948. *A Quantitative Treatment of Electrophilic Aromatic Substitution.*

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Application of the Hammett equation to electrophilic aromatic substitution is found to be of only limited use because it fails to take into account the different extents of resonance interaction between the substituent and the aromatic system in the transition state in reactions where the reagent has different electronic requirements. A new equation is proposed in which the partial rate factor for substitution at the *para*-position of a monosubstituted benzenoid compound is related to three parameters which measure severally the electron density at the *para*-position in the ground state of the molecule, the polarisability of the substituent, and the electronic requirements of the reagent. The equation correlates accurately the available data for the nitration, chlorination, bromination, and protodesilylation of seven monosubstituted benzenes. The anomalous results that in nitration fluorobenzene is deactivated in the *para*-position, and t-butylbenzene is more strongly activated than toluene, receive experimental confirmation and can now be understood. The mean error in the values predicted by the equation for the partial rate factors in all these reactions is 15%.

THE reactivity of the side chain, X, in an aromatic compound of the type $R\cdot C_6H_4\cdot X$, where R is a *meta*- or *para*-substituent, has been found to obey the Hammett free-energy equation,[1] $\log (k/k_0) = \sigma\rho$, in several thousand reactions.[2] The possibility that this equation might also hold for electrophilic aromatic substitution seems first to have been examined by Pearson and his co-workers.[3] They found that the equation held fairly well if σ-values different from those which apply to side-chain reactions were employed for each group.

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[1] Hammett, " Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, 1940, Chapter VII.

[2] Jaffé, *Chem. Rev.*, 1953, **53**, 191.

[3] Pearson, Baxter, and Martin, *J. Org. Chem.*, 1952, **17**, 1511.

Roberts *et al.*[4] found that when the original σ-values were used in an attempt to correlate nuclear substitutions, large deviations occurred for *para*-substituents, and they concluded that this was because resonance interactions are present between the substituent group and the aromatic system in nuclear substitution to a larger extent than in side-chain reactions. The same conclusion was reached by Kochi and Hammond[5] from their measurements of the rates of solvolysis of *para*-substituted benzyl toluene-*p*-sulphonates. Brown and his associates[6] accordingly proposed that a new substituent constant, denoted by σ^+, should be used to correlate electrophilic substitutions according to the equation $\log (k/k_0) = \sigma^+\rho$. The new constant differed from the σ-constant by an amount depending on the resonance interaction between the substituent concerned and the aromatic ring in the transition state of the reaction. Brown *et al.*[7] later determined a large number of σ^+ values from measurements of the solvolysis rates of *meta*- and *para*-substituted cumyl chlorides, utilising the fact that the transition state in the rate-determining step of this reaction resembles that in aromatic substitutions. They showed that σ^+-values obtained in this way agreed well with the values found from aromatic substitutions, such as nitration and bromination,[8] and they extended their study of σ^+ values to a large number of electrophilic substitutions and to equilibria such as the ionisation of triarylmethanols in which resonance interaction occurs between an electron-deficient carbon atom and the *para*-substituent.[9] They showed that the σ^+-value of a particular group determined from a number of different reactions is essentially independent of the reaction, and suggested that there must be some fundamental property of substituent groups which is represented by the individual σ^+-constants.

Nevertheless, despite the success of Brown's treatment of aromatic substitution, there is evidence that a substituent cannot be represented by a single σ^+-value.[10,11] An examination of the σ^+-values quoted by Brown reveals that, although for some substituents σ^+ is effectively constant over a wide range of values of ρ, yet for other substituents there is a considerable variation in σ^+ with change in ρ. More significantly, the σ^+-value of a substituent decreases (or becomes increasingly negative) in a fairly regular manner as ρ becomes larger, having its largest positive value (or smallest negative value if it is negative in sign) when ρ has its smallest value. σ^+-Values for seven substituent groups are recorded in Table 1.[9]

TABLE 1. *Values of σ^+ calculated from various reactions and equilibria.*

Substit.	Ionisation of $Ar_3C{\cdot}OH$ $\rho = -3{\cdot}44$	Protonolysis of $Ar{\cdot}SiMe_3$ $\rho = -4{\cdot}32$	Solvolysis of $Ar{\cdot}CMe_2Cl$ $\rho = -4{\cdot}54$	Nitration $\rho = -6{\cdot}22$	Uncatalysed chlorination $\rho = -8{\cdot}06$	Uncatalysed bromination $\rho = -12{\cdot}14$
p-Me	−0·297	−0·305	−0·311	−0·278	−0·365	−0·278
p-Ph		−0·127	−0·179	−0·167		−0·262
p-OMe	−0·721	−0·736	−0·778			−0·826
p-F		+0·028	−0·073	+0·012	−0·100	
p-Cl		+0·201	+0·114	+0·133	+0·055	
p-Br		+0·231	+0·150	+0·152	+0·074	
p-CH_2Cl				+0·035	−0·062	

From an inspection of these figures it would be reasonable to assume that the σ^+-value of the methyl group is independent of ρ, the variation in the recorded values being due to experimental errors in the measurements from which these values were obtained. For the other six groups, however, there is reason to believe that the variations are not due to

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[4] Roberts, Sanford, Sixma, Cerfontain, and Zagt, *J. Amer. Chem. Soc.*, 1954, **76**, 4525.

[5] Kochi and Hammond, *J. Amer. Chem. Soc.*, 1953, **75**, 3445.

[6] McGary, Okamoto, and Brown, *J. Amer. Chem. Soc.*, 1955, **77**, 3037.

[7] Brown, Brady, Grayson, and Bonner, *J. Amer. Chem. Soc.*, 1957, **79**, 1897; Brown, Okamoto, and Ham, *ibid.*, p. 1906; Brown and Okamoto, *ibid.*, p. 1909.

[8] Brown and Okamoto, *J. Amer. Chem. Soc.*, 1957, **79**, 1913.

[9] Brown and Okamoto, *J. Amer. Chem. Soc.*, 1958, **80**, 4979.

[10] de la Mare, *J.*, 1954, 4450.

[11] Deno and Schriesheim, *J. Amer. Chem. Soc.*, 1955, **77**, 3051.

inadequacies in experimentation. In the first place, the changes in σ^+ with ρ, as a fraction of σ^+, are large: for chlorine and bromine the values vary over a range of about three times the lowest value recorded. Secondly, the variation is in almost every case in the same direction; for example, the largest negative values of σ^+ recorded for the phenyl and methoxyl substituents both occur in the reaction of largest ρ-value (uncatalysed bromination); and the smallest positive values for chlorine and bromine also occur in the reaction of largest ρ-value for which these groups have been examined (uncatalysed chlorination).

These variations in σ^+ seemed not to be random but rather to follow a trend. Further, we were puzzled by other observations of aromatic reactivities. For instance, fluorobenzene is deactivated in the *para*-position in nitration,[12] in chlorination by Cl^+,[13] and in protodesilylation,[14] but is activated in chlorination by molecular chlorine;[12] the *para*-position in toluene is more reactive than that in biphenyl in nitration but is less reactive in bromination by molecular bromine;[12] and the *para*-position in t-butylbenzene is more reactive than that in toluene in nitration[12] but is less reactive in chlorination and bromination by molecular halogens.[12] Yet the Hammett relation in the form used by Brown, $\log (k/k_0) = \sigma^+\rho$, requires that if one position is activated relative to another in one reaction, it will be activated in all reactions.

Before attempting to elucidate the reason for these discrepancies, we decided to confirm that two anomalies which seemed particularly pertinent to any new treatment of aromatic substitution were experimentally valid. These were: the deactivation of the *para*-position of fluorobenzene in nitration; and the greater reactivity, in nitration at the *para*-position, of t-butylbenzene than of toluene.

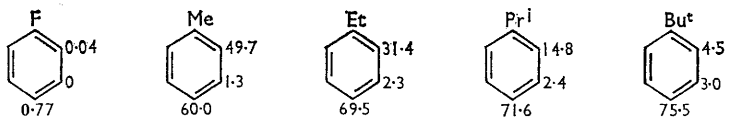
The partial rate factors for the nitration of fluorobenzene reported in the literature depend upon isomer ratios determined under preparative conditions[15] coupled with the value for the reactivity of fluorobenzene relative to benzene determined by Bird and Ingold.[16] We have determined new values for fluorobenzene, using fuming nitric acid in acetic anhydride solution at 25° as the nitrating agent, and gas chromatography for analysis. The results of the isomer distribution and overall reactivity experiments are recorded in Table 2, and the partial rate factors derived from them are set out in Table 3.

TABLE 2.

Substit.	Relative reactivity	Orientation (%) *o*-	*m*-	*p*-
F	0·14 ± 0·01 *	8·7	0	91·3
Me	1	61·4	1·6	37·0
Et	0·85 ± 0·08	45·9	3·3	50·8
Pr^i	0·65 ± 0·03	28·0	4·5	67·5
Bu^t	0·56 ± 0·03	10·0	6·8	83·2

* Relative to benzene, not toluene.

TABLE 3.



A comparison of the reactivities in nitration in aqueous acetic acid of toluene and t-butylbenzene has previously been reported, although no experimental details were

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[12] de la Mare and Ridd, "Aromatic Substitution," Butterworths Scientific Publications, 1959, p. 237.

[13] de la Mare, Ketley, and Vernon, *Research*, 1953, **6**, 12S.

[14] Eaborn, *J.*, 1956, 4858.

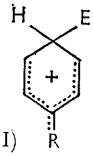
[15] Holleman, *Chem. Rev.*, 1925, **1**, 187.

[16] Bird and Ingold, *J.*, 1938, 918.

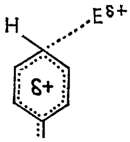
published.[17] We chose different conditions (nitration by fuming nitric acid in acetic anhydride solution at 0°) and studied both toluene and t-butylbenzene, and also ethylbenzene and isopropylbenzene, for which previously only isomer distributions in nitration have been reported.[18-20] Isomer distributions and overall reactivities relative to toluene are recorded in Table 2. When use is made of Ingold's value [21] of 27 for the reactivity of toluene relative to benzene under the same conditions as ours, the partial rate factors recorded in Table **3** are obtained.

Our results agree substantially with those obtained by previous investigators, and in particular confirm two of the anomalies mentioned above. We have confidence in our results on the relative reactivities of toluene and t-butylbenzene, not only because they were reproducible with high precision and agreed with results obtained previously, but also because the reactivities of the *para*-positions in the four alkylbenzenes which we examined show a steady trend ($\mathrm{Bu^t} > \mathrm{Pr^i} > \mathrm{Et} > \mathrm{Me}$), pointing to some feature governing the reactivities of these compounds in nitration which is not manifest in the Hammett equation.

We were prompted, both by these anomalies and by the trends apparent in σ^+, to re-examine the assumptions which underlie the application of the Hammett equation to electrophilic aromatic substitution. The difference between this type of reaction and the reaction at a side chain lies, as has been mentioned, in the greater resonance interaction between substituent and aromatic ring in the transition state for aromatic substitution than for side-chain reactions. If the Hammett equation is obeyed rigorously for side-chain reactions (as it appears to be), and is not obeyed rigorously for aromatic substitution, it is because this resonance interaction is not constant for a given substituent in different reactions. It has previously been suggested that the resonance interaction will vary markedly in different reactions so as to make it impossible to represent the effect of **a** substituent by a single constant.[5,11] Now, it is expected that the resonance interaction between substituent and aromatic ring will vary with the nature of the reaction for the following reason: if the transition state in an electrophilic aromatic substitution were always accurately represented by the structure of the Wheland intermediate, (I; where E = the attacking electrophile), then the extent of resonance in the transition state between R and the aromatic ring would be independent of the nature of the reaction and could be represented by a constant for each substituent. There is, however, evidence that in reactions of aromatic compounds with very reactive species, the transition state resembles (II) rather than (I),[22,23] the new covalent bond being only partly formed. It follows that the more reactive the reagent, the smaller is the resonance interaction of the substituent with the ring in the transition state. Since ρ is a measure of the reactivity of the reagent (a small numerical value of ρ indicating a very reactive reagent such as NO_2^+ and a large value indicating an unreactive reagent such as Br_2), it would be expected that the amount of resonance interaction in the transition state would increase with increasing



(I)



(II)

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[17] Cohn, Hughes, Jones, and Peeling, *Nature*, 1952, **169**, 291.
[18] Cline and Reid, *J. Amer. Chem. Soc.*, 1927, **49**, 3150.
[19] Brown and Bonner, *J. Amer. Chem. Soc.*, 1954, **76**, 605.
[20] Vavon and Callier, *Bull. Soc. chim. France*, 1927, **41**, 357.
[21] Ingold, Lapworth, Rothstein, and Ward, *J.*, 1931, 1959.
[22] Dewar, Mole, and Warford, *J.*, 1956, 3581.
[23] Mason, *J.*, 1958, 4329.

size of ρ. In other words, the potential of a substituent to accommodate the electron-deficiency of the transition state in an aromatic substitution is only fully realised when the transition state is closely similar in structure to the Wheland intermediate.

We therefore attempted to find whether there was some simple dependence of σ^+ upon ρ. No simple relation was apparent from the available data, and we approached the problem from a different aspect, which can be explained as follows. In an aromatic substitution in which the reagent is of extremely high reactivity, the transition state resembles the starting state, or ground state, of the aromatic compound. Thus there is no resonance interaction in the transition state which is not also present in the ground state of the molecule. Therefore the rate of reaction at the *para*-position of a benzenoid compound relative to the rate of reaction at any one position in benzene (*i.e.*, k/k_0, henceforward referred to as f_p, the partial rate factor for substitution at the *para*-position of the substituted benzene) will be governed by the ground-state electron densities and we may write a modified Hammett relation in the form:

$$\log_{10} f_p = \sigma_G\phi \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where σ_G is a measure of the ground-state density at the *para*-position in the compound relative to that at any carbon atom in benzene, and ϕ is a measure of the demand of the reagent for electrons in the transition state. On the other hand, if the reagent is less reactive, so that the transition state has a structure between the ground state and the Wheland intermediate, a resonance interaction between substituent and aromatic ring will be present, depending in extent on the degree to which the transition state resembles the Wheland intermediate. For such a reaction we may write:

$$\log_{10} f_p = \sigma_G\phi + \sigma_R\phi \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where σ_R, the resonance interaction, is itself dependent on ϕ, since ϕ provides a measure of the extent of formation of the Wheland intermediate at the transition state. Thus, $\sigma_R = \sigma_P f(\phi)$, where σ_P is the ability of the substituent to supply electrons by the resonance mechanism at the demand of the reagent; *i.e.*, σ_P measures a polarisability of the substituent. Equation (2) becomes:

$$\log_{10} f_p = \sigma_G\phi + \sigma_P f(\phi).\phi \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

We assumed that the function is a simple one, of the form ϕ^n. Then equation (3) is:

$$\log_{10} f_P = \sigma_G\phi + \sigma_P\phi^{n+1} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

σ_G, which measures the ground-state electron density at the *para*-position, is clearly related to the Hammett substituent constant, σ, and the two were at first taken to be identical. (This assumption receives further comment below.) Then, to evaluate n, an approximation, later shown to be justified, was made: *viz.*, that the t-butyl group is not polarisable, *i.e.*, $\sigma_P(\text{Bu}^t) = 0$. We then obtained ϕ for five reactions of t-butylbenzene for which rate data are known, using the Hammett σ-constant as σ_G for the Bu^t group.[24] The ϕ-values so derived are listed in Table 4. (For convenience in arguments presented below, opposite signs are given to the σ-constants used in this paper. Electron-releasing groups thus have positive σ-values and electron-attracting groups have negative values.) Equation (4) was then written in the form:

$$\log_{10} (\log_{10} f_P - \sigma_G\phi) = \log_{10} \sigma_P + (n + 1) \log_{10} \phi \quad . \quad . \quad . \quad . \quad (5)$$

and $\log_{10} (\log_{10} f_P - \sigma_G\phi)$ was plotted against $\log_{10} \phi$ for the *p*-Ph group, using the ϕ-values obtained from the reactions of t-butylbenzene and taking the Hammett σ-value for σ_G.[24]

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[24] McDaniel and Brown, *J. Org. Chem.*, 1958, **23**, 420.

The resulting graph is shown in Fig. 1. As required by equation (5) the graph is linear. The gradient is 2, so that $n = 1$, and equation (4) may be rewritten:

$$\log_{10} f_p = \sigma_G\phi + \sigma_P\phi^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

It emerges that the resonance effect, σ_R, is directly proportional to the parameter which measures the electronic demand of the reagent.

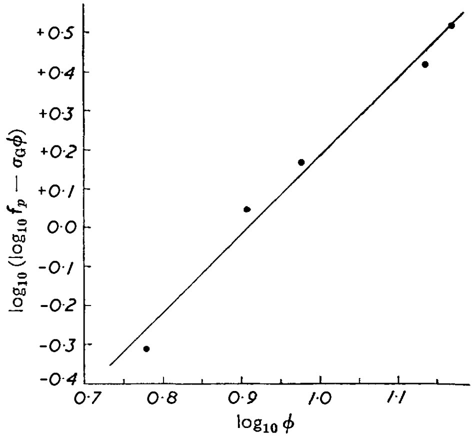
TABLE 4. *ϕ-Values derived from data for* t-*butylbenzene.*

Reaction	Protonolysis of p-$SiMe_3{\cdot}C_6H_4Bu^t$	Bromination by Br^+	Nitration	Uncatalysed chlorination	Uncatalysed bromination
$\log_{10} f_p$	1·19	1·59	1·88	2·70	2·88
ϕ	6·04	8·07	9·54	13·71	14·62

Values of $\log_{10} f_p$ for protodesilylation are taken from Eaborn's results,[14] and for the remaining reactions from the list compiled by de la Mare and Ridd.[12]

The choice of the p-Ph substituent should be explained. Only for the p-Me and p-Ph groups are data recorded in the literature for a number of electrophilic substitutions.

FIG. 1.



For the p-Me group the value of $(\log_{10} f_p - \sigma_G\phi)$ is invariably obtained as a small difference between two large quantities and is subject to large variations with small percentage errors in $\log_{10} f_p$, rendering it difficult to obtain a satisfactory graph. As will be seen below, this results from the very small polarisability of the p-Me group.

To test the validity and application of equation (6) it is necessary to obtain values of σ_G and σ_P for different substituents and values of ϕ for different reactions, and then to show that $\log_{10} f_p$ is correctly predicted for aromatic substitutions for which these parameters are known. For six substituents (Me, Ph, OMe, F, Cl, Br) we obtained values of σ_G and σ_P by writing equation (6) in the form:

$$\log_{10} f_p/\phi = \sigma_G + \sigma_P\phi$$

and plotting $\log_{10} f_p/\phi$ against ϕ. The values of σ_G and σ_P obtained from the intercept and gradient of the graph respectively depend on a number of different reactions and are more reliable parameters than ϕ, which was obtained from only one reaction in each case. By inserting the derived values of σ_P and σ_G into equation (6), mean values of ϕ for each reaction were determined. These values were used in turn to obtain new values of the sigma-parameters, and this procedure was repeated until self-consistent values of the three parameters were obtained. The final values of these parameters are recorded in

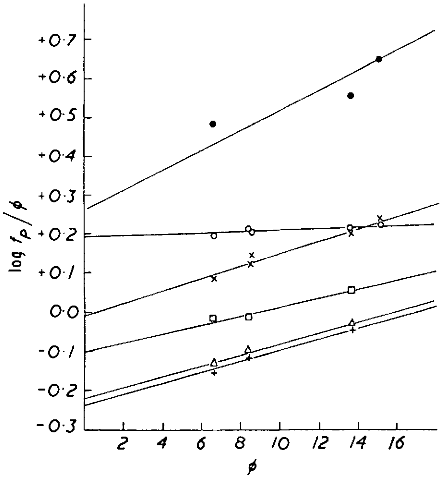
Table 5, and the graph from which the sigma-parameters for each substituent were obtained is shown in Fig. 2.

TABLE 5.

Reaction	Protonolysis of p-SiMe$_3$·C$_6$H$_4$R	Nitration		Bromination by Br$^+$	Uncatalysed chlorination	Uncatalysed bromination
ρ	6·6	8·4		8·5	13·7	15·1
Substit.	p-OMe	p-Me	p-Ph	p-F	p-Cl	p-Br
σ_G	+0·27	+0·19	−0·01	−0·10	−0·22	−0·235
$10^2\sigma_P$	2·55	0·2	1·6	1·11	1·35	1·35

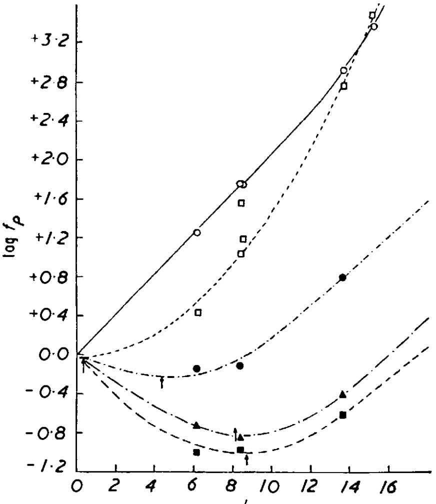
Equation (6) may now be tested. In Table 6 the values of $\log_{10} f_p$ predicted by the equation with the use of the three derived parameters are compared with the experimental values of $\log_{10} f_p$. An analysis shows that the equation predicts partial rate factors for substitution in the *para*-position (*i.e.*, f_p) with a mean error of 15%, which is surprisingly small since the range of reactivities is about 10^{12}.

FIG. 2.



X in PhX: ● = OMe, ○ = Me, X = Ph, □ = F, △ = Cl, + = Br.

FIG. 3.



X in PhX: ○ = Me, □ = Ph, ● = F, ▲ = Cl, ■ = Br.

TABLE 6. *Comparison of predicted and observed values of* $\log_{10} f_p$.*

Subst.	Protonolysis of p-SiMe$_3$·C$_6$H$_4$R		Nitration		Bromination by Br$^+$		Uncatalysed chlorination		Uncatalysed bromination	
	pd.	od.	pd.	od.	pd.	od.	pd.	od.	pd.	od.
p-OMe	2·89	3·18					8·48	7·6 [a]	9·89	9·80
p-Me	1·32	1·32	1·74	1·76	1·76	1·77	2·98	2·91	3·33	3·38
p-Bu^t	1·30	1·19	1·66	1·88	1·67	1·59	2·70	2·70	2·97	2·88
p-Ph	0·63	0·55	1·04	1·04 1·58	1·07	1·19	2·87	2·78	3·50	3·48
p-F	−0·18	−0·12	−0·06	−0·11 [b]			0·82	0·80		
p-Cl	−0·86	−0·87	−0·89	−0·85			−0·48	−0·40		
p-Br	−0·96	−1·00	−1·02	−0·96			−0·68	−0·60		

* pd. = predicted; od. = observed.

Observed values of $\log_{10} f_p$ for protodesilylation are taken from Eaborn's results,[14] and for the remaining reactions from the list compiled by de la Mare and Ridd,[12] except for b which is taken from our results. [a] This value is taken from unpublished work quoted in ref. 12.

Some interesting results of the application of equation (6) to aromatic substitution are revealed when experimental values of $\log_{10} f_p$ are plotted against ρ. Graphs for all the substituents we have studied save OMe and Bu^t are shown in Fig. 3. Each line must pass through the origin, since $f_p = 1$ when $\phi = 0$ (for this value of ϕ implies that the reagent is of infinite reactivity and therefore non-selective). The first feature of note is that the graph for toluene is very nearly linear, showing distinct curvature only at rather high values of ϕ. This reflects the very low polarisability of the methyl group. In a similar graph for the t-butyl group (not shown) it is difficult to detect any deviation from linearity. Herein lies justification for the assumption from which our equation was derived, namely, that the t-butyl group is non-polarisable. Equally, this original assumption is justified by the satisfactory correlation obtained from the equation.

Secondly, the lines for the substituents F, Cl, and Br have minima, and the curve for Ph is compatible with existence of a minimum. This is expected if equation (6) is applicable, for it is a property of this equation that a minimum value of $\log_{10} f_p$ occurs when $\phi = \sigma_G/2\sigma_P$, so that minima occur at positive values of ϕ for all substituents which have negative values of σ_G. The calculated minima for these substituents are illustrated on the graphs by arrows. The physical significance of the minima is this: for reagents of high reactivity, resonance between the substituent and the aromatic ring is not of much importance in the transition state, and those substituents with negative values of σ_G produce deactivated *para*-positions. With less reactive reagents, resonance between the substituent and aromatic ring becomes increasingly important, and the polarisability effect, which can only facilitate reactions, begins to outweigh in influence the unfavourable ground-state polarisation, so that the graph reaches a minimum and then rises. In this way the *para*-deactivation of fluorobenzene in protodesilylation and in nitration and its activation in chlorination are understood. This also leads us to expect that chlorobenzene will be activated relatively to benzene with reagents of very strong electron-demand. Likewise, the greater reactivity of the *para*-position in t-butylbenzene than in toluene in nitration reflects the relative ground-state electron densities in these two positions, a measure of which is provided by the σ-values of the two groups [$\sigma(p\text{-Me}) = -0{\cdot}170$; $\sigma(p\text{-Bu}^t) = -0{\cdot}197$ [24]].

Brown and McGary [25] have recently predicted that substitution of a monosubstituted benzene can be represented by a linear graph passing through the origin when $\log_{10} f_p$ is plotted against the selectivity factor, S_f, for each reaction. Both S_f and ϕ are measures of the electron-demand of the reagent and are therefore related, so on the basis of our results this prediction is incorrect since the plots of $\log_{10} f_p$ against ϕ are not straight lines and for polarisable substituents deviate considerably from linearity. de la Mare and Ridd [26] have previously pointed out that Brown's linear relation is not likely to be maintained by substituents such as phenyl which have conflicting inductive and electromeric effects. It is not surprising that Brown and Stock [27] obtained linear graphs for the reactions of toluene and t-butylbenzene because, as we have shown, both groups are virtually non-polarisable.

The Ground-state Polarisation Constant, σ_G.—It is apparent that the values of σ_G derived from this treatment are similar in numerical value, though of opposite sign, to the values of the Hammett σ-constant for the same *para*-substituent. The change in sign arises solely from our mathematical treatment and has no significance.* That the numerical values are similar was to be expected, for σ_G measures a ground-state electron

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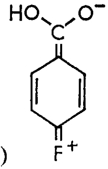
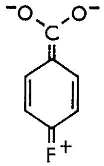
* The change is rendered necessary because, in equation (6), $\log_{10} f_p$ must always increase with increasing polarisability of the substituent. Thus $\sigma_P\phi^2$ must be positive and so, regardless of the sign of ϕ, σ_P must be positive. It is convenient that a group which releases electrons by virtue both of its permanent polarity and of its polarisability should have values of σ_G and σ_P of the same sign, or it would appear that the two effects were opposing each other. Hence σ_G is positive for an electron-releasing group. For an electron-attracting group σ_G is negative, and in this case the permanent polarisation brought about by the group and its polarisability do oppose each other.

[25] Brown and McGary, *J. Amer. Chem. Soc.*, 1955, **77**, 2300.
[26] Ref. 12, p. 242.
[27] Stock and Brown, *J. Amer. Chem. Soc.*, 1959, **81**, 3323; Brown and Stock, *ibid.*, p. 5621.

density and so does the Hammett σ-function. It was not, however, expected that the two values should coincide, for the Hammett σ-constant has usually been derived from reactions in which some resonance interaction occurs between the substituent group and the functional centre. Consider, for example, the derivation of the σ-value for the *p*-F group from the dissociation constant of *p*-fluorobenzoic acid. There is evidence that the benzene ring interacts by resonance with the carboxyl group to a greater extent than with the carboxylate ion, the acid being stabilised in this way by about 1 kcal. mole^{-1} more than the ion.[28] It is expected that the *p*-F substituent will interact more strongly with the carboxyl group than with the carboxylate ion for the same reason [*i.e.*, structure (III) will

(III)





(IV)

contribute more than structure (IV)], and this resonance interaction must reduce the acidity of *p*-fluorobenzoic acid. Thus the σ-value obtained from this acid dissociation constant will be less positive than if this particular interaction did not occur. (The bearing of interaction between substituent groups and the functional centre on σ-values has recently been examined in great detail by Van Bekkum, Verkade, and Wepster.[29]) Now, σ_G measures the electron density in a molecule in which no such *para*-resonance interaction occurs between substituent and functional centre because σ_G is obtained by extrapolation to zero interaction. Fluorobenzene is therefore expected to have a more positive value of σ_G than the values of σ obtained from acid dissociation constants and related reactions and equilibria. The difference in sign of the two scales of σ-values being borne in mind, this is what is found, for the σ-value from the dissociation constant of *p*-fluorobenzoic acid is $+0{\cdot}062$,[24] and from our treatment it is $-0{\cdot}1$. Again, the Ph group has a small negative σ-value, indicating weak electron-release to the *para*-position in *p*-phenylbenzoic acid,[24] whereas its small negative σ_G-value indicates resulting electron-attraction from the *para*-position when there is no resonance interaction between the phenyl group and the functional centre. This result is in accord with the deactivating effect of the *m*-Ph group in electrophilic substitutions.[12] Groups which withdraw electrons from the ring by the inductive effect but release them to the ring by the mesomeric effect will therefore appear to be more strongly electron-withdrawing when examined by our extrapolatory procedure than when their σ-values are determined from dissociation constants. Indeed, a better indication of the electron distribution in a benzenoid compound can probably be obtained by the method we have used, provided that enough experimental data are available for the substituent in question to enable an accurate extrapolation to be made.

The Polarisability Constant, σ_P.—The values of σ_P derived from equation (6) require two comments. First, the methyl group is essentially non-polarisable. Its σ_P-value is less than one-fifth of that of any other group we examined save t-butyl This argues that hyperconjugative electron-release must be, at most, a small factor in determining the reactivity of toluene and related compounds; it is certainly small compared with the strong conjugative effects observed, for example, with the phenyl group. Secondly, it might not have been expected that fluorine would be a less polarisable substituent than chlorine or bromine. Of the halogens, fluorine seems best able to conjugate with aromatic systems, as shown by its having the smallest σ-value of these groups in the *para*-position. It would seem

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[28] Taft in " Steric Effects in Organic Chemistry," ed. M. S. Newman, John Wiley and Sons, Inc., New York, 1956, p. 581.

[29] Van Bekkum, Verkade, and Wepster, *Rec. Trav. chim.*, 1959, **78**, 815.

that fluorine ought also to be the most capable of the halogens in conjugating with the aromatic ring in the transition state. Our interpretation of its small σ_P-value is this: the greater conjugation between fluorine and the aromatic ring than between chlorine or bromine and the aromatic ring in the ground state means that chlorine and bromine are electron-rich relatively to fluorine in this state and they are therefore the more readily able to donate electrons to the aromatic ring in the transition state. Further speculation on these polarisabilities is not at present justified because the experimental results available do not enable parameters to be calculated with a high degree of accuracy.

The Electron-demand Constant, ϕ.—The ϕ-value of a reaction is a measure of the reactivity of the reagent. Electrophilic reagents have positive ϕ-values, ϕ being zero for a reagent of infinite reactivity, and increasing with decrease in the reactivity of the reagent. The ϕ-value also yields information about the extent to which the Wheland intermediate is formed at the transition state, and therefore there should be a maximum ϕ-value corresponding to complete formation of the Wheland intermediate at the transition state. Mason has recently adduced evidence that in uncatalysed bromination this situation probably obtains,[23] from which it may be concluded that ϕ has a maximum value equal to, or not much greater than, the value for this reaction (15·1).

In summary, equation (6) shows promise of being able to correlate aromatic reactivities with a degree of precision not attainable by means of the Hammett equation. Application of the equation necessitates the evaluation of two parameters for each substituent group, one being associated with the ground-state electron distribution evoked by that group, and the other with the capacity of the group to stabilise the electron-deficient transition state by the resonance mechanism. Thus the equation amounts to a quantitative expression of Ingold's views on aromatic reactivities in which static effects and time-variable effects are separately treated.[30] We do not consider we have yet achieved a close approximation to finality in the values for the parameters which have been derived. The treatment is now being extended both to other reactions for which data are available and to *meta*-substituent groups, and it is hoped later to publish a more detailed analysis.

EXPERIMENTAL

Materials.—Benzene, the alkylbenzenes, fluorobenzene, *o*-, *m*-, and *p*-nitrotoluene, and *o*-, *m*-, and *p*-nitrofluorobenzene were commercial materials. *p*-Nitrotoluene was recrystallised to constant m. p., and the remainder were purified by fractional distillation and their purities were checked by gas chromatography. Fuming nitric acid (B.D.H. " AnalaR "; *d* 1·5) was employed for all nitrations.

The *o*-, *m*-, and *p*-nitro-derivatives of ethylbenzene, isopropylbenzene, and t-butylbenzene were prepared by nitration of the parent alkylbenzenes. The individual isomers were separated by gas chromatography. The column (446 cm. × 2·58 cm.) was packed with Apiezon " L " grease (30% w/w) coated on Embacel and was operated at 175° and 180° (see Table 7) with a carrying stream of nitrogen (800 ml./min.) at an inlet pressure of 20 lb./in.^{2} and atmospheric pressure at the outlet. The eluting material passed into a cold trap at −70°, followed by an electrostatic precipitator at 15,000 v. Collection efficiency was higher than 90%. A small proportion (less than 1%) of the eluting compounds was simultaneously detected by a hydrogen-inject flame ionisation detector. Under these conditions complete resolution of *o*-, *m*-, and *p*-nitro-isomers occurred, and gram quantities of all isomers were obtained. The order of elution of compounds from Apiezon " L " grease is known to be generally that of the boiling points. This order was confirmed for each set of three isomers by the physical properties and infrared spectra of the materials obtained. The column temperatures, retention times, and refractive indices are shown in Table 7.

Alkylbenzenes.—(a) *Isomer distribution.* Nitrations were carried out at 0°. A mixture of nitric acid (0·005 mole) and acetic anhydride (0·005 mole) was added to the alkylbenzene (0·01 mole) during 1 hr. with shaking. The temperature variation was not more than 0·5°. After

[30] Ingold, " Structure and Mechanism in Organic Chemistry," G. Bell and Sons, London, 1953.

2 hr. water was added and the whole was extracted four times with ether. The ether extract was concentrated and analysed by gas chromatography. The column (400 cm. × 4·5 mm.) was packed with Apiezon " L " grease (20% w/w) coated on Embacel and was operated at temperatures between 130° and 180° (see Table 8). Nitrogen (30 ml./min.) was used as the carrier gas, at an inlet pressure of 72 cm., with atmospheric pressure at the outlet. A hydrogen-inject flame ionisation detector coupled to a Sunvic recorder gave a linear response.

TABLE 7. *Retention times and physical properties of mononitroalkylbenzenes.*

Compound	Column temp.	Retention time (min.)	Refractive index (20°)	Lit. value
o-Ethylnitrobenzene	175°	44	1·5280	1·5352 [a]
m-Ethylnitrobenzene	175	56	1·5370	1·5390 [a]
p-Ethylnitrobenzene	175	68	1·5455	1·5459 [a]
o-Isopropylnitrobenzene	178	52	1·5233	1·5248 [a]
m-Isopropylnitrobenzene	178	72	1·5301	1·5303 [a]
p-Isopropylnitrobenzene	178	110	1·5363	1·5369 [a]
o-Nitro-t-butylbenzene	180	50	1·5177	1·5171 [b]
m-Nitro-t-butylbenzene	180	72	1·5269	1·5273 [b]
p-Nitro-t-butylbenzene	180	96	1·5335 (m. p. 27°)	1·5337 [b] (m. p. 28°) [b]

[a] Brown and Bonner, *J. Amer. Chem. Soc.*, 1954, **76**, 605. Nelson and Brown, *J. Amer. Chem. Soc.*, 1951, **73**, 5605).

The injection of standard mixtures of each set of isomers showed that the ratio of the peak areas was proportional within 2% to the ratio of the quantities of the three materials. Peak areas were measured by constructing triangles made up of tangents to the Gaussian curves and the intercepts on the base line. The analysis of standard mixtures of isomers submitted to the same extraction procedure showed that the extraction was quantitative. The retention times of the isomers on the columns described, and the isomer proportions obtained, are set out in Table 8.

TABLE 8. *Isomer distributions and retention times of nitro-derivatives.*

	Isomer distribution			Retention times			
Compound	*o*-nitro (%)	*m*-nitro (%)	*p*-nitro (%)	*o*-nitro (min.)	*m*-nitro (min.)	*p*-nitro (min.)	Column temp.
Toluene	61·6	1·7	36·7	40	50	57	135°
	63·0	1·5	35·5				
	61·5	1·4	37·1				
	59·5	1·8	38·7				
average	61·4	1·6	37·0				
Ethylbenzene	45·8	3·2	51·0	20	26	31	178
	45·6	3·3	51·1				
	46·2	3·3	50·5				
average	45·9	3·3	50·8				
Isopropylbenzene	28·1	5·6	66·3	22	31	38	178
	27·9	3·8	68·3				
	28·0	4·1	67·9				
average	28·0	4·5	67·5				
t-Butylbenzene	9·9	6·9	83·2	25	34	45	178
	10·1	6·7	83·2				
average	10·0	6·8	83·2				
Fluorobenzene	8·7	0	91·3	50	35	42	130
	8·7	0	91·3				
average	8·7	0	91·3				

(b) *Overall reactivities.* A mixture of toluene (0·02 mole), the competing alkylbenzene (0·02 mole), and a standard material (decane or undecane) (approx. 2 g.) was made up and divided into two parts. To one portion was added a mixture of nitric acid (0·007 mole) and acetic anhydride (0·007 mole) as in the direct nitrations described above. To the other portion acetic anhydride (0·007 mole) alone was added. After 2 hr. the reaction was stopped and the mixtures were extracted as before. The extracts from each mixture were injected consecutively into the same gas-chromatographic column as was used for the isomer-ratio determinations. By comparison of the heights of the peaks of toluene and the competing alkylbenzene relative to the standard in the two mixtures, the amounts of each used up in the nitration were calculated. By using the relation derived by Ingold *et al.*[21] $k_x/k_y = (\log x/x_0)/(\log y/y_0)$, the reactivities with respect to toluene were obtained. These are shown in Table 9. To check this method, standard mixtures of varying proportions of the three compounds involved were injected. The changes in peak heights relatively to the standard were shown to be proportional to the differences in amounts of the other two components present. It was also shown that, under the conditions of the nitrations, the internal standard material did not react. This was done by adding equal amounts of an *external* standard to equal amounts of the internal standard before and after the attempts to nitrate it, and comparing peak heights produced by the mixtures at each stage.

Fluorobenzene.—(a) *Isomer distribution.* The nitration of fluorobenzene was carried out at 25°. Amounts of materials similar to those used for the alkylbenzenes were employed, and the reaction mixture was left for 12 hr. The extraction procedure was as previously described, and the isomer ratio was determined by gas chromatography. The column (400 cm. × 4·5 mm.) was packed with Apiezon " L " grease (20% w/w) coated on firebrick (50—90 mesh) and was operated at 130°. Hydrogen (30 ml./min.) was used as the carrier gas, at an inlet pressure of 58·5 cm. with atmospheric pressure at the outlet. A flame-ionisation detector coupled to a Honeywell-Brown recorder gave a linear response. As before, standard mixtures of isomers were used to demonstrate the proportionality of peak height and amount of material, and to show that extraction was quantitative. The retention times and the proportions of the isomers obtained in the reaction are shown in Table 8. No evidence of the formation of the *meta*-isomer was obtained, even though the instrument was capable of detecting about 0·2% of a component in a mixture.

(b) *Overall reactivity.* The rate of nitration of fluorobenzene relatively to benzene was determined in a competitive reaction between the two compounds, decane being used as the internal standard. The procedures of nitration and extraction were essentially the same as for the alkylbenzenes, except that nitration was allowed to continue for 12 hr. Care was taken to prevent any loss of material by evaporation, and under the conditions used it was found that no such loss occurred. Gas chromatography was used as before to follow the reaction. The column (200 cm. × 4·5 mm.) was packed with polyethylene glycol (5% w/w) and stearic acid (2% w/w) coated on Embacel, and was operated at 51°. Hydrogen (42 ml./min.) was used as the carrier gas, at an inlet pressure of 29·5 cm., with atmospheric pressure at the outlet. Under these conditions complete resolution of the three components was observed. The values for the reactivity of fluorobenzene relative to benzene are shown in Table 9.

TABLE 9. *Competitive experiments.*

	Reactivity relative to	
Compound	toluene	benzene
Toluene	1	27 [a]
Ethylbenzene	0·763	
	0·892	
	0·810	
	0·760	
	0·929	
	0·936	
average	0·848 ± 0·077	22·8 ± 1·9
Isopropylbenzene	0·622	
	0·685	
	0·682	
	0·640	
average	0·652 ± 0·026	17·7 ± 0·7
t-Butylbenzene	0·530	
	0·526	
	0·574	
	0·611	
average	0·560 ± 0·032	15·1 ± 0·8
Fluorobenzene		0·143
		0·141
		0·135
		0·144
		0·141 ± 0·003

[a] Value reported in ref. 21.

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