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Chlorine Abstraction from Arenesulphonyl Chlorides by Substituted Phenyl Radicals[1]

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The relative reactivities of *p*-methoxy- and *p*-nitro-phenyl radicals (produced by iododediazoniation of the corresponding arenediazonium tetrafluoroborates) towards substituted benzenesulphonyl chlorides have been determined in competition experiments at several temperatures. The *p*-methoxyphenyl radical is more selective than *p*-nitrophenyl, but both show a small tendency to behave nucleophilically. The effect of substituents on the benzene ring of the arenesulphonyl chloride is of secondary importance, in accordance with the early transition state and the fact that sulphonyl radicals are not appreciably stabilized by delocalization over the ring.[2]

Relative Arrhenius activation energies and pre-exponential factors, determined from the relative reactivities, do not correlate with the polar characteristics of the substituents but may combine together to give relative rates which yield good Hammett correlations (in the case of *p*-methoxyphenyl radicals).

Arenesulphonyl radicals can be generated from sulphonyl halides by free-radical halogen abstraction, by such free radicals as phenyl, 1-cyano-1-methylethyl, benzyl, and trichloromethyl.[3,4] The reaction with arenesulphonyl bromides and iodides, at 60–70 °C, is very fast and it is little affected by the presence of substituents on the benzene ring of the arenesulphonyl halide but it depends strongly on the nature of the halogen atom.[3] The abstraction of chlorine (more endothermic than the abstraction of bromine and iodine) is more sensitive to the presence of substituents; relative reactivities of benzyl and trichloromethyl radicals towards arenesulphonyl chlorides, determined in competition experiments, have shown the presence of polar effects in these reactions.

Benzyl radicals react faster with arenesulphonyl chlorides carrying electron-withdrawing substituents in the benzene ring ($\rho^+ = +0.31$); trichloromethyl radicals show the opposite behaviour ($\rho^+ = -1.1$) at the same temperature (70 °C).[3]

The aim of the work is to explore the behaviour of phenyl radicals of different philicity (*p*-methoxy- and *p*-nitro-phenyl radicals) towards substituted benzenesulphonyl chlorides and to study the temperature effect on the reactivity. Although the explanation of polar effects in atom abstraction reactions is usually based upon enthalpic reasons, Wright and Gilliom[5] have concluded that these arguments are unsatisfactory and that an entropic effect must be considered. The importance of this effect in the chlorine abstraction from sulphonyl chlorides was also reported.[6] Since relative reactivities of halogen abstraction from arenesulphonyl halides, studied at one single temperature, differ by only small amounts, it should be interesting to analyse the enthalpic and entropic contributions by studying the temperature dependence of selectivities (measured by ρ and ρ^+ values).

Results and Discussion

Substituted phenyl radicals may be produced by iododediazoniation of arenediazonium tetrafluoroborates with tetrabutylammonium iodide, in acetonitrile, following Sing and Kumar[7] [equation (1)].

$$XC_6H_4N_2^+ + I^- \longrightarrow XC_6H_4^{\bullet} + N_2 + I^{\bullet} \qquad (1)$$

The intermediacy of aryl radicals in these reactions is well established.[8] The method is very useful since it allows the production of aryl radicals over a wide range of temperatures and the yield of aryl radical is essentially quantitative.[9]

The relative reactivities of chlorine abstraction by substituted phenyl radicals were measured in competition experiments based on reactions (2) and (3) by using equation (4), following Tilset and Parker.[9]

$$XC_6H_4^{\bullet} + \begin{cases} YC_6H_4SO_2Cl \xrightarrow{k_Y} XC_6H_4Cl + YC_6H_4SO_2^{\bullet} & (2) \\ CH_3CN \xrightarrow{k_0} XC_6H_5^{\bullet} + CH_2CN & (3) \end{cases}$$

$$k_Y/k_0 = ([CH_3CN]_0/[YC_6H_4SO_2Cl]_0)\cdot([XC_6H_4Cl]/[XC_6H_5]) \qquad (4)$$

Equation (4) was established by assuming a constant ratio of the concentrations of CH_3CN and $YC_6H_4SO_2Cl$ during the total reaction time [this was obtained by using a large excess of CH_3CN (the solvent) and $YC_6H_4SO_2Cl$ relative to the total amount of aryl radicals generated]. The ratio of $[XC_6H_4Cl]$ and $[XC_6H_5]$ was determined by g.l.c. by using a calibration curve. A typical set of results of relative reactivities is given in Table 1. Table 2 shows that *p*-methoxyphenyl radicals remove chlorine from sulphonyl chlorides much faster than hydrogen from acetonitrile; electron-withdrawing substituents in the benzene ring of arenesulphonyl chlorides increase the reactivity at all the temperatures examined, showing nucleophilic behaviour of the radical. Relative reactivities of *p*-methoxyphenyl radicals yield good Hammett correlations with positive ρ and ρ^+ values (*ca.* 0.1–0.2) at all the temperatures examined, that is, the selectivity is almost independent of the temperature (Table 3). The better fit of σ may be an indication of the unimportance of the delocalization over the benzene ring in the transition state. On the other hand, in the addition of arenesulphonyl radicals to substituted styrenes[10] and substituted phenyl acetylenes[11] (where the small positive charge developed in the transition state in the benzylic carbon atom can be easily delocalized into the benzene ring) relative reactivities correlate better with σ^+ than with σ.

The *p*-nitrophenyl radical reactivity is less dependent on the nature of the substituents in the ring of the arenesulphonyl chloride; the Hammett correlations obtained for these reactions are very poor and the ρ and ρ^+ values are nearly zero (Table 3).

Table 1. Competition reaction of *p*-$MeOC_6H_4SO_2Cl$ and CH_3CN with *p*-methoxyphenyl radicals, at 0 °C.

Expt.	*p*-$MeOC_6H_4SO_2Cl$ mg	mmol	$[CH_3CN]_0{}^a$/[*p*-$MeOC_6H_4SO_2Cl]_0$	[*p*-$MeOC_6H_4Cl$]/[*p*-$MeOC_6H_5$]	k_Y/k_0
1	113.43	0.55	69.51	1.04	72.6
2	87.67	0.42	89.91	0.96	86.0
3	78.33	0.38	100.63	0.84	84.2
4	98.58	0.48	79.96	0.99	79.5
5	87.02	0.42	90.58	0.89	80.5
6	78.85	0.38	99.97	0.79	79.1
7	71.59	0.35	110.11	0.73	80.2
8	99.20	0.48	79.46	1.01	80.1
9	87.05	0.42	90.55	0.82	74.6
10	78.70	0.38	100.16	0.83	82.9
11	71.06	0.34	110.93	0.76	84.6

Mean value of $k_Y/k_0 = 80.4$. Standard deviation = 4.1 (5%). [a] −38.15 mmol/2.1 cm^3

Table 2. Relative reactivities (k_Y/k_0) of chlorine abstraction (k_Y) from arenesulphonyl chlorides, $YC_6H_4SO_2Cl$, and hydrogen abstraction (k_0) from CH_3CN, by substituted phenyl radicals.

(*a*) *p*-Methoxyphenyl radicals

Y	0 °C	10° C	25 °C	40 °C	60 °C
p-MeO	80.4 (5%) (11)[a]	64.1 (7%) (6)	49.9 (5%) (16)	44.9 (2%) (8)	34.1 (9%) (9)
p-Me	87.0 (8%) (11)	73.1 (7%) (11)	64.0 (5%) (9)	50.3 (3%) (10)	32.1 (10%) (6)
H	87.1 (4%) (6)	71.5 (3%) (7)	61.7 (5%) (16)	50.4 (4%) (15)	39.6 (7%) (7)
p-Cl	103.0 (7%) (10)	93.0 (7%) (10)	72.9 (8%) (15)	54.4 (8%) (9)	49.5 (6%) (8)
m-NO_2	117.1 (7%) (6)	108.2 (5%) (8)	77.8 (9%) (18)	68.6 (8%) (12)	51.1 (10%) (9)

(*b*) *p*-Nitrophenyl radicals

Y	0 °C	10° C	25 °C	40 °C	60 °C
p-MeO	46.2 (14%) (6)	50.5 (13%) (8)	42.0 (13%) (12)	38.4 (10%) (8)	35.4 (9%) (13)
p-Me	45.3 (18%) (8)	40.1 (14%) (11)	38.5 (8%) (8)	32.4 (2%) (7)	27.0 (11%) (9)
H	61.9 (18%) (8)	46.5 (8%) (8)	52.5 (8%) (8)	47.2 (5%) (8)	29.9 (5%) (7)
p-Cl	79.9 (7%) (8)	58.8 (8%) (7)	60.6 (4%) (7)	42.9 (8%) (10)	38.3 (4%) (7)
m-NO_2	46.9 (14%) (6)	53.9 (6%) (8)	41.3 (10%) (10)	38.9 (13%) (11)	37.3 (6%) (6)

[a] Mean value (% standard deviation) (runs).

Table 3. Hammett ρ values, correlation coefficients and goodness of fit for the chlorine abstraction from substituted benzenesulphonyl chlorides by substituted phenyl radicals, in acetonitrile.

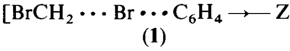
	p-Methoxyphenyl radicals				
	0 °C	10 °C	25 °C	40 °C	60 °C
ρ	0.17	0.23	0.17	0.17	0.21
r[a]	0.98	0.96	0.86	0.98	0.90
±ts (95%)[b]	0.05	0.10	0.14	0.06	0.15
ρ^+	0.12	0.16	0.13	0.12	0.15
r	0.93	0.92	0.93	0.95	0.85
±ts (95%)	0.07	0.10	0.08	0.06	0.13
	p-Nitrophenyl radicals				
ρ	0.04	0.09	0.03	0.03	0.09
r	0.15	0.57	0.14	0.21	0.55
±ts (95%)	0.40	0.20	0.31	0.22	0.21
ρ^+	0.05	0.05	0.03	0.03	0.04
r	0.24	0.40	0.22	0.28	0.33
±ts (95%)	0.29	0.16	0.22	0.16	0.17

[a] Correlation coefficient. [b] 't value' times 'standard deviation of the regression coefficient' (level of confidence).

The correlations are not good enough to decide which σ or σ^+ yield the better fit. The presence of the nitro group in the ring of the phenyl radical is not sufficient to give it an electrophilic character.

Since both radicals are nucleophilic in these reactions, the more reactive should be the *p*-methoxyphenyl, since its electron density in the carbon bearing the unpaired electron is bigger. The same conclusion can be obtained from frontier orbital considerations:[12] if the dominant interaction in the chlorine abstraction by a nucleophilic radical is SOMO–LUMO, then the reactivity of the radical increases with the energy of the SOMO, that is, the reactivity increases with the electron-donating capacity of the substituent present in the aryl radical. The greater selectivity of the more nucleophilic (more reactive) *p*-methoxyphenyl radicals seems to be another example of the violation of the reactivity–selectivity principle.

The selectivities of *p*-substituted phenyl radicals in hydrogen, deuterium and bromine atom abstraction from CH_3CN and CH_2Br_2 at 20 °C, have been determined by Tilset and Parker.[13] The values of k_{Br}/k_H decrease in the order *p*-nitrophenyl > *p*-bromophenyl > *p*-methoxyphenyl (the more electrophilic the aryl radical, the more favourable the abstraction of bromine relative to the abstraction of hydrogen from CH_3CN). However, for arenesulphonyl chlorides (Table 2), the more nucleophilic the aryl radical, the more favourable the halogen abstraction relative to the abstraction of hydrogen. This different behaviour is the result of an opposite polarization of the C–Br and S–Cl bonds in the transition states (**1**) and (**2**).



$$[\overrightarrow{BrCH_2}\cdots Br\cdots \overrightarrow{C_6H_4}\rightarrow\!\!-\,Z]^{\ddagger}$$

(**1**)

Table 4. Relative Arrhenius parameters, correlation coefficients and goodness of fit for the reaction of substituted phenyl radicals with arenesulphonyl chlorides, $YC_6H_4SO_2Cl$, and acetonitrile.

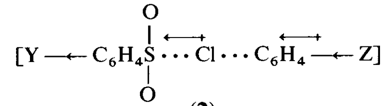
p-Methoxyphenyl radicals:

Y	A_Y/A_0	$(E_Y - E_0)$/kcal mol^{-1}	r[a]	±ts[b]	A_Y/A_H	$(E_Y - E_H)$/kcal mol^{-1}
p-MeO	0.82	−2.47	0.991	0.51	0.66	−0.17
p-Me	0.47	−2.86	0.979	0.89	0.38	−0.56
H	1.24	−2.30	0.998	0.24	(1)	(0)
p-Cl	1.27	−2.39	0.986	0.60	1.02	−0.09
m-NO_2	1.12	−2.54	0.990	0.053	0.91	−0.24

p-Nitrophenyl radicals:

Y	A_Y/A_0	$(E_Y - E_0)$/kcal mol^{-1}	r[a]	±ts[b]	A_Y/A_H	$(E_Y - E_H)$/kcal mol^{-1}
p-MeO	8.33	−0.96	0.917	0.62	3.41	+0.79
p-Me	3.00	−1.48	0.984	0.39	1.23	+0.27
H	2.44	−1.75	0.856	1.56	(1)	(0)
p-Cl	1.58	−2.10	0.954	0.98	0.65	−0.35
m-NO_2	8.17	−0.99	0.848	0.93	3.35	+0.76

[a] Correlation coefficient. [b] 't value' times 'standard deviation of the regression coefficient' (level of confidence = 95%)



$$[Y \leftarrow C_6H_4\overleftrightarrow{\overset{O}{\underset{O}{S}}\cdots Cl}\cdots \overleftrightarrow{C_6H_4} \leftarrow Z]^\ddagger$$

(2)

Similar behaviour was found in the abstraction of bromine from benzyl bromide and bromotrichloromethane,[14] where the relative reactivities of *p*-substituted phenyl radicals decrease in the order phenyl > *p*-chlorophenyl > *p*-nitrophenyl (for Cl_3CBr) but increase in the opposite order for $PhCH_2Br$ [transition states (**3**) and (**4**)].

$$[\overleftarrow{Cl_3C\cdots}Br\cdots\overleftarrow{C_6H_4}\leftarrow Z]^\ddagger$$

(3)

$$[\overrightarrow{PhCH_2\cdots}Br\cdots\overrightarrow{C_6H_4}\rightarrow Z]^\ddagger$$

(4)

In both cases of chlorine abstraction from $YC_6H_4SO_2Cl$, the effect of substituents on the benzene ring of the arenesulphonyl chloride is of secondary importance, in accordance with the early transition state of the chlorine abstraction and with the fact that arenesulphonyl radicals are not appreciably stabilized by delocalization over the ring.[2]

Plots of $\ln(k_Y/k_0)$ against 1/T yielded $E_Y - E_0$ and A_Y/A_0, from which relative Arrhenius parameters for the chlorine abstraction from $YC_6H_4SO_2Cl$ and from $C_6H_5SO_2Cl$, $E_Y - E_H$ and A_Y/A_H, were obtained. Results are given in Table 4. If the activation energy were the dominating factor in the reaction of *p*-methoxyphenyl radicals, the reactivity would follow the order

$$p\text{-Me} > m\text{-NO}_2 > p\text{-MeO} > p\text{-Cl} \approx \text{H} \qquad (5)$$

but if the pre-exponential factor dominates, we would expect

$$p\text{-Cl} \approx \text{H} > m\text{-NO}_2 > p\text{MeO} > p\text{-Me} \qquad (6)$$

that is, all the substituents should increase the reactivity of the arenesulphonyl chloride if the activation energy were the dominating factor but, if the A factor were dominating, all the substituents should decrease the reactivity. The order of expected reactivities (5) and (6) do not parallel the magnitude of the corresponding substituent constants σ and σ^+. In spite of this, quite good Hammett correlations were obtained. This result is interesting since it shows that polar effects may be related to enthalpic and entropic factors simultaneously, although the rationalizaton of the separate contribution of each may be very difficult when the variations of relative reactivities are small, as in the present case.

Relative Arrhenius activation energies and pre-exponential factors, determined for the reaction of *p*-nitrophenyl radicals, are generally bigger than those for *p*-methoxyphenyl radicals, but they combine to yield smaller relative reactivities at all the temperatures studied. No correlation between the relative Arrhenius activation parameters and the polar characteristics of the substituents was found.

Experimental

Materials.—Arenesulphonyl chlorides ($YC_6H_4SO_2Cl$) were prepared from the corresponding aromatic compounds and chlorosulphonic acid (Y = H,[15] *p*-MeO,[16] *m*-NO_2[17]). Toluene-*p*-sulphonyl chloride (BDH), *p*-chlorobenzenesulphonyl chloride (Aldrich), acetonitrile (Merck), tetrabutylammonium iodide (Aldrich), fluoroboric acid (BDH), anisole (BDH), nitrobenzene (Merck), *p*-chloronitrobenzene (EGA-Chemie) and pentane (Carlo Erba) were good quality products and were used after distillation or recrystallization, when necessary. *p*-Methoxy- and *p*-nitro-benzenediazonium tetrafluoroborates[18] were obtained from diazotization of *p*-methoxy- and *p*-nitroaniline (Aldrich), respectively, and stored at low temperature, below 0 °C. *p*-Chloroanisole was obtained from anisole and sulphuryl chloride (BDH).[19]

Competition Experiments.—(a) *Reactions with* p-*methoxyphenyl radicals.* A solution of the arenesulphonyl chloride (0.4–0.6 mmol), *p*-methoxybenzenediazonium tetrafluoroborate (4 mg, 18 μmol) and acetonitrile (2.0 cm^3) was allowed to come to thermal equilibrium at the required temperature, under an atmosphere of N_2, in a Buhler 7400 Tubingen UKT thermostat. A solution of tetrabutylammonium iodide in acetonitrile (100 mm^3; 0.15 g/2.0 cm^3) was then injected into the solution, with stirring. The solution was allowed to stand for 0.5 h. The reaction mixture was then treated with 2 cm^3 of aqueous 10% $Na_2S_2O_3$ and extracted with pentane (2 cm^3). The pentane solution was dried ($MgSO_4$) and analysed by g.l.c.

(b) *Reactions with* p-*nitrophenyl radicals.* Competition experiments were carried out under similar conditions by using a solution of the arenesulphonyl chloride (150–300 mg) and *p*-

nitrobenzenediazonium tetrafluoroborate (6 mg, 25 μmol) in acetonitrile (2.00 cm^3) and tetrabutylammonium iodide in acetonitrile (100 mm^3; 0.30 g/2.0 cm^3).

G.L.C. Analysis.—Yields of reaction products were determined by g.l.c. analysis using chromatographs equipped with flame ionization detectors and coupled to electronic integrators. Nitrogen was the carrier gas. Analysis of *p*-chloroanisole/anisole reaction products was carried out in a Tracor 565 chromatograph using an Hewlett Packard 3390 A electronic integrator. The column (glass, 1.8 m × 4 mm i.d.) was 3% OV-1 on Supelcoport 80/100 mesh. The temperature was linearly programmed: 65 °C for 10 min, 65–190 °C, 10 °C/min. Analysis of *p*-chloronitrobenzene/nitrobenzene reaction products were carried out in a Varian 3700 chromatograph using a Perkin Elmer M.2 electronic integrator. The column (glass, 2 m × 6 mm i.d.) was 15% OV-275 on Chromw-AW, 80/100 mesh. The temperature was linearly programmed: 117 °C for 35 min, 117–180 °C, 20 °C/min. Standard mixtures of *p*-chloroanisole and anisole, and *p*-chloronitrobenzene and nitrobenzene were prepared and analysed by g.l.c.

Calibration curves relating ratios of areas to ratios of number of moles were then constructed and used to determine the relative concentrations [*p*-chloroanisole]/[anisole] and [*p*-chloronitrobenzene]/[nitrobenzene].

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