The S_N Mechanism in Aromatic Compounds. Part XL.[1] Activating Effects of Groups attached to the Ring by a Sulphur Atom

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Kinetic data are presented for the alkaline methanolysis of a series of 4-substituted fluorobenzenes. in which the substituents are joined to the ring through sulphur. *viz.* SMe. SPh. SCF_3. SOMe. SO_2Me. SO_2Ph. and SO_2CF_3. The Hammett substituent constants (σ^-) estimated at 100° are: 0.27: 0.36: 0.66: 0.77: 1.00: 1.04; 1.40. These are compared with values for COMe. NO. and NO_2 groups. It is suggested that in the sequence of saturated groups SCH_3 to SCF_3. a small conjugative effect becomes evident. The possibility of a favourable polarizability effect is also considered. The ability of SR groups to activate both S_E and S_NAr reactions is discussed and brief comparison made with OR groups.

IN two earlier studies,[2,3] using different series of compounds, we showed that the methylthio-group is activating in S_NAr reactions, as it is in S_EAr reactions.[4] We also compared some SO_2X and COX groups.

In the present work using a simpler aromatic series we have extended the alkylthio and sulphonyl comparisons, linking them through the methylsulphinyl group.

EXPERIMENTAL

Literature methods were used for the preparation of the compounds p-FC_6H_4X (X = SMe,[5] SPh,[6] SCF_3,[7] SOMe,[8] SO_2Me,[5] SO_2Ph,[6] and SO_2CF_3[7]). Reagent and solvent were prepared as in previous Parts.

For runs between 130—220° a metal block thermostat was used. Sealed ampoules contained in steel bomb tubes [9] were placed in wells in the block containing Woods metal. Liquid bath thermostats were used at lower temperatures (oil between 70 and 130°; water up to 70°). Runs above 45° were carried out using sealed ampoules.

Reactions were followed by measuring the consumption of the reagent (OMe^-) using potentiometric titrations. Satisfactory second-order rate constants (first order in reagent and substrate) were obtained in all cases.

RESULTS AND DISCUSSION

Experimental and derived kinetic data are presented in Tables 1 and 2. As a sample, Table 3 presents experimental data for the calculation of the rate constant for reaction of the sulphinyl compound at 100°.

There are few substituents which are activating in both S_EAr and S_NAr reactions; and most of them do so because they can conjugate with an aromatic ring by $\pm R$ effects. The methylthio group (and its congeners) does so, however, by a shift in the relatively close balance of inductive electron withdrawal and conjugative electron release.

The $-I$ effect varies little between S_E and S_NAr reactions, but only in the S_EAr reactions is there an electromeric component of the $+R$ effect, enabling the group to be electron releasing and activating. In the S_NAr reactions the inductive effect is the greater. There the overall weak electron attraction makes the group weakly activating also.

Because the OMe group has a greater conjugative effect than the SMe group, the former is electron-releasing in S_N as well as S_EAr reactions. It is thus weakly deactivating in the former [10] and strongly activating in the latter,[3] a typical inversion pattern.

In S_NAr reactions, the SPh group should be more activating than the SMe group. This follows from (i) the greater electronegativity of Ph than Me and (ii) the alternative pathway for conjugation of the unshared electron pair on sulphur. Neither effect is large, however, and the change in σ^- (100°) is only from 0.27 to 0.36.

Powerful electron attraction by a CF_3 group is well known and it should make the SCF_3 group considerably more activating than SCH_3. The experimental value of σ^- (0.66) is in accord with this. The σ^- value is close to that derived by Sheppard [11] from phenol acidity measure-

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[1] Part XXXIX, J. Miller and H. W. Yeung, *J.C.S. Perkin II*, 1972, 1553.

[2] N. J. Daly, G. Kruger, and J. Miller, *Austral. J. Chem.*, 1958, **11**, 290.

[3] R. L. Heppolette and J. Miller, *J. Chem. Soc.*, 1956, 2329.

[4] C. K. Ingold, 'Structure and Mechanism in Organic Chemistry,' Bell, London 1969, 2nd. edn., p. 298.

[5] H. Zahn and H. Zuber, *Chem. Ber.*, 1953, **86**, 172.

[6] N. J. Leonard and L. E. Sutton, *J. Amer. Chem. Soc.*, 1948, **70**, 1564.

[7] L. M. Yagupol'skii and B. E. Gruz, *Zhur. obshchei Khim.*, 1961, **31**, 1315 (*Chem. Abs.* 1961, **55**, 24,721).

[8] R. W. Taft, E. Price, I. R. Fox, I. C. Lewis, K. K. Andersen, and G. T. Davis, *J. Amer. Chem. Soc.*, 1963, **85**, 709, 3146.

[9] N. J. Daly and J. Miller, *Chem. and Ind.*, 1961, 826.

[10] J. Miller, 'Aromatic Nucleophilic Substitution,' Elsevier, Amsterdam, London and New York 1968 (*a*) p. 8; (*b*) p. 84.

[11] W. A. Sheppard and D. R. Eabon, *J. Amer. Chem. Soc.*, 1962, **84**, 3072; 1963, **85**, 1310, 1314.

ments (0.64). A comparison of the change in activating power on going from CH_3 to CF_3[10b] and from SCH_3 to SCF_3 leads to a value for a transmission coefficient of electronic effects across divalent sulphur. The value is close to 0.4.

For a more informative analysis of other substituents we now discuss jointly the SOMe and SO_2Me groups; and compare them with COMe, NO, and NO_2 groups.

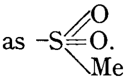
However the combined relationships of the SOMe and SO_2Me, and the NO and NO_2 groups, suggest that the sulphone would better be represented as  $-\mathrm{S}(=\mathrm{O})(=\mathrm{O})\mathrm{Me}$. This representation is well supported by the generally held views on the prevalence of S=O bonds due to p_π–d_π back bonding.

TABLE 1

Activation parameters (at 100° unless stated) for the alkaline methanolysis of some 4-substituted fluorobenzenes

Substituent	$10^4\ k_2$/l mol^{-1} s^{-1} (t/°C)						$\log_{10}$ (B/ l mol^{-1} s^{-1})	$\Delta E^‡$/ kJ mol^{-1}	$\Delta H^‡$/ kJ mol^{-1}	$\Delta S^‡$/ J mol^{-1} K^{-1}	$\Delta G^‡$/ kJ mol^{-1}
H[a]	0.400	0.402	0.808	0.810	1.50	1.52	11.95	146	143	−26.4	153
	(193.2)		(202.5)		(210.5)						
SCH_3	1.39	7.64	18.0	33.3			12.0	$134._5$	$131._5$	−25.3	141
	(169.5)	(192.5)	(202.2)	(212.2)							
SC_6H_5	4.55	14.3	23.7	28.0			11.7_5	128	125	−30.1	136
	(167.0)	(181.7)	(187.7)	(189.5)							
SCF_3	6.08	12.6	18.3	40.8	72.5		11.7_5	115	112	−30.1	123
	(127.8)	(135.0)	(142.0)	(152.8)	(159.2)						
$SOCH_3$	0.560	0.833	2.25	7.70	16.7		11.9	111	108	−27.3	118
	(84.0)	(88.4)	(100.0)	(112.3)	(121.5)						
SO_2CH_3	9.90	14.8	24.2	48.3	72.0		12.4_5	104	101	−16.7	107
	(73.9)	(84.4)	(90.0)	(95.7)	(100.2)						
$SO_2C_6H_5$	17.3	29.2	82.0	114			12.3	$101._5$	$98._5$	−19.6	106
	(79.3)	(84.4)	(95.7)	(100.2)							
SO_2CF_3	16.5	17.4	46.6	64.2	193		11.4	$80._5$	$77._5$	−36.8	91
	(22.3)	(23.7)	(32.7)	(35.5)	(47.3)						
NO_2[b]	5.87	10.4	18.8	21.8	52.1	52.1	11.7_5	$88._5$	$77._5$	−30.1	$88._5$
	(35.6)	(40.2)	(47.3)	(48.1)	(82.0)						

[a] M. Liveris, P. G. Lutz, and J. Miller, *J. Amer. Chem. Soc.*, 1956, **78**, 3375. [b] Compare m-NO_2: $\Delta E^‡ = 120$ kJ mol^{-1}; $\log_{10} B = 12.5_5$.

TABLE 2

Comparative kinetic data for the alkaline methanolysis of some 4-substituted fluorobenzenes at 100° (Hammett reaction constant $\rho = 6.35$)

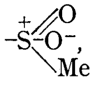
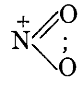
Substituent	H	SCH_3	SC_6H_5	SCF_3	$SOCH_3$	SO_2CH_3	$SO_2C_6H_5$	SO_2CF_3	NO_2
k_2/l mol^{-1} s^{-1}	3.18×10^{-9}	1.55×10^{-7}	6.03×10^{-7}	4.57×10^{-5}	2.32×10^{-4}	7.18×10^{-3}	1.19×10^{-2}	2.57	2.21×10^{-1}
Substituent rate factor	1	4.87×10	1.90×10^2	1.44×10^4	7.30×10^4	2.26×10^6	3.74×10^6	8.08×10^8	6.92×10^7
Hammett substituent constant	0	0.27	0.36	0.66	0.77	1.00	1.04	1.40	1.27

Although the inductive effect of the NO_2 group is greater than that of the NO group, its internal conjugation so competes with its external conjugation that the NO group has the greater external effect in S_NAr reactions: $\sigma^- = 1.49$ by comparison with 1.27.[12]

TABLE 3

Reaction (100° in MeOH) of equimolar quantities (0·048 3M) of sodium methoxide and p-fluorophenyl methyl sulphoxide. Portions (2·50 ml) titrated against 0·018 4M HNO_3

Time (min)	0	12.5	27.5	47.5	135	250	300	500
Titre(ml)	5.76	5.71	5.63	5.62	5.33	5.06	4.91	4.35

In contrast the SOMe group is less activating than SO_2Me (σ^-, 0.77 and 1.00). Also the SO_2Me group is less activating than NO_2. The latter comparison would be consistent with a representation of the SO_2Me group as  $-\overset{+}{\mathrm{S}}(=\mathrm{O})(\mathrm{O}^-)\mathrm{Me}$, analogous to  $\overset{+}{\mathrm{N}}(=\mathrm{O})\mathrm{O}^-$; since S^+ is less electronegative than N^+, and there is a methyl group in the sulphone.

The difference between SOMe and NO groups (σ^- 0.77 and 1.49) is the expected direction (S less electronegative than N) but the difference is rather large, and it is reasonable to relate this to differences in electron release of the unshared pair of electrons on S and N into the ring in S_NAr reactions. The conjugation of the N=O double bond implies that the unshared pair on N does not conjugate. In contrast, the p_π–d_π SO double bond does not have the same spatial restrictions, permitting conjugation of the sulphur unshared pair also.

The implication that the activating power of the SOMe group is unusually weak gains support from the fact that the SOMe group is also less activating than COMe (σ^- 0.77 and 0.87 [13]).

The two reasons offered for the difference between SMe and SPh combine differently when SO_2Me and SO_2Ph are compared. The electronegativity difference stands, but in the latter the conjugative effect is in the direction

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[12] B. A. Bolto, J. Miller, and A. J. Parker, *Austral. J, Chem.*, 1957, **11**, 93.

[13] J. Miller, *Austral. J. Chem.*, 1956, **9**, 74.

phenyl to SO_2, by comparison with S to phenyl. The counterbalancing effect thus implied in the pair of sulphones is well supported by the near identity of σ^- values (SO_2Me 1.00, SO_2Ph 1.04).

As with SCH_3 and SCF_3, a substantial difference $SO_2CF_3 > SO_2CH_3$ is expected, and found. Values of σ^- are 1.00 and 1.40, the difference being about the same as the SCH_3 and SCF_3 pair and corresponds to a transmission coefficient across SO_2 of *ca* 0.4. The SO_2CF_3 group is thus among the most powerful electrically neutral activating groups. Our σ^- value may be compared with the two different values obtained by Sheppard[11], *viz.* 1.36 and 1.65, the former based on phenol, and the latter on anilinium ion acidities. Phenol acidities seem to be a better guide for σ^- values in S_NAr reactions.

The σ^- values for SMe (0.27), SOMe (0.77), and SO_2Me (1.00) serve as type values for di-, tetra- and hexa-valent sulphur substituent groups in S_NAr reactions.

Inspection of the Arrhenius parameters shows that the activating effects of all the groups are essentially enthalpy dependent. There is a smooth gradation of $\Delta E^{\ddagger}$ ($\simeq \Delta H^{\ddagger}$) with activating power, whereas $\log_{10} B$ values vary little, falling in the approximate range $11.9_5 \pm 0.5$ (11.9_5 is the value for fluorobenzene) with no discernible pattern in the variations.

It is also noteworthy that there is no significant discontinuity between the SX, SOX, and SO_2X groups, though only the latter have an obvious $-R$ effect. This suggests the possibility that with increasing electronegativity in the sequence SCH_3 to SCF_3 a weak $-R$ effect becomes evident. Some support for this interpretation comes from a comparison with kinetic data for *m*-nitrofluorobenzene. In relation to σ^- the value of $\Delta E^{\ddagger}$ is significantly higher for the *m*-NO_2 compound.

The possibility that the polarizability of the sulphur atom contributes to the activating power of SX groups, as suggested by Streitweiser[14] is not excluded, but we feel the incursion of a $-R$ effect is a more appropriate explanation, especially as one expects the polarizability of sulphur to decrease in the sequence SCH_3 to SCF_3.

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[14] (*a*) A. Streitweiser and S. P. Ewing, *J. Amer. Chem. Soc.* 1975, **97**, 190; (*b*) A. Streitweiser and J. E. Williams, jun., *ibid.*, p. 191.