

7. *Homolytic Aromatic Substitution. Part III.* Ratio of Isomerides formed in the Phenylation of Chlorobenzene. Competitive Experiments on the Phenylation of p-Dichlorobenzene and 1 : 3 : 5-Trichlorobenzene. Partial Rate Factors for Chlorobenzene.*

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The proportions of the three isomeric chlorodiphenyls formed in the phenylation of chlorobenzene by means of both benzoyl peroxide and the Gomberg reaction have been determined. Together with the results reported in Part II,* these provide a direct assessment of the partial rate factors for the phenylation process. The three nuclear positions are activated slightly towards attack by phenyl radicals, the sequence of the partial rate factors being $o > p > m$. A brief comparison of these results with theoretical predictions is made. Competitive experiments have been carried out on the action of phenyl radicals derived from benzoyl peroxide on mixtures of *p*-dichlorobenzene and of *s*-trichlorobenzene with nitrobenzene, and the relative rates of phenylation of the polysubstituted benzenes so obtained are compared with values for the same quantities calculated from the partial rate factors for chlorobenzene on the assumption that the substituents contribute additively and independently to the energy of activation for substitution at any one position.

In Part II * was reported the determination by direct and indirect methods of the rate of attack by phenyl radicals on chlorobenzene relatively to that on benzene. This quantity, $\frac{\text{PhCl}}{\text{PhH}}K$, enables a complete specification to be made of the influence of the substituent chlorine atom on the homolytic substitution reaction in terms of the partial rate factors for the *o*-, *m*-, and *p*-positions, provided that the ratio of isomerides formed in the phenylation of chlorobenzene is known. Analytical methods based on the isolation of the individual isomerides are fundamentally unsuitable for use in the determination of the composition of the mixture of isomerides, since the large differences in solubility prevent assessment of the amounts present. In particular, in comparing the results of the present determinations with those of previous preparative experiments (Grieve and Hey, *J.*, 1934, 1797; Hey, *ibid.*, p. 1966; Butterworth, Heilbron, Hey, and Wilkinson, *J.*, 1938, 1386; France, Heilbron, and Hey, *ibid.*, p. 1364; Heilbron, Hey, and Wilkinson, *J.*, 1938, p. 113; Hey and Waters, *J.*, 1948, 882), it is apparent that the loss of the 2- and the 3-isomeride is much more serious than that of the 4-isomeride, and the orienting influence of the chlorine atom given by such experiments is liable to serious distortion (cf. Waters, *J.*, 1948, 727). Hence, in the present determination, no attempt has been made to isolate the individual isomerides from the mixture obtained in the phenylation reaction, but, rather, the mixture has been analysed by comparison of its infra-red spectrum with the spectra of the three pure isomerides, which were prepared independently. The proportions so obtained are very much more reliable than any obtained previously, and the accuracy of the determination is of the order of $\pm 2\%$.

It has been shown (Bradfield and Jones, *Trans. Faraday Soc.*, 1941, 37, 726; Bird and Ingold, *J.*, 1938, 918), for heterolytic (electrophilic) substitution, that the effect of substituents is concerned mainly with the energy of activation for substitution at the various positions in the nucleus, and that the frequency factor is substantially independent of the nature of the directing substituent. The same conditions are probably fulfilled in homolytic aromatic substitution, and such an assumption is implicit in theoretical treatments of organic reactivity towards free radicals (cf. Brown, *J.*, 1950, 691, 2730, 3249; 1951, 1612, 1950).

If the partial rate factors for *o*-, *m*-, and *p*-substitution in a monosubstituted benzene derivative PhX are F_o , F_m , and F_p , respectively, then, provided the two substituents contribute additively and independently to the activation energy for substitution at any

* Part II, *J.*, 1952, 2094.

given position, the relative rate of substitution in the disubstituted compound $p\text{-C}_6\text{H}_4\text{X}_2$ is given by

$$p\text{-C}_6\text{H}_4\text{X}_2K = \frac{1}{8}(4F_oF_m) \quad \dots \quad (1)$$

since in this compound four equivalent positions are available for substitution, each of which is *ortho* with respect to one substituent X, and *meta* with respect to the other. In the compound 1:3:5- $\text{C}_6\text{H}_3\text{X}_3$ there are three equivalent positions available for substitution, each of which is *ortho* with respect to two of the substituents X, and *para* with respect to the third. The relative rate of substitution in this compound is therefore given by

$$s\text{-C}_6\text{H}_3\text{X}_3K = \frac{1}{6}(3F_o^2F_p) \quad \dots \quad (2)$$

Thus, comparison of the measured values of the above two quantities K with the values obtained from equations (1) and (2) by substitution of the measured values of F_o , F_m , and F_p for chlorobenzene affords a check on the assumption of the additivity of substituent effects, on the basis of which these relations are derived.

EXPERIMENTAL METHODS AND RESULTS

Preparation of Mixtures of Isomeric Chlorodiphenyls.—(i) *Gomberg reaction.* Redistilled aniline (15.5 g.; 1/6 mole) was dissolved in a warmed mixture of water (13 ml.) and hydrochloric acid (35 ml.). When cooled, the resulting suspension of the hydrochloride was diazotised at 5° with sodium nitrite (13 g.) in water (24 ml.). Chlorobenzene (200 ml.) was added to the diazotised solution, and the mixture was stirred vigorously while 5*N*-sodium hydroxide (ca. 40 ml.) was added dropwise, and then for a further 10 hours. In experiment (a) the mixture was acidified; much tar separated, and the organic material was extracted with benzene. In experiment (b) the organic layer was separated directly from the aqueous alkali. After being dried (CaCl_2), the solutions were distilled, and the products collected as orange-coloured oils, b. p.s (a) 82–120°/0.1 mm., (b) 82–160°/0.1 mm. These distillations, and all subsequent distillations mentioned in this paper, were carried out with great care, the apparatus and techniques described in Part II (*loc. cit.*) being used. The yields obtained are given in Table I. Product (a) was redistilled. Product (b) was dissolved in benzene, and when light petroleum (b. p. 60–80°) was added to the solution a small quantity of flocculent material was precipitated. This was redissolved by gentle warming, and the solution was passed through a short alumina column, and eluted with benzene–light petroleum (b. p. 60–80°). The mixture of isomerides was obtained by distillation of the eluate, a little involatile resin remaining. Both products were divided into two portions, one of which was repeatedly washed in light petroleum solution with small quantities of concentrated sulphuric acid to remove the orange colour. The solutions were then washed with aqueous sodium hydrogen carbonate and water. In each case the spent acid and aqueous washes were extracted with light petroleum (b. p. 60–80°), and the extracts combined with the main petroleum solutions. These were dried (Na_2SO_4) and distilled. The mixtures of isomerides were obtained as colourless oils. Very little material was lost as a result of this treatment (Table I). From each experiment two mixtures (one orange and the other colourless) were thus obtained for analysis (a,1), (a,2), (b,1), and (b,2). Mixtures (a,2) and (b,2) were those which had been treated with sulphuric acid, and were therefore colourless.

The differences in yields are thought to be due to the different procedures used for the separation of the organic and the aqueous phases in the preparation. Some tar had separated in (a) but not in (b), owing to the acidification of (a), and any coprecipitation of chlorodiphenyls with the tar would reduce the yield of final product.

TABLE I.

Expt.	Product, g.	Yield, %	H_2SO_4 treatment	
			Wt. treated, g.	Wt. of product, g.
(a)	2.940	15.6	1.847	1.672
(b)	6.200	32.8	2.408	2.200

(ii) *Peroxide reaction.* The standardised procedure outlined in Part II (*loc. cit.*) was used for the isolation of the diaryl fraction from the products of reactions (c), (d), and (e). In experiment (c), 9 g. of benzoyl peroxide and 300 ml. of chlorobenzene were used, and in experiments (d) and (e), 6 g. and 200 ml., respectively. A portion of product (e) was chromatographed before redistillation; hence two portions (e,1) and (e,2) were obtained, one of which had

been chromatographed. In each case a high-boiling resin was collected at 0.1 mm. (bath-temp. 200—350°). The combined resin was refluxed for 12 hours with 2.5N-sodium hydroxide in 50% aqueous ethanol. The solution was then extracted with warm benzene after the alcohol had been distilled off. 0.39 G. of benzoic acid was isolated from the aqueous solution and the resin was fractionally distilled out from the dried benzene extract. The resin was a yellow glassy solid, b. p. 194—250°/17 mm., as the main product. This was redistilled, and the middle fraction collected and shown by analysis to consist mainly of chloroterphenyls (Found : C, 82.4; H, 5.2; Cl, 12.8. Calc. for $C_{18}H_{13}Cl$: C, 81.7; H, 4.2; Cl, 13.4%). The formation of resins in this reaction was expected in the light of the experience of their formation gained in the competitive experiments with benzene and chlorobenzene, and with chlorobenzene and pyridine (see Part II, *loc. cit.*). The results are summarised in Table 2.

TABLE 2.

Expt.	Diaryl fraction, g.	Resin, g.	Benzoic acid, g.	(Ph·CO ₂) ₂ accounted for, %
(c)	3.770	3.783	2.14	88.5
(d)	2.360	2.692	1.45	90.2
(e)	2.487	2.329	1.44	86.0

Spectrographic Analysis.—For the infra-red spectrographic analysis of the mixtures of 2-, 3-, and 4-chlorodiphenyl a Grubb Parsons instrument was used with an automatic pen recorder. In order to determine the range in which the suitable absorption bands of the chlorodiphenyls lay and so to enable a choice of solvent to be made, the spectra of the three pure isomerides were taken. The 2- and the 4-isomeride were used as crystalline powders in Nujol mulls, and the liquid 3-chlorodiphenyl as a capillary film between rock-salt plates. The 3- and the 4-isomeride possessed characteristic bands in the region 11—15 μ . The corresponding band for the 2-isomeride was very close to a strong band common to all three and, consequently, was of no use for quantitative analysis. Nitromethane, which has no pronounced absorption bands in this region, was used as solvent. Its spectrum was first recorded in a 130- μ cell, the speed of the wave-length scanning and of the slit closing being adjusted so that, as nearly as possible, the energy of transmission recorded was constant over the required range.

The spectra of the solutions under examination were then taken, under strictly reproducible conditions. The "calibration" spectra of the three pure isomerides were obtained by using solutions containing about 0.4 g./10 ml. In order to check the accuracy of the determination, the spectra of three test solutions (f), (g), and (h), containing known amounts of the pure isomerides, were taken, and their compositions calculated from the spectra by the procedure outlined below. The results are given in Table 3.

TABLE 3. Analysis of mixtures of chlorodiphenyls.

Solution	Known compositions, %			Compositions calc. from spectra, %		
	2-	3-	4-	2-	3-	4-
(f)	39.15	32.15	28.7	42.4	30.6	27.1
(g)	44.3	32.5	23.2	48.8	29.5	21.7
(h)	0	61.9	38.1	0	62.4	37.6

Finally, the spectra of the experimental mixtures (a,1), (a,2), (b,1), (b,2), (c), (d,1), (d,2), (e,1), and (e,2)* were taken, solutions containing about 1.5 g./10 ml. being used, and the compositions of the mixtures calculated by the procedure outlined below. The results are given

TABLE 4. Analysis of products obtained in phenylation of chlorobenzene.

Solution	Composition, %			Solution	Composition, %		
	2-	3-	4-		2-	3-	4-
(a,1)	64.5	21.3	14.2	(d,1)	61.4	25.0	13.6
(a,2)	65.8	20.5	13.7	(d,2)	57.6	27.1	15.3
(b,1)	63.4	22.7	13.9	(e,1)	60.3	25.9	13.8
(b,2)	64.5	22.2	13.1	(e,2)	59.5	27.0	13.5
(c)	62.8	24.6	12.6	Mean	62.2	24.0	13.8

in Table 4. The figure shows the spectra obtained for the three pure isomerides, and one experimental mixture (a,2), all corrected for background absorption (including solvent).

Calculation of Ratios of Isomerides.—The Beer-Lambert law, $-\log(I_t/I_i) = kc$, is assumed, where I_t and I_i represent respectively the transmitted and the incident radiation, k is the

* The solutions (d,1) and (d,2) arise from the fact that two separate analyses were performed on mixture (d).

product of the extinction coefficient and the cell thickness, and c is the concentration of the absorbing substance in moles/l. For a mixture of substances x , y , and z at concentration C_x , C_y , and C_z respectively, at a fixed wave-length (in practice the absorption peak of one of the substances x , y , and z),

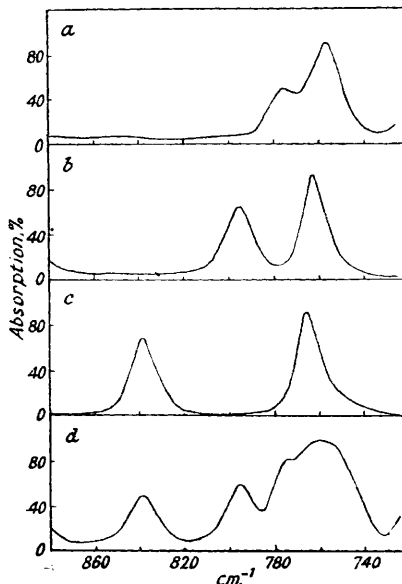
$$-\log(I_t/I_i) = k_1C_x + k_2C_y + k_3C_z = Y \quad (3)$$

Similarly, at another wave-length,

$$-\log(I_t/I_i) = k_4C_x + k_5C_y + k_6C_z = Z \quad (4)$$

The quantities Y and Z are obtained by measurement from the spectra of the mixture, and of the solvent, and the six values of k from the spectra of the pure substances at the wave-length

a, 2-Chlorodiphenyl (0.4065 g.).
 b, 3-Chlorodiphenyl (0.4005 g.).
 c, 4-Chlorodiphenyl (0.4111 g.).
 d, Mixture a,2 (1.4219 g.).
 All quantities per 10 ml. of nitromethane.
 Cell thicknesses, 130 μ .



concerned, by the use of the Beer-Lambert equation, the concentrations in these cases being known. Since the total weight X of the mixture to be analysed is equal to the sum of the weights of the individual isomerides composing the mixture,

$$C_x + C_y + C_z = X \quad (5)$$

By solution of the simultaneous equations (3), (4), and (5) the values of C_x , C_y , and C_z , and hence the composition of the mixture of isomerides, are obtained. The wave-lengths used for obtaining the quantities Y and Z were 795 and 839 cm^{-1} , which are the absorption maxima of the 3- and the 4-isomeride respectively.

Direct Determination of $p\text{-C}_6\text{H}_4\text{Cl}_2\text{K}$.—Benzoyl peroxide (6 g.) was allowed to decompose in an equimolar mixture (200 g.) of nitrobenzene and p -dichlorobenzene in a thermostat at 80° for 72 hours. The mixed product was isolated and analysed by estimation of the nitro-compound by titration with titanous chloride. The standard procedure described in Part II (*loc. cit.*) was employed. The results are given in Table 5.

TABLE 5.

Expt. no.	Diaryl fraction, g.	Nitro-diphenyl, %	Fore-run, g.	Cl, % in fore-run	Cor-rection $\text{Cl}_2\text{C}_6\text{H}_3\text{Ph}$, mg	Corr. wt. of diaryl fraction, g.	Nitro-diphenyl, % (corr.)	$p\text{-C}_6\text{H}_4\text{Cl}_2\text{K}$, %	$(\text{Ph}\cdot\text{CO}_2)_2$ accounted for, %
1	4.287	57.00	0.419	2.39	32	4.319	56.58	0.685	84.7
2	4.418	58.82	0.631	5.11	101	4.519	57.51	0.660	89.9

Hence, $p\text{-C}_6\text{H}_4\text{Cl}_2\text{K} = 0.672$

After a portion of the product had been used for the analysis, the remainder was warmed with a little light petroleum (b. p. 60—80°), in which the nitrodiphenyls are only sparingly soluble, and the yellow solution decanted from the remaining orange oil. This was repeated twice, and the combined petroleum extracts were washed four times with concentrated sulphuric acid. The spent acid was extracted with light petroleum, and the extracts were all added to the main petroleum solution. This colourless solution was washed with aqueous sodium hydrogen carbonate, and with water, and dried (Na_2SO_4). The solvent was then evaporated, and the remaining oil distilled (b. p. 157°/10 mm.; 112°/1 mm.; 100°/0.3 mm.). The 2 : 5-dichlorodiphenyl was obtained as a colourless oil (n_D^{20} 1.6167) in 37% yield (calc. on weight of benzoyl peroxide) (Found : Cl, 32.1. Calc. for $\text{C}_{12}\text{H}_8\text{Cl}_2$: Cl, 31.8%).

Direct Determination of $s\text{-C}_6\text{H}_4\text{Cl}_2\text{K}$.—Expts. 3 and 4 were carried out with benzoyl peroxide (5 g.) in an equimolar mixture of 1 : 3 : 5-trichlorobenzene (100 g.) and nitrobenzene (56.5 ml.), and Expt. 5 with benzoyl peroxide (5 g.) in a mixture of 1 : 3 : 5-trichlorobenzene (97 g.) and nitrobenzene (70 ml.), *i.e.*, a molar ratio of 1 : 1.2767. The agreement between the results of these experiments confirms the conclusion (Part II, *loc. cit.*) that the proportions in which the competing compounds are present have no effect on the relative rates derived from the competitive experiments. No fore-runs were collected in these experiments, since the b. p.s of 2 : 4 : 6-trichlorodiphenyl and the nitrodiphenyls are very similar. The results are in Table 6.

TABLE 6.

Expt. no.	Wt. of diaryl fraction, g.	Nitro-diphenyl, %	$s\text{-C}_6\text{H}_4\text{Cl}_2\text{K}$ PhNO_2K	($\text{Ph}\cdot\text{CO}_2$) ₂ accounted for, %
3	3.427	38.15	1.254	75.1
4	3.337	37.60	1.283	72.9
5	3.521	44.64	1.224	71.1

Hence, $s\text{-C}_6\text{H}_4\text{Cl}_2\text{K} = 1.25$.

2 : 4 : 6-Trichlorodiphenyl was isolated from the mixed product by the procedure employed above for the isolation of 2 : 5-dichlorodiphenyl. The b. p.s recorded in the final distillation were 172°/15 mm., 163°/10 mm., and 124°/1 mm. The colourless oil, obtained in 42% yield (calculated on the weight of benzoyl peroxide), solidified, and the solid was crystallised from dilute acetic acid to a constant m. p. of 62.5° (Found : C, 55.2; H, 2.8; Cl, 42.2. $\text{C}_{12}\text{H}_7\text{Cl}_3$ requires C, 56.0; H, 2.7; Cl, 41.3%).

Reagents.—Nitromethane (Light & Co.) was boiled under reflux in a stream of dry nitrogen, passed through an alumina column (30 × 3 cm.), dried (CaCl_2), and distilled through a 4-ft. helix-packed column (b. p. 101°/760 mm.). *p*-Dichlorobenzene (B.D.H.) was twice distilled through a similar column (b. p. 174°/760 mm.).

The preparation of 1 : 3 : 5-trichlorobenzene recorded in *Org. Synth.* (7, 592) was modified. 2 : 4 : 6-Trichloroaniline (175 g.) was dissolved in a warm mixture of 95% ethanol (1780 ml.) and benzene (469 ml.). Sulphuric acid (125 ml.) was added slowly, followed by powdered sodium nitrite (125 g.), added as quickly as possible. The mixture was stirred for 1 hour at room temperature and then boiled under reflux for a further 3 hours. Two such batches were combined at this stage. The mixture was filtered, and the filtrate diluted to *ca.* 12 l. with water and extracted several times with benzene (2500 ml. in all). The residue from the filtration was added to this benzene solution, which was then dried (CaCl_2). After removal of the benzene, the residue was distilled *in vacuo*, and the portion of b. p. 97—100°/17 mm. was collected. This was steam-distilled, distilled twice *in vacuo*, and finally crystallised from glacial acetic acid until constant m. p. (63°); the yield was 260 g. (88.7%).

2-, 3-, and 4-Chlorodiphenyl were prepared by means of the Gomberg reaction from *o*-, *m*-, and *p*-chloroaniline and benzene. The benzene layers, after separation, were washed with water and dried (CaCl_2). The solutions were distilled, and the fractions containing the chlorodiphenyls taken up in light petroleum (b. p. 40—60°) and washed repeatedly with concentrated sulphuric acid until the solutions were colourless. After being washed with aqueous sodium hydrogen carbonate and finally with water, the solutions were dried (Na_2SO_4) and distilled. The 2- and the 4-isomeride were recrystallised to constant m. p., and the 3-chlorodiphenyl, which was an oil, was redistilled until its refractive index did not change on redistillation. 2-Chlorodiphenyl was obtained in 13% yield as colourless needles (m. p. 33.5°) from aqueous ethanol. 3-Chlorodiphenyl was a colourless oil (b. p. 152°/11 mm.; n_D^{20} 1.6186) (yield 22%). 4-Chlorodiphenyl was obtained in 28% yield as colourless plates (m. p. 77°) from light petroleum (b. p. 60—80°).

DISCUSSION

Partial Rate Factors for Phenylation.—(i) *Chlorobenzene.* The relative rate of substitution in chlorobenzene, $\frac{\text{PhCl}}{\text{PhH}}K$, may be obtained from the values of $\frac{\text{PhCl}}{\text{PhNO}_2}K$ and $\frac{\text{PhNO}_2}{\text{PhH}}K$, both of which were determined as reported in Part II (*loc. cit.*), since

$$\frac{\text{PhCl}}{\text{PhH}}K = \frac{\text{PhCl}}{\text{PhNO}_2}K \times \frac{\text{PhNO}_2}{\text{PhH}}K$$

In this way, $\frac{\text{PhCl}}{\text{PhH}}K$ is found to be equal to 1.44. Using this value, and the mean values obtained by spectrographic analysis for the ratio of isomerides (Table 4), we obtain the following values for the partial rate factors:

$$\frac{\text{PhCl}}{\text{PhH}}F_o = 2.7; \quad \frac{\text{PhCl}}{\text{PhH}}F_m = 1.03; \quad \frac{\text{PhCl}}{\text{PhH}}F_p = 1.2$$

Thus, the *o*-position is activated to the greatest extent, the *p*-position slightly, and the *m*-position hardly at all. The *amounts* of the isomerides formed vary in the order $o > m > p$. This is an entirely unexpected result since, as pointed out on p. 44, preparative experiments had led to the isolation of the three isomerides in amounts varying in the order $p > o > (m)$. These partial rate factors may be compared with the corresponding quantities for heterolytic substitution (nitration), which were measured by Bird and Ingold (*J.*, 1938, 918). For that reaction $F_o = 0.030$, $F_m = 0.000$, and $F_p = 0.139$; $\frac{\text{PhCl}}{\text{PhH}}K$ was then equal to 0.0332.

(ii) *p-Dichlorobenzene and s-trichlorobenzene.* The rates of phenylation relative to benzene of *p*-dichlorobenzene and *s*-trichlorobenzene are obtained from the values of $\frac{p\text{-C}_6\text{H}_4\text{Cl}_2}{\text{PhNO}_2}K$ and $\frac{s\text{-C}_6\text{H}_3\text{Cl}_3}{\text{PhNO}_2}K$ (pp. 47, 48, respectively) by multiplication by 4, since $\frac{\text{PhNO}_2}{\text{PhH}}K$ is equal to 4 (Part II, *loc. cit.*). Thus, we obtain

$$\frac{p\text{-C}_6\text{H}_4\text{Cl}_2}{\text{PhH}}K = 2.7 \quad \text{and} \quad \frac{s\text{-C}_6\text{H}_3\text{Cl}_3}{\text{PhH}}K = 5.0$$

Hence, the partial rate factors for substitution at any position in *p*-dichlorobenzene and *s*-trichlorobenzene are 4.05 and 10.0, respectively. The values of the relative rates predicted from the effect of one chlorine atom on the three nuclear positions, which are obtained by substitution of F_o , F_m , and F_p in equations (1) and (2), are

$$\frac{p\text{-C}_6\text{H}_4\text{Cl}_2}{\text{PhH}}K = 1.8 \quad \text{and} \quad \frac{s\text{-C}_6\text{H}_3\text{Cl}_3}{\text{PhH}}K = 4.4$$

These are of the correct order of magnitude, showing that the assumption made on p. 44 with regard to the additivity of the effects of the substitution is true, at least as a first approximation.

Comparison with Theoretical Predictions.—Two of the quantities which have been used in the theoretical treatment of substitution reactions, namely, free valences (cf. Coulson, *Trans. Faraday Soc.*, 1946, 42, 265) and atom localisation energies (cf. Wheland, *J. Amer. Chem. Soc.*, 1942, 69, 900) are relevant to a discussion of homolytic reactivity. Both may be calculated by the molecular-orbital method, provided certain parameters are known or assumed. These parameters are the electronegativity of the hetero-atom, in this case chlorine, from which its Coulomb integral α_{Cl} may be estimated, and the resonance integral $\beta_{\text{C-Cl}}$ of the C-Cl bond. In addition, "auxiliary inductive parameters" are sometimes included in order to allow for the changes in the Coulomb integrals of $C_{(1)}$, $C_{(2)}$, and $C_{(6)}$ of the aromatic nucleus brought about by the inductive effect of the hetero-atom. Both the atom localisation energies and the free valences have been calculated for chlorobenzene, and it is of interest to compare the theoretical predictions with the experimental results.

Partial rate factors may be calculated from atom localisation energies by means of equation (6):

$$\log F = (A_r^\circ - A_r)/2.303RT \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where A_r is the atom localisation energy for homolytic substitution at the position to which F refers, and A_r° is the corresponding localisation energy at any position in benzene. By using the localisation energies calculated by Wheland (*loc. cit.*) and the currently accepted value of -34 kcal. for the standard bond integral, the following values are obtained for the partial rate factors for chlorobenzene :

$$F_o = 4.48; F_m = 1.32; F_p = 1.75$$

These values lead to the relative rate $\frac{\text{PhCl}}{\text{PhH}}K = 2.22$. The agreement with experiment is surprisingly good, especially when it is remembered that the partial rate factors depend exponentially on the small energy-difference $A_r^\circ - A_r$. It should be remembered also that the parameters used were chosen so as to predict correctly the observed phenomena of heterolytic substitution and the resonance moment of the compound. Wheland's calculations were also performed at a time when no quantitative data on homolytic reactivity were available. That the order of magnitude of these partial rate factors, in addition to the order of reactivity of the nuclear positions ($o > p > m$), are thus correctly predicted is regarded as a notable achievement.

Partial rate factors are related to free valences by the relation (7) (cf. Brown, *Quart. Reviews*, 1952, 6, 63),

$$\log F_r = 2x\beta(f_r - f_b)/2.303RT \quad . \quad . \quad . \quad . \quad . \quad (7)$$

where F_r is the partial rate factor of the r th position of the molecule, f_r is the free valence of that position, f_b is the free valence of any position in benzene, and $x\beta$ is the change in the resonance integrals $\beta_{rm}, \beta_{rn} \dots$ brought about by the reagent. Since $x\beta$ is not known, partial rate factors cannot be calculated directly from free valences. The necessary free valences, which are obtained from the bond-orders calculated by Sandorfy (*Bull. Soc. chim.*, 1949, 16, 615) are as follows :

$$f_o = 0.410; f_m = 0.400; f_p = 0.404; f_b = 0.398$$

Once again, it is seen that the order of reactivity ($o > p > m$) is correctly predicted, though the absolute magnitudes of the partial rate factors to which these calculations lead must remain unknown in the absence of knowledge of the changes in the resonance integrals $\beta_{rm}, \beta_{rn} \dots$ which accompany the reaction.

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