655. *The S_N Mechanism in Aromatic Compounds. Part XXIX.*[1] *Some* para-*Substituted Chlorobenzenes.*

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Measurements of the rate of methanolysis of four *para*-substituted chlorobenzenes (*p*-Cl, *p*-CF_3, *p*-Ac, *p*-NO_2) have been made. By use of the Hammett equation the rates and Arrhenius parameters for methanolysis of chlorobenzene have been estimated; direct measurement is unsatisfactory since reaction is very slow; the rate constant may be estimated, even at the critical temperature of methanol (232°), as only $6{\cdot}55 \times 10^{-7}$ l. mole^{-1} sec.$^{-1}$.

By relation to fluorobenzene, a high F/Cl rate replacement ratio is found, typical of aromatic S_N reactions with first-row nucleophiles in protic solvents.

CHLOROBENZENE reacts very slowly with methoxide in methanol even near the critical temperature (232°),[2] and direct measurements are unsatisfactory except perhaps when radioactive tracers are used. The rate constant is, however, required, for example, for discussions of relative reactivity[4] of fluoro-[5,6] and other halogeno-benzenes, and in gauging the effects of replacing carbon atoms of a benzene ring by heteroatoms. In view

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[1] Part XXVIII, Liveris and Miller, preceding paper.
[2] Golik and Ravikovich, *Dopovidi Akad. Nauk Ukrain. R.S.R.*, 1950, 101.
[3] Liveris and Miller, *Chem. and Ind.*, 1957, 954.
[4] Beckwith, Miller, and (in part) Leahy, *J.*, 1952, 3552 and subsequent papers.
[5] Bevan and Bye, *J.*, 1954, 3091.
[6] Bolto, Liveris, and Miller, *J.*, 1956, 750.

of the general reliability of the Hammett equation [7-9] in simple unhindered systems, the reaction of a series of compounds (p-Cl·C_6H_4X) with methoxide in absolute methanol has been measured for this purpose and for general information on aromatic S_N reactions.

Hammett substituent constants are already known for the substituents chosen and have already been used for aromatic S_N reactions with methoxide ion.[9] From the experimental rate constants and activation energies, rate constants at a number of standard temperatures have been calculated, and at each a Hammett plot has been drawn and extrapolated to $\sigma^* = 0$. From these values at the different temperatures, values of E_{act} and $\log_{10} B$ have been estimated for methanolysis of chlorobenzene.

EXPERIMENTAL

Materials.—p-*Chlorobenzotrifluoride*. The commercial product, purified by distillation, had b. p. 138°/750 mm. (lit.,[10] 139·8°/770·5 mm.).

4-*Chloroacetophenone*. Prepared from chlorobenzene by the Friedel–Crafts reaction as described by Noller and Adams,[11] this had m. p. 20·5° (lit.,[11] 20—21°)

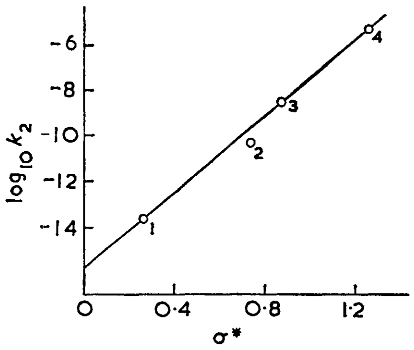

FIG. 1. Hammett plot for methanolysis of 4-substituted chlorobenzenes at 50°. 1, Cl. 2, CF_3. 3, Ac. 4, NO_2.

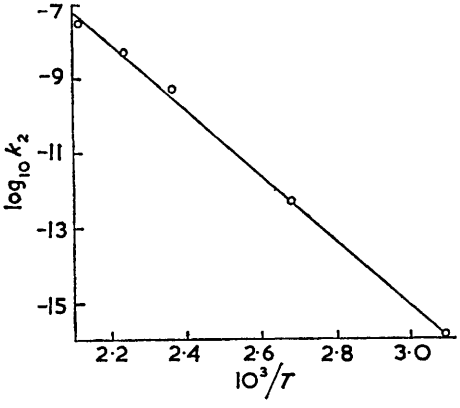

FIG. 2. Activation energy plot for chlorobenzene (k_2 values from Hammett plots).

p-*Dichlorobenzene*. The commercial product was purified by sublimation at reduced pressure and had m. p. 53° (lit., 53°,[12] 54° [13]).

Products.—All are known compounds.

Kinetic Procedure.—Runs were carried out with equimolar concentrations of chloro-compound and sodium methoxide in absolute methanol. Rate constants (k_2) were obtained by graphical plots after estimation of chloride ion potentiometrically in aliquot parts quenched in an excess of dilute chloride-free nitric acid. The values of activation energy (E_{act}) were determined from plots of $\log_{10} k_2$ against the reciprocal of temperature, and from them the values of $\log_{10} B$ and S_{act} were computed. Estimated errors based on reproducibility of rates to ±2% are E_{act} ±0·5 kcal. mole^{-1}, $\log_{10} B$ ±0·4, S_{act} ±1·3 e.u. Oil-bath or aluminium-block thermostats were used and runs carried out in bomb tubes of the type described by Daly and Miller.[14] Values of rates for p-chloronitrobenzene are taken from Miller's results.[15] The Hammett plot at 50° is shown as Fig. 1. The E_{act} plot for chlorobenzene is shown as Fig. 2.

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[7] Hammett, *J. Amer. Chem. Soc.*, 1937, **59**, 96; *Trans. Faraday Soc.*, 1938, **34**, 156.
[8] Jaffe, *Chem. Rev.*, 1953, **53**, 191.
[9] Miller, *Austral. J. Chem.*, 1956, **9**, 61.
[10] Borth, Elsey, and Burchfield, *J. Amer. Chem. Soc.*, 1935, **57**, 2066.
[11] Noller and Adams, *J. Amer. Chem. Soc.*, 1924, **46**, 1895.
[12] Errera, *Phys. Z.*, 1926, **27**, 766.
[13] Sugden, *J.*, 1924, **125**, 1167.
[14] Daly and Miller, *Chem. and Ind.*, 1961, 826.
[15] Miller, *J.*, 1952, 3550.

Kinetic data are tabulated. For *p*-dichlorobenzene, for symmetry reasons, the rate constants were halved in making calculations.

Rate constants and some derived parameters for reaction of sodium methoxide in methanol with *p*-substituted chlorobenzene.

k_2 (l. mole^{-1} sec.$^{-1}$) at temperatures shown in parenthesis

				(*b*) Calculated at					
4-Subst.	(*a*) Experimental			50°	100°	200°	E_{act}	$\log_{10} B$	S_{act}
Cl	3·86 × 10^{-6} (195·4°) 1·00; 1·015 × 10^{-5} (207·6°)	6·95; 6·96 × 10^{-5} (203·3°)		4·55 × 10^{-14}	1·17 × 10^{-10}	5·39 × 10^{-6} *	37·6$_5$	11·8 [11·5] †	−6·70 [−8·07] †
CF_3	1·36 × 10^{-5} (159·6°)	1·92 × 10^{-5} (161·8°)	5·56 × 10^{-5} (176·7°)	5·46 × 10^{-11}	3·91 × 10^{-8}	3·10 × 10^{-4}	31·5	11·0$_5$	−10·1
	6·60 × 10^{-5} (178·0°)	7·22 × 10^{-5} (179·2°)	1·50 × 10^{-4} (189·0°)						
Ac	3·18 × 10^{-4} (159·5°)	3·56 × 10^{-4} (160·8°)	5·35 × 10^{-4} (164·9°)	3·22 × 10^{-9}	1·43 × 10^{-6}	5·88 × 10^{-3}	29·2	11·2$_5$	−9·21
	6·66 × 10^{-4} (169·0°)	9·75 × 10^{-4} (173·2°)	1·13 × 10^{-3} (175·3°)						
NO_2	8·12; 8·68 × 10^{-5} (71·0°) 1·37$_5$; 1·37$_5$ × 10^{-3} (100·8°)	2·35 × 10^{-4} (81·6°)		8·47 × 10^{-6}	1·28 × 10^{-3}	1·21 × 10^{-0}	24·0$_5$	11·2	−9·44
H	—	—	—	1·20 × 10^{-16}	5·01 × 10^{-13}	3·39 × 10^{8} ‡	39·9$_5$	11·1	−9·90

* For the Hammett plot half these values were used. † Values of $\log_{10} B$ and S_{act} corresponding to half-rate constant values. ‡ From Hammett plots of the other compounds at these temperatures extrapolated to $\sigma^* = 0$.

DISCUSSION

Aromatic substitutions are very sensitive to substituent effects, particularly for single substituents,[8,9] and aromatic S_N reactions have been shown to fit the Hammett equation well.[9] By using σ^* values quoted by Miller [9] and measurements reported here, it is simple to compute values of ρ for methanolysis of p-substituted chlorobenzenes and k_2 for chlorobenzene (from $\sigma^* = 0$ for H as substituent) at different temperatures.

In each case it is found the CF_3 point is somewhat off an otherwise reasonably straight line (cf. Fig. 1) obtained from points of the other three compounds. At 50°, for example, $\rho = 8{\cdot}47$, as compared with $\rho = 7{\cdot}55$ for monosubstituted fluorobenzenes,[9] while k_2 is estimated to be $1{\cdot}20 \times 10^{-16}$. Values of k_2 computed by extrapolation at 100°, 150°, 175°, and 200° are $5{\cdot}01 \times 10^{-13}$, $5{\cdot}01 \times 10^{-10}$, $5{\cdot}25 \times 10^{-9}$, and $3{\cdot}39 \times 10^{-8}$, respectively. From the five values a satisfactory $\log_{10} k_2$–reciprocal temperature plot is obtained, giving $E_{\text{act}} = 39{\cdot}9_5$, and correspondingly $\log_{10} B = 11{\cdot}1$ and $S_{\text{act}} = -7{\cdot}92$. The values are very satisfactory in relation to the other four compounds. After allowance for symmetry in *p*-dichlorobenzene by reducing $\log_{10} B$ by 0·3 unit, frequency factors are all within the range $11{\cdot}0_5$—11·5. Such values are normal for aromatic S_N reactions in unhindered cases and are essentially constant (within experimental error).

In comparison with fluorobenzene the F/Cl rate replacement ratio is similar to that in *p*-halogenonitro- and 1-halogeno-2,4-dinitro-benzenes, but opposite to that in aliphatic S_N reactions. It is clear, therefore, that the transition states for all these aromatic series are similar. The order F > Cl is determined by electronegativity [15-17] and not bond strength, even in the unsubstituted halogenobenzenes; and as with the common aromatic S_N reactions this is taken as indicating that reaction proceeds through an intermediate complex with transition state 1 (bond formation) [16] rate-determining.

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[16] Miller, *J. Amer. Chem. Soc.*, 1963, **85**, in the press.

[17] Bolto and Miller, *Austral. J. Chem.*, 1956, **9**, 74, 304; Bolton, Miller, and Parker, *Chem. and Ind.*, 1960, 1026; Parker and Read, *J.*, 1962, 9.

From an attempt at 202·5° to make direct measurements of the methanolysis of chlorobenzene, Liveris and Miller estimated k_2 to be more than 10^{-7} but less than 10^{-6}, and quoted[3] the latter as a very crude estimate, since even that, giving the order F > Cl and a F/Cl rate replacement rate ~100, was in marked contrast with a report by Tronov and Kruger[18] giving the rate replacement ratio PhF/PhCl as 0·55. It appears that Liveris and Miller's crude estimate was high, the calculated value of k_2 at 202·5° being $\sim 5 \times 10^{-8}$

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[18] Tronov and Kruger, *J. Russ. Phys. Chem. Soc.*, 1926, **58**, 1270; *Chem. Abs.*, 1927, **21**, 3887.