

## THE $S_N$ MECHANISM IN AROMATIC COMPOUNDS\*

### XXXV.† COMPARATIVE REACTIVITY OF PENTACHLOROFLUOROBENZENE, HEXAFLUOROBENZENE, AND FLUOROBENZENE

By J. MILLER‡§ and H. W. YEUNG‡

In a recent paper<sup>1</sup> dealing with  $S_N$  reactions of perhalogenobenzenes it was predicted that pentachlorofluorobenzene would be more reactive, replacing fluorine, than hexafluorobenzene, and this is now confirmed. Hammett substituent constants ( $\sigma^-$ ) for pentachlorophenyl and pentafluorophenyl groups are derived and compared with values for *ortho*- and *para*-nitrophenyl groups.

#### Experimental

##### Materials

The solvent and reagent were prepared as described.<sup>1</sup>

2,3,4,5,6-Pentachloro-1-fluorobenzene was prepared according to the procedure of Finger and Kruse<sup>2</sup> from the commercially available pentachloronitrobenzene, using anhydrous potassium fluoride in dimethylformamide. The product, recrystallized from 95% ethanol, was obtained as long white needles of m.p. 137–138° (lit.<sup>2</sup> 137–138°).

##### Kinetic Procedure

Generally as described,<sup>1</sup> but runs were followed by estimating the concentration of reagent (OMe<sup>-</sup>) by potentiometric back-titration of excess quenching acid. A check by estimation of fluoride confirmed the reaction as simple replacement of F by OMe. Good second-order plots were obtained, more precise by the acid-base method. Experimental kinetic data were measured over a range of about 30°. Values of rate constants  $10^3k_2$  (l. mole<sup>-1</sup> sec<sup>-1</sup>) and temperature are: 3·30, 49·9°; 3·38, 50·1°; 5·53, 59·9°; 13·9, 65·1°; 21·6, 70·1°; 37·3 and 39·6, 80·1°. The Arrhenius parameters and other derived values are included in Table 1. The error in  $\Delta E^\ddagger$  computed by least squares is less than the estimated error in  $\Delta E^\ddagger$  of  $\pm 0.5$  kcal mole<sup>-1</sup>. Estimated error in  $\log_{10}B$  is about  $\pm 0.3$ .

##### Product

The product, pentachloroanisole, was isolated from a reaction mixture allowed to proceed to "infinity", and was obtained as fine white needles, m.p. 108–109° (lit.<sup>3</sup> 108–110°).

\* Manuscript received June 14, 1966.

† Part XXXIV, *J. Chem. Soc. B*, 1966, 310.

‡ Department of Chemistry, University of Hong Kong.

§ Present address: Department of Supply, Defence Standards Laboratories, P.O. Box 50, Ascot Vale, W.2., Vic.

<sup>1</sup> Ho, K. C., and Miller, J., *Aust. J. Chem.*, 1966, **19**, 423.

<sup>2</sup> Finger, G. C., and Kruse, C. W., *J. Am. chem. Soc.*, 1956, **78**, 6034.

<sup>3</sup> Rocklin, A. L., *J. org. Chem.*, 1956, **21**, 1478.

### Results and Discussion

On the basis of well-known theories of electron displacement and transmission of electronic effects, such as are discussed by Ingold,<sup>4</sup> and using known substituent effects of halogens in aromatic  $S_N$  reactions<sup>5-8</sup> it was predicted<sup>1</sup> that activation by *para*-chlorine exceeds that of *para*-fluorine by a greater margin than that by which *meta*-fluorine exceeds *meta*-chlorine, and that the difference between *ortho*-chlorine and *ortho*-fluorine is unlikely to affect this relationship. This leads to the conclusion that in aromatic  $S_N$  reactions the pentachlorophenyl group is more activating than the pentafluorophenyl group, and this view is supported by the known greater acidity of pentachlorophenol<sup>9</sup> than of pentafluorophenol.<sup>10</sup>

TABLE I  
COMPARATIVE KINETIC DATA FOR REPLACEMENT OF FLUORINE IN ArF COMPOUNDS  
BY METHOXIDE ION IN METHANOL AT 50°

Parameter	Ar in ArF		
	C <sub>6</sub> H <sub>5</sub> *	C <sub>6</sub> F <sub>5</sub> †	C <sub>6</sub> Cl <sub>5</sub>
Rate constant $k_2$ (l. mole <sup>-1</sup> sec <sup>-1</sup> )	$2.16 \times 10^{-12}$	$3.01 \times 10^{-4}$	$3.34 \times 10^{-3}$
Rate ratios	1 (—)	$1.39 \times 10^8$ (1)	$1.54_5 \times 10^9$ (11.1)
Hammett‡ substituent constant ( $\sigma^-$ )	0	0.976§	1.217
$\Delta E^\ddagger$ (kcal mole <sup>-1</sup> )	34.9	20.4	18.9
$\log_{10} B$	11.9 <sub>5</sub>	10.2 <sub>5</sub>	10.3 <sub>5</sub>
$\Delta S^\ddagger$ (e.u.)	-6.0	-13.8	-13.3
$T\Delta S^\ddagger$ (kcal mole <sup>-1</sup> )	-1.9 <sub>5</sub>	-4.5	-4.3
$\Delta G^\ddagger$ (kcal mole <sup>-1</sup> )	36.5 <sub>5</sub>	24.9	23.2

\* Bolto, B. A., Liveris, M., and Miller, J., *J. chem. Soc.*, 1956, 750; Miller, J., *Aust. J. Chem.*, 1956, 9, 61.

† Ref. 1.

‡ Using Hammett reaction constant ( $\rho$ ) = 7.55 (see Miller, J., *Aust. J. Chem.*, 1956, 9, 61).

§ Using ‡th rate ratio (=  $2.32 \times 10^7$ ) for statistical reasons (see text).

|| Equal to  $\Delta H^\ddagger$  in these solution reactions.

With first row nucleophiles in protic solvents the mobility of aromatic fluorine is substantially greater than that of chlorine,<sup>11</sup> the mobility ratio being of the order of  $10^3$  with methoxide ion, so that with one mole of reagent only replacement of

<sup>4</sup> Ingold, C. K., "Structure and Mechanism in Organic Chemistry." Ch. II. (G. Bell: London 1953.)

<sup>5</sup> Miller, J., and Wrightson, J. M., Abstr. 112th Meeting Am. chem. Soc., 1947, 16J.

<sup>6</sup> Heppollette, R. L., and Miller, J., *J. Am. chem. Soc.*, 1953, 75, 4265.

<sup>7</sup> Heppollette, R. L., Liveris, M., Lutz, P. G., Miller, J., and Williams, V. A., *Aust. J. Chem.*, 1955, 8, 454.

<sup>8</sup> Bolto, B. A., Heppollette, R. L., Leung, H. W., Miller, J., Parker, A. J., and Williams, V. A., unpublished data.

<sup>9</sup> Tiessens, G. J., *Recl. Trav. chim. Pays-Bas Belg.*, 1929, 48, 1068.

<sup>10</sup> Forbes, E. J., Richardson, R. D., Stacey, M., and Tatlow, J. C., *J. chem. Soc.*, 1959, 2019.

<sup>11</sup> Miller, J., *Rev. pure appl. Chem.*, 1951, 1, 171; Bolto, B. A., and Miller, J., *Aust. J. Chem.*, 1956, 9, 74, 304; Miller, J., and Parker, A. J., *J. Am. chem. Soc.*, 1961, 83, 117; Miller, J., *J. Am. chem. Soc.*, 1963, 85, 1628; Miller, J., and Wong, K. W., *Aust. J. Chem.*, 1965, 18, 117; Hill, D. L., Ho, K. C., and Miller, J., *J. chem. Soc. B*, 1966, 299.

fluorine occurs in reaction with pentachlorofluorobenzene. The predicted relationship can then be readily confirmed by comparing the mobility of fluorine in this compound with hexafluorobenzene, which has already been reported.<sup>1,12</sup> Hammett substituent constants for the halogenophenyl group may be obtained by further comparison with fluorine mobility in fluorobenzene.<sup>13</sup> The experimental data are given in Table 1.

The relative reactivity  $C_6Cl_5F/C_6F_6$  is 11.1 at 50°. Allowance for there being six equivalent replaceable fluorine atoms in hexafluorobenzene and only one in pentachlorofluorobenzene leads to the relative group activating power  $C_6Cl_5/C_6F_5 = 66.6$ . This results from the relative activating power  $p\text{-Cl} > p\text{-F}$  substantially exceeding  $m\text{-F} > m\text{-Cl}$ ,<sup>5-8</sup> and being unchanged by the effects in the *ortho* position. The difference in reactivity of 11.1 is due entirely to a lower value of  $\Delta E^\ddagger$  in pentachlorofluorobenzene, the values of  $\log_{10} B$  being the same as in hexafluorobenzene within experimental error. Like the pentafluorophenyl group, the pentachlorophenyl group is therefore powerfully activating. The Hammett substituent constants ( $\sigma^-$ ) for  $C_6F_5$  and  $C_6Cl_5$  groups obtained by comparisons with fluorobenzene are 0.976 and 1.217 respectively, the  $C_6Cl_5$  group being about as activating as *ortho*- or *para*- $C_6H_4NO_2$  groups, values for which at 50° are 1.219 and 1.270 respectively.<sup>14</sup>

<sup>12</sup> Burdon, J., Hollyhead, W. B., and Patrick, C. R., *J. chem. Soc.*, 1964, 4663.

<sup>13</sup> Bolto, B. A., Liveris, M., and Miller, J., *J. chem. Soc.*, 1956, 750; Miller, J., *Aust. J. Chem.*, 1956, 9, 61.

<sup>14</sup> Miller, J., *J. chem. Soc.*, 1952, 3552; Miller, J., and Wan, K. Y., *J. chem. Soc.*, 1963, 3492.