Nucleophilic Displacement in Polyhalogenoaromatic Compounds. Part 1. Kinetics of Reaction of Polychlorofluorobenzene Derivatives

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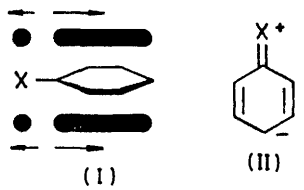
The rates of displacement of fluorine from some polychloropolyfluorobenzene derivatives by sodium methoxide in methanol have been studied. The second-order rate constants show a dependence upon halogen substituent effects similar to that found in aromatic nucleophilic displacement reactions with other activating groups. The mechanisms by which halogen substituents activate benzene systems to such attack are discussed; only two, classical, electronic interactions are needed. A simple numerical method is described which enables the prediction of rates and orientations of displacement, and of ^{19}F n.m.r. shifts, in polyhalogenobenzene derivatives.

HALOGEN substituents in an aromatic system usually show a composite electronic effect ($-I + M$) which activates the system to nucleophilic displacement.[1,2] The ready reactivity of polyfluoro-aromatic compounds to such displacement, used extensively in preparing such compounds [3] and in kinetic studies of the electronic properties of such systems,[4,5] appears to arise from the much greater solubility of these compounds in common solvents (*cf.* ref. 6) and the comparative ease of displacement of fluorine as fluoride ion (*cf.* refs. 6 and 7). Excepting when bond-breaking becomes significant,[8] the order of displacement of groups attached to the aromatic system is usually $F > NO_2 > Cl, Br$ when activation by nitro [1] or by halogen [1,4,5] substituents occurs.

Halogen substituent effects have been described in terms of two electronic effects ($-I + M$),[2] to which a third (I_π) has been added,[9] further complicating the explanation (*cf.* ref. 10). The relevance of these effects towards an understanding of aromatic nucleophilic displacement reactions may be argued.

Electronic Effects of Halogen Substituents.—The relative contributions of inductive and mesomeric effects of halogen substituents attached to aromatic systems have been carefully analysed.[11] The third (I_π) effect was found when Clark, Murrell, and Tedder [12] sought to rationalise the disparity between spectroscopically derived mesomeric effects of halogen substituents and those found in kinetic or thermodynamic measurements. Its use [9] to explain the results of such measurements in nucleophilic aromatic substitution presupposed that the classical inductive and mesomeric effects, already successfully applied to a wealth of electrophilic substitution reactions, could not be used in this particular instance. This was in addition to the reservation that spectroscopic effects are associated with the transition of an electron between energy levels in the same molecule, whereas kinetic effects arise in the passage of a molecule or molecules from a ground state to a transition state of quite different structure.

The term I_π has also been used by some authors [13] who, finding a canonical structure in which positive charge is located upon a highly electronegative element to be improbable, suggest a repelling interaction between *p* orbitals of the halogen group and the aromatic π-system (I). However, the formal positive charge upon halogen in (II) only arises from the need to describe electron donation ($+M$ effect). As the mesomeric effect only partly reverses the inductive effect, the total state of the halogen substituent attached to an aromatic system is always electron-*rich* compared with hydrogen. This I_π term appears to be an alternative to the mesomeric effect, differing only in the way in which the effect is brought about; it will therefore be discarded in favour of the term M effect.



(I) (II)

Since nucleophilic substitution by methanolic sodium methoxide is a process showing considerable sensitivity to substituent effects, and in which steric effects are small, we have studied the rates of reaction of a number of polychloropolyfluorobenzene derivatives in this system, so that the electronic effects of halogen could be determined.

DISCUSSION

Pentafluorohalogenobenzenes.—Earlier kinetic studies [5] dealt with fluorine displacement from hexafluorobenzene, pentafluorobenzene, and chloropentafluorobenzene at positions *ortho* and *para* to the heavier halogen. We have extended the series to include bromo- and iodopentafluorobenzene (Table 1). The effect upon the ease

[1] J. Miller, 'Aromatic Nucleophilic Substitution,' Elsevier, Amsterdam, 1968; J. F. Bunnett and R. E. Zahler, *Chem. Rev.*, 1951, **49**, 273; J. Miller, *Rev. Pure Appl. Chem.*, 1951, **1**, 171.

[2] C. K. Ingold, 'Structure and Mechanism in Organic Chemistry,' Cornell University Press, Ithaca, New York, 1969, 2nd edn., pp. 293 *et seq.*

[3] W. A. Sheppard and C. Sharts, 'Organic Fluorine Compounds,' Benjamin, New York, 1969.

[4] K. C. Ho and J. Miller, *Austral. J. Chem.*, 1966, **19**, 423.

[5] J. Burdon, W. B. Hollyhead, and J. C. Tatlow, *J. Chem. Soc.*, 1965, 6375.

[6] T. de Crauw, *Rec. Trav. chim.*, 1931, **50**, 753.

[7] A. L. Rocklin, *J. Org. Chem.*, 1956, **21**, 1478.

[8] M. Liveris and J. Miller, *Austral. J. Chem.*, 1958, **22**, 297; C. W. L. Beavan and G. C. Bye, *J. Chem. Soc.*, 1954, 3091; C. W. L. Beavan, T. A. Emokpae, and J. Hirst, *J. Chem. Soc.* (*B*), 1968, 238.

[9] J. Burdon, *Tetrahedron*, 1965, **21**, 3373.

[10] J. F. Dippy and R. H. Lewis, *J. Chem. Soc.*, 1936, 644.

[11] R. G. Coombes, D. H. G. Crout, J. G. Hoggett, R. B. Moodie, and K. Schofield, *J. Chem. Soc.* (*B*), 1970, 347.

[12] D. T. Clark, J. M. Murrell, and J. M. Tedder, *J. Chem. Soc.*, 1963, 1250.

[13] L. M. Stock, 'Aromatic Substitution Reactions,' Prentice-Hall, Englewood Cliffs, New Jersey, 1968, p. 56.

of nucleophilic displacement of the '*para*'-fluorine substituent in pentafluorobenzene of replacing hydrogen by halogen lies in the order X = F < H < Cl,Br < I. This order is consistent with those found in many

TABLE 1

Second-order rate constants, and relative rates, for OMe^- attack upon C_6F_5X (MeOH; 333 K)

X	10^4k_2/ l mol^{-1} s^{-1}	10^4k_o [a]	10^4k_p [a]	k_o^{rel}	k_p^{rel}
H	3.0 ± 0.1	0.05	3.0	1	1
F	10.1 [b]	1.68	1.68	34	0.6
	9.7 ± 0.2	1.62	1.62	33	0.5
Cl [b,c]		6.8	53.2	130	17
Br	58 ± 1.2	3.6	50	70	17
I	120 ± 1.0	3	114	60	38

[a] Orientations of nucleophilic attack from J. Burdon, P. L. Coe, C. R. Marsh, and J. C. Tatlow, *Tetrahedron*, 1966, **22**, 1183. [b] J. Burdon, K. R. Hollyhead, and J. C. Tatlow, *J. Chem. Soc.*, 1965, 6375. [c] 10^4k_m = 1.1 (*cf.* for C_6F_6).

nucleophilic and electrophilic processes, although in the latter case it is an order of increasing *de*activation.[1,2,14] The corresponding replacement has a less consistent effect upon the displacement of '*ortho*'-fluorine substituents, where the order is H ≪ F < Br,I < Cl. The simplest explanation of this sequence, apart from the large $-I$ effect of the halogen groups, is the imposition of a steric retardation upon the displacement of fluorine adjacent to the larger halogen substituents (*cf.* ref. 15) causing a depression of rate in the *ortho*-attack of bromo- and iodo-pentafluorobenzene to below that found in the analogous reaction of chloropentafluorobenzene.

Miller has reported [1a] the displacement of fluorine by nucleophiles in mixed solvents from various halogenopentafluorobenzene derivatives. The rates of these displacements are similar to, but less regularly ordered than, the present values which are the first in which all four halogenopentafluorobenzenes have been studied in the same solvent.

Polyhalogenobenzene Derivatives.—Rates of nucleophilic displacement by methanolic sodium methoxide upon some polychlorofluorobenzene derivatives, and upon pentachloro- and 1,2,4,5-tetrachloro-3-nitrobenzene, are summarised in Table 2. The purity of the kinetic samples was checked by ^{19}F n.m.r. spectroscopy, after it was found that samples of fluoropentachlorobenzene considerably contaminated with tetrachlorodifluorobenzene isomers and with tetrachlorofluoronitrobenzene showed sharp m.p.s.

In contrast to earlier reports,[16] we found that pentachloronitrobenzene loses both chlorine and the nitro-group during attack by methoxide ion. At 317.7 K, 58 ± 1.5% of the methoxide ion consumed gave chloride ion; during a kinetic study in which the formation of chloride ion and the loss of methoxide ion were followed simultaneously, this value did not change over 60% reaction. At 328.4 K, chloride ion accounted for 61 ± 1.5% of the consumed reagent. ^1H N.m.r. spectroscopy showed three methoxy-absorptions in the solid organic product; although the peaks overlapped, and did not allow accurate integration, the apparent ratio of the three absorptions (2 : 1 : 2) was consistent with the presence of pentachloroanisole (40%) and both *ortho*- and *para*-nitrotetrachloroanisoles (60%) required from the titration results. In addition, the first peak was identified, by comparison with an authentic sample, as due to pentachloroanisole.

1,2,4,5-Tetrachloro-3-nitrobenzene also lost both chlorine and the nitro-group under these conditions; chloride ion accounted for 24% of the methoxide ion consumed at 323.2 K. ^1H N.m.r. spectroscopy showed two derivatives of anisole, 2,3,5,6-tetrachloroanisole and (probably) 3,4,6-trichloro-2-nitroanisole, in the ratio 3 : 1.

TABLE 2

Second-order rate constants and derived Arrhenius activation energies for OMe^- attack upon polysubstituted benzenes (MeOH)

$C_6Cl_5NO_2$:	10^3k_2 = 13.0 ± 0.4 (333.2 K); 7.2 ± 0.2 (328.2 K); 5.0 ± 0.3 (323.2 K); 2.62 ± 0.04 (317.7 K)
	ΔE = 20.9 ± 1.1 kcal mol^{-1}
4*H*-$C_6Cl_4NO_2$:	10^4k_2 = 10.4 ± 0.3 (333.5 K); 6.6 ± 0.3 (328.6 K); 4.9 ± 0.5 (328.2 K); 1.75 ± 0.04 (311.0 K)
	ΔE = 18.8 ± 0.6 kcal mol^{-1}
C_6Cl_5F:	10^3k_2 = 9.3 ± 0.3 (335.2 K); 3.3 ± 0.2 (323.2 K); 1.29 ± 0.2 (313.2 K)
	ΔE = 18.9 ± 0.2 kcal mol^{-1}
m-$C_6Cl_4F_2$:	10^3k_2 = 20.4 ± 0.2 (332.2 K); 9.5 ± 0.4 (323.2 K); 3.62 ± 0.04 (312.7 K).
	ΔE = 18.6 ± 0.1 kcal mol^{-1}
sym-$C_6Cl_3F_3$:	10^3k_2 = 20.5 ± 0.4 (323.2 K); 8.7 ± 0.2 (313.3 K); 1.92 ± 0.1 (298.2 K)
	ΔE = 18.2 ± 0.1 kcal mol^{-1}
4*H*-C_6Cl_4F:	10^4k_2 = 14.0 ± 0.4 (333.1 K); 5.7 ± 0.1 (323.2 K); 2.15 ± 0.03 (313.2 K)
	ΔE = 19.4 ± 0.4 kcal mol^{-1}
Crude $C_6Cl_2F_4$	(79% *meta*-, 10% *ortho*-, 0.6% *para*-, and 10% 2,4-dichloro-1,3,5-trifluorobenzene): 10^3k_2 = 20.6 ± 0.4 (333.2 K); 7.8 ± 0.1 (323.2 K); 3.2 ± 0.1 (313.3 K)
	ΔE = 18.8 ± 0.5 kcal mol^{-1}

Chlorine loss did not occur with carefully purified samples of pentachlorofluorobenzene, although less thoroughly purified material of the same m.p. gave chloride ion, perhaps from the presence of pentachloronitrobenzene; none of the other polychloropolyfluorobenzene derivatives lost chlorine on treatment with methanolic sodium methoxide.

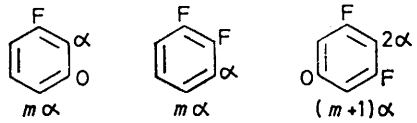
Substituent Effects of Halogen Groups.—The result of combining the effects of a number of substituents is usually based upon the assumption of complete additivity, which is strictly true only when the substituent effects are independent of the electron density of the centre upon which they act, and upon the absence of appreciable specific interactions between reagent and substrate.[17] Additivity of substituent effects has been

[14] R. O. C. Norman and R. Taylor, 'Electrophilic Substitution of Benzenoid Compounds,' Elsevier, Amsterdam, 1965.
[15] H. C. Brown and Y. Okamoto, *J. Amer. Chem. Soc.*, 1957, **79**, 1907.
[16] V. S. F. Berckmans and A. F. Holleman, *Rec. Trav. chim.*, 1925, **44**, 851.
[17] J. Burdon, D. R. King, and J. C. Tatlow, *Tetrahedron*, 1966, **23(3)**, 1347.

found in aromatic nucleophilic substitution [1a] without evidence of the saturation of effect noticed by Nishida.[18] The present results (Tables 1 and 2) parallel a Hammett plot obtained for methoxide ion attack upon many derivatives of *ortho*- and *para*-chloronitrobenzene in methanol; the basic substituent constant, σ, is used in the absence of satisfactory values of σ^- which do not show scatter.[1a] Classical concepts of electronic effects interpret this result in terms of the $-I$ effect of halogen being partly neutralised by the $+M$ effect acting specifically at positions *ortho* and *para* to the halogen substituent. Positions *meta* to halogen substituents therefore have the lowest electron density in a halogenobenzene; the values of the Hammett substituent constant (σ) summarise the wealth of evidence (see ref. 19; *cf.* ref. 20) in both electrophilic (also σ^+) and nucleophilic aromatic substitution.[1,14] The orientation of displacement, as well as the observed rate constants (Tables 1 and 2) confirm this.

We now describe a simple, empirically derived method by which the orientation and relative rates of substitution of polyhalogenoaromatic compounds may be deduced.

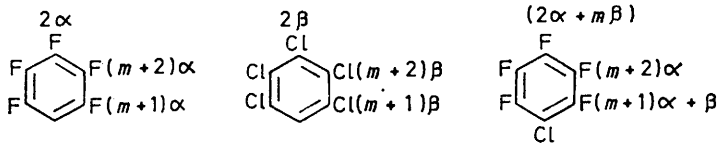
Electrophilic substitution of halogenobenzenes (PhX) takes place mainly at the *para*-positions, but also *ortho* to the halogen substituent. The orientation may be explained by suggesting either an attenuation of the $-I$ effect in transmission around the ring, or a preferential relaying of the $+M$ effect to the *para*-position. The relative activation of these sites in the electrophilic attack of fluorobenzene are shown as α [$\alpha = -RT\ln(k_o/k_m) = -2.3RT(\sigma_o - \sigma_m)\rho$] and $m\alpha$ [$m\alpha = -RT\ln(k_p/k_m) = -2.3RT(\sigma_p - \sigma_m)\rho$] in formula (III),



(III) (IV) (V)

with the *meta*-position being taken as substantially unaffected by the process which determines orientation. By extension, the orientation of attack of *ortho*- (IV) and *meta*- (V) difluorobenzenes may be deduced, and the corresponding parameters (β, γ, and δ) may be applied to considerations of chloro-, bromo-, and iodo-benzene. In these terms, $m > 1$ (*i.e.* preferential attack at *para*-position), and $\alpha > \beta > \gamma > \delta$ follows from the comparative reactivities of *ortho*- and *para*-positions (k_o/k_p) in each of the four halogenobenzenes [*e.g.* $RT\ln(k_o/k_p) = (m-1)\alpha$ for fluorobenzene]. This order is not altered by changes in the numerical value of ρ, the Hammett reaction constant; it becomes an order of *de*activation when applied to reactions for which ρ is positive (*i.e.* nucleophilic displacement). This allows the application of these terms to predicting the orientation of such reactions, as in nucleophilic attack on pentafluorobenzene (VI), pentachlorobenzene (VII), and chloropentafluorobenzene (VIII); although the numerical values of α and β are not the same in electrophilic and nucleophilic reactions, they are linked by the parameter ρ'/ρ. Therefore, in both pentafluoro- and pentachlorobenzene the predicted orientation of attack relative to the hydrogen substituent is *para* > *ortho* > *meta*, since this is the order in which the deactivation terms [*e.g.* $(m+2)\alpha$] increase. As $\alpha > \beta$, the *ortho* : *para* ratio (k_o/k_p) is less in pentafluorobenzene than in pentachlorobenzene. In chloropentafluorobenzene, the same orientation relative to the heavier halogen substituent (Cl) is predicted; the term governing the *ortho* : *para* ratio [$(m-1)(\alpha-\beta)$] suggests that there will be more *ortho*-displacement in chloropentafluorobenzene than in pentafluorobenzene, for which the term is $(m-1)\alpha$, and that this *ortho* : *para* ratio will decrease when chlorine is replaced by heavier halogens because the terms $(\alpha-\gamma)$ and $(\alpha-\delta)$ tend more closely to α. Some of the evidence [9] supporting these conclusions is shown in Table 1. Positions *meta* to chlorine in chloropentafluorobenzene are also predicted to show a reactivity similar to that of any site in hexafluorobenzene.

This simple calculation method may be successfully applied to all the examples used to substantiate the I_π concept; however, it cannot be used to predict the outcome of competition between molecules unless the sensitivity of the reaction to substituent effects is known, or the values of α and β can be derived experimentally. An example of the success of this approach is in the prediction of ^{19}F n.m.r. chemical shifts of derivatives of chlorofluorobenzenes (Table 3). Using fluorobenzene (chemical shift 114.0 p.p.m. upfield of trichlorofluoromethane) as standard, and the values $m = 0.28$, $\alpha = 22.3$ p.p.m., and $\beta = -2.2$ p.p.m., the chemical shifts of fifty fluorine nuclei could be predicted to within 6.5 p.p.m. and over a range of 57 p.p.m.; half of these shifts lie within 1.5 p.p.m. of the reported values.[21]



(VI) (VII) (VIII)

[18] Shinya Nishida, *J. Org. Chem.*, 1966, **32**(9), 2692, 2695, 2697.
[19] H. H. Jaffé, *Chem. Rev.*, 1953, **53**, 191.
[20] R. D. Chambers, W. K. R. Musgrave, J. S. Waterhouse, D. L. H. Williams, J. Burdon, W. B. Hollyhead, and J. C. Tatlow, *J.C.S. Chem. Comm.*, 1974, 239.
[21] C. H. Dungan and J. R. van Wazer, 'Compilation of Reported ^{19}F NMR Chemical Shifs,' Wiley–Interscience, New York, 1970.

The previous argument focuses attention entirely upon the positions *ortho* and *para* to halogen. However, in nucleophilic aromatic substitution the positions *meta* to halogen are strongly activated, since the inductive effect is not weakened by any mesomeric effect. Any attempt to predict relative rates of reaction between molecules will need to take account of this

TABLE 3

Observed and calculated † ^{19}F n.m.r. shifts for polyhalogenofluorobenzenes (quoted as displacements upfield of trichlorofluoromethane, in p.p.m.)

Substituents					Shift (calc. in parentheses)
2	3	4	5	6	
H	H	H	H	H	$\delta_1 = -114.0$ (−114.0), standard
Cl	H	H	H	H	−115.8 (−111.8)
H	Cl	H	H	H	−111.1 (−114.0)
H	H	Cl	H	H	−115.5 (−113.4)
Cl	H	Cl	H	Cl	−112.6 (−109.0)
Cl	Cl	Cl	Cl	Cl	−108.1 (−109.0)
F	H	Cl	H	H	−133.7 (−135.7)
Cl	H	H	F	H	−111.1 (−111.8); $\delta_5 = -114.1$ (−113.4)
Cl	H	F	H	H	−121.7 (−118.0); $\delta_4 = -117.0$ (−120.2)
F	H	Cl	H	Cl	−133.2 (−133.5)
Cl	H	F	Cl	H	−118.0 (−118.0)
Cl	H	F	H	Cl	−116.4 (−115.8)
F	Cl	Cl	Cl	Cl	−130.9 (−133.5)
Cl	F	Cl	Cl	Cl	−109.0 (−109.0)
Cl	Cl	F	Cl	Cl	−111.1 (−115.8)
F	H	Cl	H	F	−155.5 (−158.0)
Cl	F	Cl	F	H	−111.9 (−111.2)
F	F	Cl	Cl	Cl	−133.2 (−133.5); $\delta_2 = -158.4$ (−158.0)
Cl	F	Cl	F	Cl	−112.5 (−109.0)
F	Cl	F	Cl	Cl	−138.8 (−140.3); $\delta_2 = -134.2$ (−133.5); $\delta_4 = -114.3$ (−115.8)
F	F	Cl	F	H	−162.3 (−164.8); $\delta_2 = -132.1$ (−134.1); $\delta_5 = -116.9$ (−118.0)
F	F	F	Cl	Cl	−136.1 (−140.3); $\delta_2 = -155.6$ (−158.6)
F	Cl	F	Cl	F	−160.6 (−164.8); $\delta_2 = -134.5$ (−133.5); $\delta_4 = -118.4$ (−115.8)
F	Cl	F	F	Cl	−140.0 (−140.3)
F	F	Cl	F	F	−156.4 (−158.0); $\delta_2 = -161.5$ (−164.8); $\delta_3 = -140.8$ (−140.3)
F	F	F	F	F	−163.7 (−164.8)
F	F	F	F	H	−141.3 (−142.5); $\delta_2 = -164.5$ (−164.8); $\delta_3 = -156$ (−158.6)
F	H	F	F	H	−139.8 (−142.5)
H	F	H	F	H	−107.6 (−114.0)
F	F	H	H	H	−136.2 (−136.2); $\delta_2 = -163.0$ (−158.6)
F	H	F	H	H	−143.5 (−142.5); $\delta_2 = -134.0$ (−136.3); $\delta_4 = -115.5$ (−120.2)
H	H	F	H	H	−119.8 (−120.2)
H	F	H	H	H	−110.1 (−114.0)
F	H	H	H	H	−139.0 (−136.3)

† Using fluorobenzene as standard, taking $m = 0.28$, $\alpha = 22.3$, and $\beta = -2.2$. Experimental values taken from C. H. Dungan and J. R. van Wazer, 'Compilation of Reported ^{19}F NMR Chemical Shifts,' Wiley–Interscience, New York, 1970.

activation. In applying the calculation method to our kinetic results and those of Burdon *et al.*[5,20] the values $m = 3.8$, $\alpha = -1.1$ kcal mol^{-1}, and $\beta = -0.45$ kcal mol^{-1} were needed to reflect the effect of replacing fluorine in hexafluorobenzene by chlorine (Table 4). In addition, the parameters $I_F = 3.95$ kcal mol^{-1} and $I_{Cl} = 3.72$ kcal mol^{-1} were needed to show the effect of replacing either halogen with hydrogen. These terms were necessary regardless of the position of the halogen substituent with respect to the site under attack. Thus the relative reactivities of the *para*-position of chloropentafluorobenzene and a position in hexafluorobenzene are defined by equation (i), where $\Delta\Delta G = -RT\ln k_2$,

$$\Delta\Delta G(C_6F_5Cl) = \Delta\Delta G(C_6F_6) - I_F + I_{Cl} + (\beta - \alpha)m \quad \text{(i)}$$

$$\Delta\Delta G(C_6H_5F) = \Delta\Delta G(C_6F_6) - 5I_F - (m + 2)\alpha \quad \text{(ii)}$$

and that of fluorobenzene itself by equation (ii). Using these five parameters, fourteen rate constants could be calculated with an average error of ±25% over seven orders of magnitude (Table 4). Using the results for bromo- and iodo-pentafluorobenzene (Table 1), $I_{Br} = 3.6$ kcal mol^{-1}, $I_I = 3.25$ kcal mol^{-1}, $\gamma = -0.3$, and

TABLE 4

Calculated and experimental second-order rate constants [a] for ArF + NaOMe ⟶ ArOMe + NaF (MeOH; 323 K)

Substrate		10^6k_2(obs.)	10^6k_2(calc.)
Hexafluorobenzene		75.6 [b]	75.6
Chloropentafluorobenzene:	*p*-F	2 520	2 410
	m-F	53	48
	o-F	150	400
Pentafluorobenzene	*p*-F	101	108
	o-F	*ca.* 2	0.8
1,3-Dichlorotetrafluorobenzene (4-F)		5 300	4 780
1,3,5-Trichlorotrifluorobenzene		6 800	9 200
1,3-Difluorotetrachlorobenzene		4 800	6 100
Pentachlorofluorobenzene		3 300	4 500
1,2,3,4-Tetrafluorobenzene (2-F)		0.4	0.24
1,2,3,5-Tetrafluorobenzene (1-F)		1.2	1.26
1,2,4,5-Tetrafluorobenzene		0.0025	0.0019
1,2,4,5-Tetrachloro-3-fluorobenzene		570	200
Fluorobenzene		2×10^{-6} [c]	2×10^{-8}

[a] Calculated using $\Delta\Delta G = -RT\ln k_2$, with $I_F = -3.95$ kcal mol^{-1}, $I_{Cl} = -3.72$ kcal mol^{-1}, $\alpha = -1.1$ kcal mol^{-1}, $\beta = -0.45$ kcal mol^{-1}, and $m = 3.8$; values also taken from refs. 4, 5, and 20; k_2 quoted in l mol^{-1} s^{-1}. [b] Standard; allowance is made for compounds in which more than one of the displaced groups are equivalent. [c] Extrapolated over 100 °C.

$\delta = -0.25$ were obtained. The orders of these sets of parameters, $I_F > I_{Cl} > I_{Br} > I_I$ and $-\alpha > -\beta > -\gamma > -\delta$, agree with those of the $-I$ and $+M$ effects.

EXPERIMENTAL

Hexafluorobenzene, bromopentafluorobenzene, pentafluoroiodobenzene, and pentafluorobenzene were gifts from Imperial Smelting Corporation (Avonmouth); we thank Dr. G. Fuller and Professor G. H. Williams for making these available. Pentachlorofluorobenzene, m.p. 138—139.5° (from ethanol) (lit.,[22] 137—138°), was obtained from pentachloronitrobenzene through ion-exchange with potassium fluoride.[22] 1,2,4,5-Tetrachloro-3-fluorobenzene, m.p. 71.5—72° (from ethanol) (lit.,[22] 71.5—72.5°), was similarly obtained from 1,2,4,5-tetrachloro-3-nitrobenzene.[22] Hexachlorobenzene and potassium fluoride in tetramethylene sulphone [23] gave 1,3,5-trichloro-2,4,6-trifluorobenzene, m.p. 58—59.5° (from ethanol) (lit.,[23] 61—62°) and a liquid, b.p. 154.5—156° at 757 mmHg, containing 1,3- (80%), 1,2- (10%), and 1,4-(0.6%)dichlorotetrafluorobenzene together with 2,4-dichloro-1,3,5-trifluorobenzene (10.4%). Under milder conditions, a tetrachlorodifluorobenzene fraction

[22] G. C. Finger and C. W. Kruse, *J. Amer. Chem. Soc.*, 1956, **78**, 6034.
[23] G. Fuller, *J. Chem. Soc.*, 1965, 6264.

could be obtained, from which 1,3-difluorotetrachlorobenzene could be crystallised. The resulting mixture of isomers, m.p. 45—50° contained 88% of the desired compound (^{19}F n.m.r.).

TABLE 5

^{19}F N.m.r. chemical shifts (p.p.m. upfield of $CFCl_3$)

Compound	δ
Pentachlorofluorobenzene	105.8 (lit.,[1] 108.07)
1,2-Difluorotetrachlorobenzene	131.1 (lit.,[1] 130.9)
1,3-Difluorotetrachlorobenzene	109.5 (lit.,[1] 109.0)
1,4-Difluorotetrachlorobenzene	111.1 (lit.,[1] 111.1)
2,4-Dichloro-1,3,5-trifluorobenzene	110.8 (lit.,[b] 110.6)
	112.0 (lit.,[b] 112.0)
1,3,5-Trichloro-2,4,6-trifluorobenzene	112.9 (lit.,[a] 112.5)
1,2-Dichlorotetrafluorobenzene	136.4 (lit.,[a] 136.1)
	155.9 (lit.,[a] 155.6)
1,3-Dichlorotetrafluorobenzene	118.4 (lit.,[a] 118.4)
	134.9 (lit.,[a] 134.5)
	161.1 (lit.,[a] 160.6)
1,4-Dichlorotetrafluorobenzene	140.3 (lit.,[a] 140.0)
2,4-Dichloro-3,5,6-trifluoroanisole	118.9
	137.2
	156.5
2,6-Dichloro-3,5-difluoroanisole	135.1
4,5-Dichloro-2,3,6-trifluoroanisole	132.4
	138.6
	151.9
1,2,4,5-Tetrachloro-3-fluorobenzene	104.0

[a] N. Boden, J. W. Emsley, J. Feeney, and L. H. Sutliffe, *Mol. Phys.*, 1964, **8**, 133. [b] P. Bladon, D. W. A. Sharp, and J. M. Winfield, *Spectrochim. Acta*, 1964, **20**, 1033.

Pentachloronitrobenzene (m.p. 144.5—145°) and 1,2,4,5-tetrachloro-3-nitrobenzene (m.p. 99.5—100°) were commercial samples which were recrystallised from ethanol to remove un-nitrated starting material which otherwise contaminated the derived polychlorofluorobenzenes.

Kinetic studies were carried out by using carbonate-free solutions of sodium methoxide in pure methanol (+99.95%; <10 p.p.m. water) which had previously been standardised by titration with acid (phenolphthalein); reactions were initiated by adding a quantity of concentrated sodium methoxide solution to a solution of the polychloroaromatic compound in methanol. Samples were withdrawn at intervals, and were quenched in water and titrated with acid to determine the amount of base consumed. Potentiometric titration of chloride ion was also carried out where appropriate.

^{19}F N.m.r. spectra were measured (Varian HA-60; 56.4 MHz) for *ca.* 10% solutions of substrate in trichlorofluoromethane (internal standard). ^{1}H N.m.r. spectra were measured at 60.0 MHz for solutions in trichloromethane (tetramethylsilane as internal standard).

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