO_3H[8] and data for equilibrium (3) have also been obtained by studying HNO_3–CF_3SO_3H–H_2O mixtures in the range 80–100 wt% CF_3SO_3H.[9]

$$CF_3SO_3H + H_2O \rightleftharpoons CF_3SO_3^- + H_3O^+ \qquad (2)$$

$$CF_3SO_3H + HNO_3 \rightleftharpoons NO_2^+ + CF_3SO_3^- + H_2O \qquad (3)$$

The results show that the acid-catalysed process for the formation of NO_2^+ is analogous to that observed in H_2SO_4[10] and this is essentially due to the fact that both H_2SO_4 and TFMSA are substantially stronger acids than HNO_3.[11] This suggests the effectiveness of NO_2^+ as a nitrating species[1–3,9,12] so that the 'true' rate constants ($k_2°$), written as in eqn. (4),[13] can be determined using the procedure already described for nitrations in sulphuric acid.[14]

$$\text{rate} = k_2°[Ar][NO_2^+] \qquad (4)$$

Our interest in studying the nitration process in TFMSA concerns some theoretical and practical topics and, in particular, the different solvent dependence of k_{2obs} in dilute and concentrated aqueous strong acids. For example, the profiles of the observed rate constants *vs.* the medium composition in H_2SO_4 show a large increase up to 90 wt% H_2SO_4 and a small decrease in 90–100 wt% H_2SO_4.[4–7] Whereas the equilibrium analogous to equilibrium (3) accounts for the large increase, different explanations have been suggested for the behaviour above 90 wt% H_2SO_4[4,15–19] where the ionization of HNO_3 to NO_2^+ is virtually complete. A comparison with the corresponding behaviour in CF_3SO_3H–H_2O mixtures can help to distinguish whether a change in rate-determining step (or other causes) are responsible. From a practical point of view the effectiveness of TFMSA appears to be useful in the nitration of compounds which, in concentrated sulphuric acid, may undergo undesirable side-reactions.[7]

A further goal of this work is to determine the $k_2°$ rate coefficients of nitration which appear in eqn. (4), in order to separate the solvent effect in equilibrium (3) from the solvent effect on the kinetics of nitration. Indeed, the solvent dependence of k_{2obs} is usually very large and, *e.g.*, between 50 and 80 wt% H_2SO_4 the rate of anisole nitration increases by a factor[20–22] of 10^{12}, and the rate of toluene nitration by a factor[22–25] of 10^9.

The present study shows that the $k_2°$ profiles of aromatics reacting as free bases are almost invariant with the medium acidity in the nitrating ranges <90 wt% H_2SO_4 and CF_3SO_3H. Moreover, the $k_2°$ rates in aqueous acid solutions are linearly related to kinetic data of analogous compounds nitrated in the gas phase.[26] The latter observation shows the reliability of the procedure reported in the present work.

Experimental

Materials.—Aromatic substrates and TFMSA were fractionally distilled from the commercially available products (99%) and samples obtained by several distillations were used. Nitric acid was distilled from concentrated sulphuric acid (1:2 v/v) and the purified material stored at −50 °C. The acid solutions

Table 1 Second-order rate constant (k_{2obs}/dm^3 mol^{-1} s^{-1}) for nitration in aqueous trifluoromethanesulphonic acid at 25 °C

CF_3SO_3H (wt%)	Mole fraction (N)	log k_{2obs}	[Ar]/10^{-3} mol dm^{-3}	[HNO_3]/10^{-3} mol dm^{-3}
Mesitylene				
63.55	0.173	−3.18	0.144	138
65.09	0.183	−2.77	0.862	133
68.12	0.204	−1.88	0.378	39
68.12	0.204	−1.97	0.224	39
71.30	0.229	−1.22	0.179	16
Toluene				
65.48	0.185	−3.71	0.248	367
66.47	0.192	−3.47	1.212	270
70.53	0.223	−2.19	0.388	63
70.59	0.224	−2.18	0.389	63
72.19	0.237	−1.67	0.195	19
74.92	0.264	−0.53	0.180	18
Benzene				
70.62	0.224	−3.61	0.546	78
72.02	0.236	−3.04	0.635	122
74.98	0.265	−1.90	0.483	48
77.91	0.297	−0.63	0.512	83
77.91	0.297	−0.70	0.375	2
Bromobenzene				
74.99	0.265	−3.20	0.367	122
78.03	0.299	−1.89	0.292	94
80.03	0.325	−0.93	0.407	98
80.03	0.325	−1.05	0.066	6
83.42	0.376	0.65	0.717	0.7
Methyl phenyl sulphone				
86.14	0.427	−4.17	52	47
87.32	0.453	−3.78	46	50
87.89	0.465	−3.39	37	37
87.97	0.467	−3.44	30	31
88.59	0.482	−3.22	23	692
89.21	0.498	−2.76	2	623
89.46	0.505	−2.53	2	174
90.17	0.524	−2.30	1	158
91.14	0.552	−1.81	3	3
91.54	0.565	−1.89	8	8
91.54	0.565	−1.86	7	7
91.65 (91.52)[a]	0.569 (0.564)[a]	−2.02	0.5	110
94.09 (94.03)	0.656 (0.654)	−2.04	0.4	38
94.10 (94.02)	0.657 (0.654)	−2.07	0.2	16
96.04 (95.92)	0.744 (0.739)	−2.18	0.6	64
98.11 (97.94)	0.862 (0.851)	−2.26	0.8	77
99.03 (98.83)	0.924 (0.910)	−2.37	0.8	81
99.61 (99.26)	0.969 (0.942)	−2.40	1.0	129
100. (99.75)	1.0 (0.980)	−2.43	0.9	217
100. (99.81)	1.0 (0.984)	−2.45	0.9	156
100. (99.86)	1.0 (0.989)	−2.48	1.0	100
100. (99.92)	1.0 (0.994)	−2.52	0.7	35

[a] Values in parentheses are corrected for added HNO_3.

for kinetic runs were prepared by mixing distilled water and TFMSA. The percentage composition was selected by weighing and checked by automatic potentiometric titration against a standard solution of sodium hydroxide. The procedure has already been described elsewhere.[19]

Kinetic Studies.—Separate solutions of aromatic and nitric acid in TFMSA of appropriate concentration were prepared using weighed samples of solvent and reagents. A small volume of the aromatic solution was transferred by micrometric syringe, at $t = 0$, to an optical cell containing a weighed sample of nitric acid in TFMSA. The cell was kept at the fixed temperature by a digital thermostat, and the change of absorbance with time at selected wavelengths was followed. In data treatment, literature density values of CF_3SO_3H–H_2O mixtures[27–29] have been used together with the more reliable value of 1.6989 g cm^{-3} for the pure TFMSA. This value was obtained at 25 °C, and used in the recent study of the TFMSA dissociation.[8,9]

Second-order rate coefficients have been determined by eqn. (1), using either excess nitric acid, or equimolar concentrations of nitric acid and aromatic. The observed rate constants obtained in CF_3SO_3H at 25 °C for mesitylene, toluene, benzene, bromobenzene and methyl phenyl sulphone are reported in Table 1.

Nitration rates in sulphuric and perchloric acid are also given in Table 2 in order to extend the range of literature data for mesitylene, toluene and methyl phenyl sulphone,[19,22–25,30–32] and/or improve their reliability. Mesitylene was nitrated in acid solutions with added acetic acid (*ca.* 10^{-3} mol dm^{-3}). As

Table 2a Second-order rate constants (k_{2obs}/dm^3 mol^{-1} s^{-1}) for nitration in aqueous sulphuric acid at 25 °C

H_2SO_4 (wt%)	Mole fraction (N)	log k_{2obs}	[Ar]/ 10^{-3} mol dm^{-3}	[HNO_3]/ 10^{-3} mol dm^{-3}
Mesitylene[a]				
58.29	0.204	−2.42	3.60	25
59.51	0.213	−2.09	1.91	39
62.65	0.235	−1.27	1.64	34
62.65	0.235	−1.35	1.64	37
65.16	0.256	−0.60	1.33	2.7
69.84	0.298	0.74	3.63	0.9
69.84	0.298	0.66	3.63	0.5
71.92	0.320	1.40	1.67	0.3
Methyl phenyl sulphone				
81.40	0.446	−3.53	1.09	535
81.40	0.446	−3.57	0.27	625
82.99	0.472	−2.89	0.16	139
84.69	0.504	−2.30	0.18	99
85.82	0.526	−2.00	0.30	33
87.74	0.568	−1.32	0.30	27
88.49	0.585	−1.24	0.28	8
89.37	0.607	−1.15	0.28	9
90.38	0.633	−1.15	0.26	8
90.38	0.633	−1.19	0.26	9
95.70	0.803	−1.60	0.22	11
96.66	0.842	−1.69	0.30	26
97.86	0.894	−1.87	0.30	34

[a] With added acetic acid (10^{-4}–10^{-3} mol dm^{-3}).

Table 2b Second-order rate constants (k_{2obs}/dm^3 mol^{-1} s^{-1}) for nitration in aqueous perchloric acid at 25 °C

H_2SO_4 (wt%)	Mole fraction (N)	log k_{2obs}	[Ar]/ 10^{-3} mol dm^{-3}	[HNO_3]/ 10^{-3} mol dm^{-3}
Mesitylene[a]				
55.53	0.183	−1.31	0.836	53
55.53	0.183	−1.26	0.836	22
56.21	0.187	−1.17	2.11	56
56.21	0.187	−1.11	0.200	26
57.63	0.202	−0.59	1.93	10
58.88	0.204	−0.17	2.61	7
58.88	0.204	−0.18	2.61	4
59.70	0.210	0.07	5.47	0.3
60.17	0.213	0.24	9.86	0.6
60.17	0.213	0.29	0.79	0.5
60.17	0.213	0.28	0.79	0.4
61.15	0.220	0.71	0.2	0.3
61.15	0.220	0.71	0.2	0.2
Toluene				
57.29	0.193	−1.46	0.17	5.3
57.35	0.194	−1.48	0.16	4.8
58.05	0.199	−1.16	0.08	8.9
59.18	0.206	−0.70	0.16	7.2
60.31	0.214	−0.24	0.09	1.8
60.38	0.215	−0.19	0.08	1.5
60.59	0.216	−0.12	0.08	1.0
60.84	0.218	0.00	0.1	1.2
61.51	0.223	0.29	0.09	7.8
61.51	0.223	0.24	0.14	2.6

[a] With added acetic acid (10^{-4}–10^{-3} mol dm^{-3}).

Table 3 The dependence upon temperature of the nitration rates of methyl phenyl sulphone

T/°C	CF_3SO_3H (wt%)	Mole fraction (N)	log k_{2obs}
25	91.92	0.577	−1.94[a]
40	91.92	0.577	−1.48
50	91.92	0.577	−1.17
55	91.92	0.577	−1.03
25	99.63	0.970	−2.44
40	99.63	0.970	−1.81
50	99.63	0.970	−1.41
55	99.63	0.970	−1.23
T/°C	**H_2SO_4 (wt%)**	**Mole fraction (N)**	**log k_{2obs}**
25	88.41	0.584	−1.10[a]
40	88.41	0.584	−0.68
50	88.41	0.584	−0.42
55	88.41	0.584	−0.31
25	99.27	0.961	−1.92
40	99.27	0.961	−1.28
40	99.27	0.961	−1.27
50	99.27	0.961	−0.89
50	99.27	0.961	−0.87
55	99.27	0.961	−0.72
55	99.27	0.961	−0.74

[a] At *ca.* 90% where the degree of conversion of HNO_3 into NO_2^+ is 50%, the condition $k_{2obs} = k_2^\circ$ is verified.

discussed previously[33] this addition increases the solubility of the aromatic without affecting the rate values.

The dependence on temperature of the rates of nitration of methyl phenyl sulphone, and the variation of this dependence with acidity in CF_3SO_3H and H_2SO_4 is shown in Table 3.

Protonation Studies.—In order to test the protonation range of methyl phenyl sulphone, UV spectra at different acidities were recorded. The UV spectra were found to be in agreement with literature data[34] and practically coincident, both at low (*ca.* 50 wt%) and high acidities (*ca.* 100 wt% CF_3SO_3H). Therefore we can surmise that the methyl phenyl sulphone is not protonated in the acidity range where the nitration rates are measured.

Preliminary measurements show that mesitylene in pure CF_3SO_3H develops an intense red colour and absorbance peaks at *ca.* 275, 320 and 355 nm, as well as a slow variation with time. The behaviour is similar to that observed in fluoridric acid[35] and suggests that the compound undergoes a protonation and an unknown reaction. No spectral changes are observed in CF_3SO_3–H_2O mixtures until 75 wt% CF_3SO_3H, so that at lower acidities mesitylene can react only as a free base.

For the values of p$K_{NO_2^+}$, $n_{NO_2^+}$ and Mc in H_2SO_4, we refer to ref. 14; the same values are used in $HClO_4$. From preliminary data in CF_3SO_3H the parameters of equilibrium (3) have been derived: p$K_{NO_2^+} = -17.3$, $n_{NO_2^+} = 3.02$. The coefficients of the polynominal expansion of Mc in CF_3SO_3H [eqn. (10) of ref. 14] are: $a_1 = -0.039$, $a_2 = 0.166$, $a_3 = -0.227$, $a_4 = -0.0029, a_5 = 9.7 \times 10^{-4}, a_6 = -2.4 \times 10^{-5}, a_7 = 8.1 \times 10^{-6}$, $a_8 = 4.8 \times 10^{-7}$.

Product Studies.—The products of nitration of toluene,[25] bromobenzene[36,37] and methyl phenyl sulphone[32] in sulphuric acid are well known. Analogous studies in TFMSA are now reported using the procedure described in ref. 25. Analysis by GLC showed the isomeric composition given in Table 4.

Results and Discussions

Nitration rates of aromatic compounds in acids of different strength have been reported,[23,31,38–40] and aqueous sulphuric acid appears to be the most commonly used solvent,[4,7] because of its ability to nitrate, in the range 40–100 wt%, substrates with very different reactivities, such as mesitylene and nitrobenzene.

Aqueous TFMSA between 50 and 100 wt% shows nitrating

Table 4 Isomeric composition for the nitration in aqueous trifluoromethanesulphonic and sulphuric acid at 25 °C

Compound	Solvent	% *ortho*	% *meta*	% *para*
ArMe	70.3 wt% CF_3SO_3H (N = 0.22)	65.9	2.6	31.5[a]
	64.4 wt% H_2SO_4 (N = 0.25)	63.1	4.2	32.9[b]
ArBr	79.1 wt% CF_3SO_3H (N = 0.31)	36.3	0.4	62.8[a]
	72.4 wt% H_2SO_4 (N = 0.32)	38.0	0.54	58.9[c]
$ArSO_2Me$	90.3 wt% CF_3SO_3H (N = 0.53)	6	94	<0.5[a]
	99.7 wt% CF_3SO_3H (N = 0.97)	1.9	98	<0.5[a]
	99.9 wt% CF_3SO_3H (N > 0.99)	1.7	98.2	<0.5[a]
	90.2 wt% H_2SO_4 (N = 0.63)	5.1	94	<2[d]
	98.5 wt% H_2SO_4 (N = 0.92)	1.5	96	<2[d]

[a] Present work. Experimental uncertainties amount to *ca.* 0.5%. [b] From ref. 25. [c] From ref. 36 and 37. [d] From ref. 32.

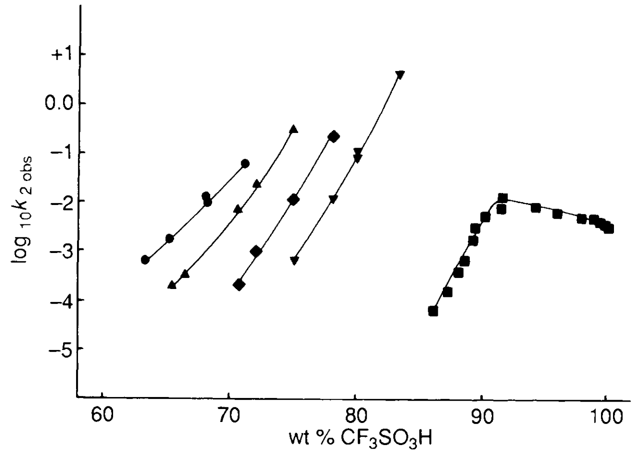

Fig. 1 Nitration in aqueous trifluoromethanesulphonic acid at 25 °C of: (●) mesitylene; (▲) toluene; (◆) benzene; (▼) bromobenzene; (■) methyl phenyl sulphone. Values of log k_{2obs} *vs.* CF_3SO_3H wt%.

properties analogous to those observed in H_2SO_4, as can be seen from the rate profiles of k_{2obs} reported in Fig. 1. Indeed, in both solvents the observed rate constants for mesitylene, toluene, benzene and bromobenzene increase with acid concentration, and the values are very close to each other, if compared at the same mole fraction of acid [see Fig. 2(*a*)].

Of particular interest are the results of Fig. 2(*b*) where the rate profiles of methyl phenyl sulphone are plotted in both concentrated TFMSA and sulphuric acid. The observed trends are very similar, but the rate in CF_3SO_3H is reduced by a factor of eight, both above and below N = 0.5 (*ca.* 90 wt%). Obviously this reduction can be related neither to the aromatic protonation nor to the concentration of nitronium ion which, in both systems, is practically the same at the same mole fraction.[9,10] Further, the viscosity of the solvents cannot help explain the experimental trends. In the range N = 0.4–1, the viscosity of CF_3SO_3H–H_2O mixtures increases up to N = 0.5, but decreases at high acidities, and the value for the pure solvent is *ca.* 3 cP.[28] In the same range the viscosity of H_2SO_4–H_2O mixtures is almost constant, and equal to *ca.* 23 cP.[41]

We suggest that the different rate of nitration of methyl phenyl sulphone in reaction media where the water behaves as a solute is related to the different ability of the pure solvents to dissociate ion pairs into free, solvated ions.[42] It is expected that the relative permittivity of pure CF_3SO_3H is lower than the exceptionally high relative permittivity of pure H_2SO_4.[7]

As regards the reaction path in TFMSA, there is kinetic evidence that the removal of the proton is not part of the rate determining step, even at very high acidities where, in principle, the removal is not favoured by a significant concentration of strong bases.[4–7] Proton-acceptor bases are not present in significant concentrations in pure CF_3SO_3H, since its autoprotolysis is very low.[12] Within the limits of experimental uncertainty, the nitration rates of methyl phenyl sulphone in pure CF_3SO_3H have been found to be independent of the concentration of nitric acid (0.03–0.3 mol dm^{-3}) used (see Table 1), and hence the concentration of base, which is proportional to the added nitric acid concentration, does not affect the nitration rate.

As regards the effectiveness and the positional selectivity of $NO_2^+CF_3SO_3^-$ there is evidence that the nitrating system in aqueous solutions of TFMSA exhibits properties analogous to those observed in aqueous H_2SO_4. The isomeric compositions of toluene, bromobenzene and methyl phenyl sulphone nitrated in CF_3SO_3H are reported in Table 4, and compared with analogous data in H_2SO_4. The results are similar in both media, within the limits of experimental uncertainties.

To get more insight into the nitration process and better compare the reaction rates in different solvents, the concentration of nitronium ion is taken into account through eqn. (4). In both aqueous H_2SO_4 and TFMSA, the equilibrium of HNO_3 to give NO_2^+ ion can be measured only in a narrow acidity range between 80 and 100 wt% (N = 0.4–1).[9,10] In the range below the experimental observations, the concentration of NO_2^+ can be calculated formally by eqn. (5), and practically estimated by eqn. (6) where the activity coefficient (a.c.) term is

$$\log[NO_2^+][H_2O]/[HNO_3][H^+] = pK_{NO_2^+} + \log(f_{HNO_3}f_{H^+}/f_{NO_2^+}f_{H_2O}) \quad (5)$$

$$\log[NO_2^+][H_2O]/[HNO_3][H^+] = pK_{NO_2^+} - n_{NO_2^+}Mc \quad (6)$$

evaluated by means of the empirical 'activity coefficient' function (or *Mc* function).[43,44] The *Mc* function, also called in the literature 'excess acidity function',[45,46] is defined formally by eqn. (7) where reactants and products pertain to a reference compound.

$$Mc = \log(\text{product of reactants' a.c.}) - \log(\text{product of products' a.c.}) \quad (7)$$

The *Mc* procedure has been tested carefully in non-ideal solutions[43,44] and evidence about its effectiveness in describing a large number of different equilibria in concentrated solutions of different acids has already been reported.[10,43–48]

We think that the $[NO_2^+]$ value estimated by eqn. (6) is not very far from the effective unknown value of $[NO_2^+]$. Clear evidence comes from the experimental observation that in H_2SO_4 and CF_3SO_3H the same $pK_{NO_2^+}$ value can be estimated from the $[NO_2^+]/[HNO_3]$ values obtained by Raman measurements.[9,10] It also seems to be of interest to point out the agreement between thermodynamic pK_{HX} values and those estimated by the same empirical procedure for the dissociation

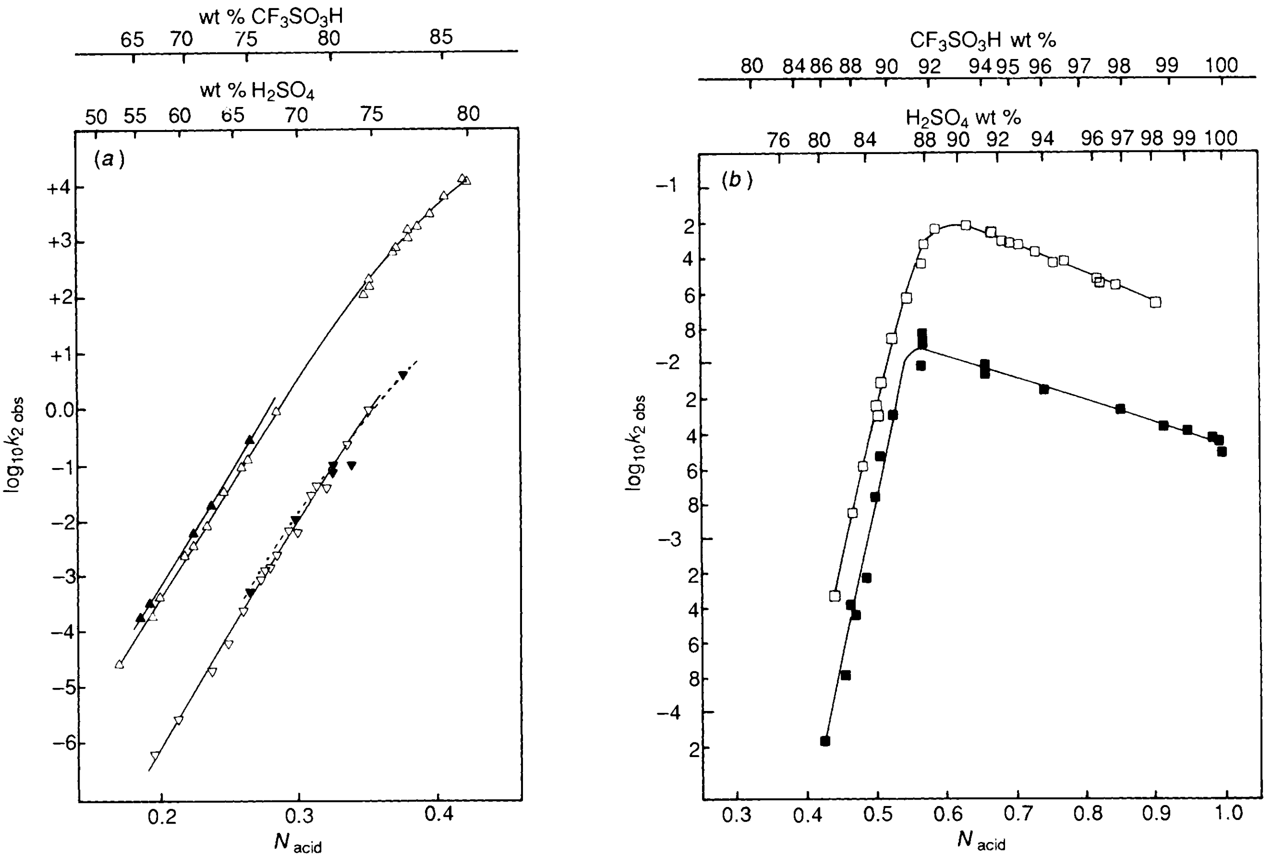

Fig. 2 (*a*) Nitration in aqueous trifluoromethanesulphonic and sulphuric acid at 25 °C of: (▲) toluene in CF_3SO_3H; (△) toluene in H_2SO_4; (▼) bromobenzene in CF_3SO_3H; (▽) bromobenzene in H_2SO_4. Values of $\log k_{2obs}$ *vs.* mole fraction of acid (N_{acid}). Experimental data in CF_3SO_3H from present work; toluene in H_2SO_4 from refs. 22–25; bromobenzene in H_2SO_4 from refs. 20, 33 and 36. (*b*) Values of $\log k_{2obs}$ *vs.* mole fraction of acid (N_{acid}) for the nitration of methyl phenyl sulphone in aqueous CF_3SO_3H (■) and H_2SO_4 (□). Experimental data in CF_3SO_3H from present work; in H_2SO_4 from present work and from refs. 19 and 32.

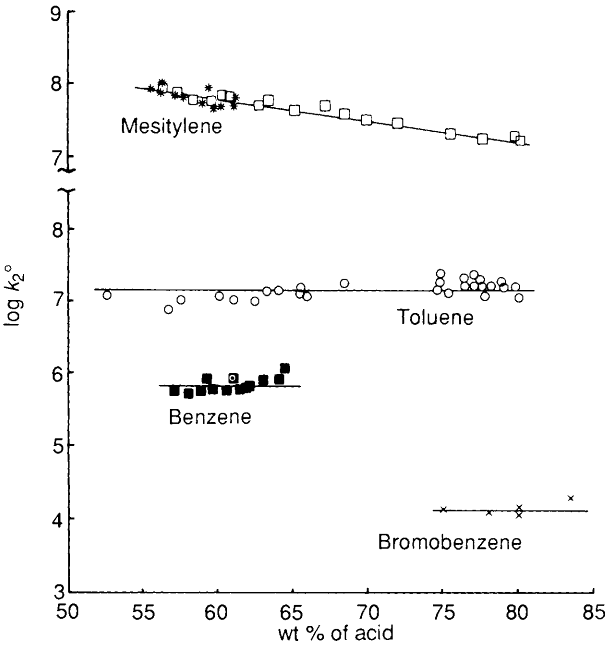

Fig. 3 Nitration in aqueous acid solutions. Values of $\log k_2°$ *vs.* percentage of acid. Experimental data of (×) bromobenzene in CF_3SO_3H (present work); (■) benzene in $HClO_4$ (refs. 23 and 49); (○) toluene in H_2SO_4 (refs. 22–25); (□) mesitylene in H_2SO_4 (refs. 23, 30 and present work), (*) in $HClO_4$ (refs. 23, 31 and present work). The $k_2°$ values have been calculated as reported in ref. 19.

($HX + H_2O \rightleftharpoons H_3O^+ + X^-$) of methanesulphonic and nitric acids in aqueous solutions (1–98 wt%).[47,48]

Examples of $k_2°$ rates estimated by eqn. (4) are shown in Fig. 3 where the rate profiles of mesitylene, toluene, benzene and bromobenzene are reported in perchloric, sulphuric and trifluoromethanesulphonic acids. The results of the study, which has been extended to a much larger number of substrates in different acids, suggest a number of items for discussion. (i) For a given compound the $k_2°$ value obtained in aqueous solutions of a given acid is almost invariant with the concentration of acid. Such behaviour is consistent with the constant involvement of NO_2^+ in the rate-determining step of the nitration process performed in the medium under investigation. (ii) The scatter of $k_2°$ values (less than a factor of ten) is not sufficient to invalidate the argument, in view of the large variation in the observed rate constants and the approximations involved in the estimation of *Mc* and $[NO_2^+]$. (iii) For mesitylene, which reacts on encounter,[4] a small decrease in rate is observed compared with the trend of those substrates which require an activation energy before reaction. (iv) The different behaviour of $k_2°$ and k_{2obs} shows that the change in k_{2obs} arises essentially from the change in the position of the HNO_3–NO_2^+ equilibrium. (v) Estimated $k_2°$ values are almost the same in both H_2SO_4 and $HClO_4$ for all the substrates studied [Fig. 4(*a*)]. (vi) For analogous compounds a linear relationship is observed [Fig. 4(*b*)] between $k_2°_{PhX}/k_2°_{PhH}$ values obtained in H_2SO_4 and k_{PhX}/k_{PhH} values obtained in the gas phase.[26] This shows that the $k_2°$ rate coefficients allow the reactivities of different aromatics in different media to be compared in a simpler way than by the use of k_{2obs} values. The improvement comes from the separation of solvent effects on the equilibria of

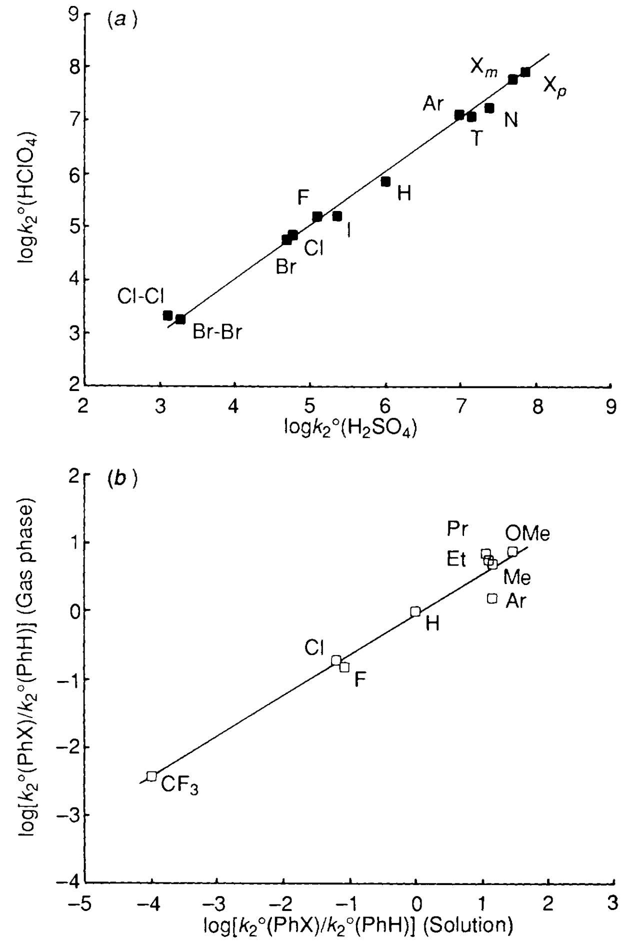

Fig. 4 (*a*) Nitration in aqueous acid solutions. Values of log k_2° (in $HClO_4$) *vs.* log k_2° (in H_2SO_4) of: (X_p) *p*-xylene (refs. 23, 25 and 31); (X_m) *m*-xylene (refs. 23, 30 and 31); (N) naphthalene (ref. 23); (T) toluene (refs. 22–25 and present work); (Ar) biphenyl (refs. 23, 30 and 50); (H) benzene (refs. 20, 23, 33 and 49); (I) iodobenzene (refs. 33, 36 and 49); (F) fluorobenzene (refs. 20, 33, 36 and 49); (Cl) chlorobenzene (refs. 20, 33, 36 and 49); (Br) bromobenzene (refs. 20, 33, 36 and 49); (Cl-Cl) *p*-dichlorobenzene (refs. 31 and 36); (Br-Br) *p*-dibromobenzene (refs. 36 and 37). (*b*) Values of log k_{PhX}/k_{PhH} (Gas-phase nitration) *vs.* log $k_2^\circ{}_{PhX}/k_2^\circ{}_{PhH}$ (nitration in H_2SO_4) of monosubstituted arenes (PhX): (OMe) anisole (refs. 26, 14 and 20–22); (Me) toluene (refs. 26 and 22–25); (Et) ethylbenzene (refs. 26 and 32); (Pr) propylbenzene (refs. 26 and 32); (Ar) biphenyl (refs. 23, 26, 30 and 50); (H) benzene (refs. 20, 23, 26 and 33); (F) fluorobenzene (refs. 20, 26, 33 and 36); (Cl) chlorobenzene (refs. 20, 26, 33 and 36); (CF_3) benzotrifluoride (refs. 26 and 51).

the reagents and solvent effects on the kinetic behaviour of the reacting species.

Solvent effects on rates become important only at very high acidities, as can be seen in Fig. 2 where rate profiles in CF_3SO_3H and H_2SO_4 are compared. Between 90 and 100 wt% a decrease in rate by a factor of three is observed, in both solvents, for the nitration of methyl phenyl sulphone carried out at 25 °C. The decreasing factor becomes smaller as the temperature increases and is halved at 55 °C (see Table 3). Indeed, methyl phenyl sulphone exhibits activation energies (E_a) which are seen to increase with increasing acidity above 90%. In H_2SO_4 the values of E_a/kcal mol^{-1} are 12.2 and 18.4 at 88.4 and 99.3 wt%, respectively, and in CF_3SO_3H appear to range between 13.3 and 13.5 at 91.9 wt% and between 18.1 and 18.3 at 99.6 wt%.

Analogous dependence of E_a on acidity has been observed for nitration of trimethylphenylammonium ion[52] and *p*-chlorophenyltrimethylammonium ion[16] in H_2SO_4 over the range 87–100 wt%. On the contrary, a different trend has been found for aromatic nitrations carried out both in acidic media below 90 wt% and in oleum, where the activation energies are seen to decrease with increasing acidity.[16,23,36]

The kinetic dependence on temperature discussed above suggests that strong interactions between ionic species, occurring at very high acidity, decrease the concentration of the nitrating agent. Independent evidence for ionic association above 90 wt% arises from studies on the solvents themselves (HA).[8] The degree of dissociation of the mixtures $H_2O–H_2SO_4$ and $H_2O–CF_3SO_3H$, estimated from the sulphonate group (SO_3^-), were found to be significantly lower than that corresponding to undissociated acid (SO_3H). This suggests the formation of ion pairs and a two step ionization–dissociation process of ionic species according[8] to the process: $AH + H_2O \rightleftharpoons A^-H_3O^+ \rightleftharpoons A^- + H_3O^+$. Furthermore, the large decrease in the nitration rates of $ArSO_3^-$ between 90 and 100 wt% H_2SO_4,[53] compared to that of $ArSO_2Me$ also supports strong interactions, with the active species now an ionic species. The concentration of $ArSO_3^-$ has been estimated, taking into account the corresponding protonation equilibrium.[53]

Acknowledgements

We are grateful to Professor J. H. Ridd for helpful discussions. Financial support by C. N. R. and G. N. S. M. is gratefully acknowledged.

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Paper 0/03551C
Received 3*rd August* 1990
Accepted 11*th October* 1990