345. *The Separation of Polar and Steric Effects. Part I. The Kinetics of the Reaction of* ortho-*Substituted Benzoic Acids with Diazodiphenylmethane.*

By N. B. CHAPMAN, J. SHORTER, and J. H. P. UTLEY.

Rate coefficients for the reactions in ethanol at 30° of a series of acids o-X·C_6H_4·CO_2H (X = Me, Et, Pr^i, Bu^t, F, Cl, Br, or I), m-X·C_6H_4·CO_2H (X = Me, or Cl), p-X·C_6H_4·CO_2H (X = Me, Et, Pr^i, Bu^t, F, Cl, or I), and of 2,6-dichlorobenzoic acid with diazodiphenylmethane have been measured. Alkyl groups in the *para*-position inhibit the reaction very slightly and almost equally; *para*-halogen facilitates the reaction weakly and more or less equally. *ortho*-Alkyl groups, except Me, facilitate the reaction noticeably with $Et < Pr^i < Bu^t$. *ortho*-Halogen facilitates the reaction more strongly still, with $F \lll Cl < Br \approx I$. 2,6-Dichlorobenzoic acid reacts ~5 times faster than o-chlorobenzoic acid. The influence of an *ortho*-alkyl group is attributed mainly to a secondary steric effect, but that of *ortho*-halogen to a polar effect stronger from the *ortho*- than from the *para*-position. This polar effect is thought to be mainly a direct field effect. The relation between acid dissociation constants (water) and (*a*) esterification rate coefficients (ethanol), and (*b*) steric parameters for other systems is discussed.

PREVIOUS attempts to separate polar and steric effects in the reactions of *ortho*-disubstituted benzene derivatives have been made by Taft.[1] In this analysis, which will be considered in detail in Part II of this series, polar substituent constants, σ^*, and steric parameters, E_S, are obtained for *ortho*-substituents from kinetic data for basic and acidic ester hydrolysis. At present there is little information on the applicability of the Taft parameters to other reaction systems, but the treatment leads to one conclusion at least which is not intuitive: comparison of Hammett[2] and Taft σ-constants reveals that for the halogens $\sigma^* \approx \sigma_{para}$, which indicates that polar effects are equal from the *ortho*- and *para*-positions. This

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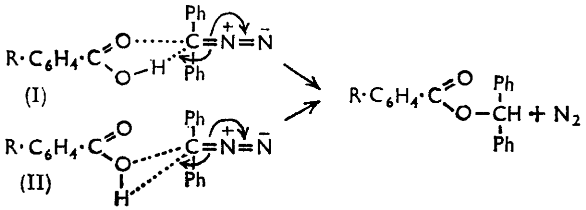
[1] Taft, " Steric Effects in Organic Chemistry," ed. Newman, Chap. 13, John Wiley and Sons, Inc., New York, 1956.

[2] Hammett, " Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, 1940, pp. 184—199.

seems unlikely even if the polar effect of the halogen operates through a mesomeric mechanism only (cf. p. 1830). Hence attempts to separate polar and steric effects by other methods are of interest. The present paper records an investigation of the effects of alkyl and halogen substituents in benzoic acid on the rate of esterification with diazodiphenylmethane in ethanol.

The mechanism of the reaction between diazodiphenylmethane and carboxylic acids has been investigated by Roberts, Watanabe, and McMahon.[3] The transition states proposed are (I) and (II). For *ortho*-substituted benzoic acids it appears that attack by



diazodiphenylmethane is at the hydroxyl group of the carboxyl group, and therefore at a point remote from substituents in the benzene ring. This implies an absence of primary steric effects in the reaction and therefore eliminates one possible contribution to the effect of an *ortho*-substituent.

EXPERIMENTAL

Materials.—Alkylbenzoic acids not available commercially were prepared by carbonation in the usual way of Grignard reagents derived from the corresponding bromo- or iodo-compounds (see Table 1).

TABLE 1.

Alkyl-substituted benzoic acids.

Subst.	M. p. obs.	M. p. lit.	Solvent for recrystn.	Overall yield (%)	Ref.
p-Et	114°	114—115°	Acetic acid	36	7
o-Et	66	65—65·5	Light petroleum (b. p. 40—60°)	45	8
o-Pr^i	57·5—58·5	59·0—59·5	,, ,, ,,	9	6
o-Bu^t	68·5—69·0	68·2—68·5	,, ,, ,,	16	5, 6

o-*Ethyliodobenzene.* This was prepared from *o*-ethylaniline by diazotisation followed by reaction with potassium iodide and had b. p. 98°/10 mm.

p-*Bromoethylbenzene,* b. p. 80°/10 mm. *p*-Bromoacetophenone was reduced by the Huang-Minlon modification of the Wolff–Kishner reaction.

o-*Bromocumene.* Cumene was nitrated by Bogert and Sterling's method [4] to yield *p*-nitrocumene, b. p. 124—128°/10 mm., and this was brominated "cationically" to give 2-bromo-4-nitrocumene,[5] b. p. 148—153°/10 mm., which was reduced in ethanol with hydrazine and Raney nickel to 4-amino-2-bromocumene, b. p. 146°/10 mm. Deamination of 4-amino-2-bromocumene by diazotisation and reaction with hypophosphorous acid resulted in *o*-bromocumene, b. p. 83—85°/10 mm. (lit.,[5] 90°/15 mm.).

o-*Bromo-t-butylbenzene.* This was prepared by Shechter's method.[6] *p*-t-Butylbenzoic acid was brominated "cationically" to yield 3-bromo-4-t-butylbenzoic acid, m. p. 176·5°, which was converted into 3-bromo-4-t-butylaniline by the Schmidt reaction. Diazotisation of the amine followed by deamination with hypophosphorous acid gave *o*-bromo-t-butylbenzene, b. p. 100°/11 mm. (lit.,[5] 106—107°/15 mm.).

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[3] Roberts, Watanabe, and McMahon, *J. Amer. Chem. Soc.*, 1951, **73**, 760.
[4] Bogert and Sterling, *J. Org. Chem.*, 1939, **4**, 20.
[5] Crawford and Stewart, *J.*, 1952, 4443.
[6] Shechter, personal communication.
[7] Bergmann and Reswik, *J. Org. Chem.*, 1952, **17**, 1291.
[8] Hauser and Weinheimer, *J. Amer. Chem. Soc.*, 1954, **76**, 1264.

o-Fluorobenzoic acid. Methyl *o*-fluorobenzoate was prepared from methyl anthranilate by the Balz–Schiemann reaction and saponified to yield *o*-fluorobenzoic acid. The acid was recrystallised from water and had m. p. 125° (lit.,[9] 125—126°).

2,6-Dichlorobenzoic acid, m. p. 141·5°, was supplied by Dr. J. G. Mather (cf. ref. 10).

The following acids were obtained commercially and recrystallised from glacial acetic acid: benzoic, *o*-toluic, *m*-toluic, *p*-toluic, *p*-fluorobenzoic, *o*-chlorobenzoic, *m*-chlorobenzoic, *p*-chlorobenzoic, *o*-bromobenzoic, *o*-iodobenzoic, *p*-iodobenzoic, *p*-isopropylbenzoic, *p*-t-butylbenzoic. They had m. p.s identical with, or very close to, those recorded in the literature.

Diazodiphenylmethane. Diazodiphenylmethane was prepared by Smith and Howard's method.[11] Approximately 0·007M-solutions in ethanol were stored in a refrigerator.

Purity of Materials.—Each carboxylic acid was esterified with diazomethane in ethereal solution, the ether was allowed to evaporate, and the residue analysed by vapour-phase chromatography. A stationary phase of 10% polypropylene sebacate on " Celite 100—120 " was usually used. The esters of *o*-toluic, *o*-ethylbenzoic, and *o*-isopropylbenzoic acids were analysed with a stationary phase of 10% Apiezon L. A column temperature of 150° was used in all cases.

Only in samples of the methyl esters of *p*- and *o*-isopropylbenzoic acid were impurities detected. About 0·5% of impurity was found for the former and 1% and 6·5%, severally, of two impurities for the latter. The preparation of *o*-isopropylbenzoic acid involves the nitration of cumene and the separation of the isomeric nitro-compounds formed, and it is probable that the impurities found in the final product are the *meta*- and *para*-isopropylbenzoic acids (see footnote to Table 3).

Solvent.—Pure ethanol was prepared by the method of Lund and Bjerrum.[12]

Measurements.—(a) *Competing reactions.* The ratio (R) of the amount of diazodiphenylmethane consumed in the reaction with each substituted benzoic acid to the total amount consumed (arising from simultaneous acid-catalysed reaction with solvent ethanol, and reaction with the acid [3]), was determined by allowing equimolecular amounts of acid and diazo-compound to react in ethanol and determining the residual acid by titration with standard alkali to Cresol Red.

(b) *Rate coefficients.* In the presence of an excess of the acid, the reaction is of the first order, and apparent first-order rate coefficients (k_1^a) were determined spectrophotometrically by Smith and Hunt's method.[13] Optical-density measurements at 525 mμ were made with 1 cm. cells and a Unicam S.P. 500 spectrophotometer. The true second-order rate coefficient (k_t) for the reaction of the acid with diazodiphenylmethane is given by $k_t = k_1^aR/[\text{acid}] = k_2^aR$.

DISCUSSION

In Table 2 are listed values of R (see above) as percentages. For the conversion of k_1^a into k_t, mean values of R (per cent) were used, *viz.*, for *p*-alkyl 58·0, for *p*-halogen 59·8, for *m*-alkyl 62·0, and for *m*-halogen 59·7. The individually determined values were used for the *ortho*-substituents. True and apparent second-order rate coefficients (k_t and k_2^a, respectively) for the esterification of substituted benzoic acids with diazodiphenylmethane

TABLE 2.

Values of R for reaction of diazodiphenylmethane with 0·01M substituted benzoic acids in ethanol at 30°.

Subst.	R (%)	Subst.	R (%)	Subst.	R (%)	Subst.	R (%)
H	61·7, 57·4 *	*o*-F	60·7	*p*-Bu^t	57·5	*m*-Me	57·7 * (62·0)
o-Me	64·3	*o*-Cl	63·6	*p*-I	58·2	*p*-F	57·1 * (61·3)
o-Et	64·1	*o*-Br	63·6	2,6-Cl$_2$	64·6	*p*-Et	54·5 * (58·5)
o-Pr^i	65·5	*o*-I	63·6	*m*-Cl	59·7		
o-Bu^t	65·8						

* Determined at 0·006M; figures in parentheses are corrected to 0·01M.

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[9] Gilman and Gorsich, *J. Amer. Chem. Soc.*, 1956, **78**, 2217.

[10] Mather and Shorter, *J.*, 1961, 4744.

[11] Smith and Howard, *Org. Synth.*, **24**, 53.

[12] Lund and Bjerrum, *Ber.*, 1931, **64**, 210.

[13] Smith and Hunt, *J. Amer. Chem. Soc.*, 1959, **81**, 590.

are listed in Table 3. The question of temperature-dependence of k_t awaits investigation, so we confine the present discussion to rate coefficients for 30°.

Polar and Steric Effects of Alkyl Substituents.—*p*-Alkyl substitution retards the reaction, as expected for electron-releasing groups, although no clear order of polar effects is discernible. It appears that there is an almost complete balance between the inductive polar effect, which releases electrons in the order Bu^t > Me, and the C–H hyperconjugative effect, which releases electrons in the order Me > Bu^t, giving a more or less constant polar effect as the series Me to Bu^t is traversed.

TABLE 3.

Esterification of substituted benzoic acids with diazodiphenylmethane in ethanol at 30°.

Subst.	k_2^a (l. mole^{-1} min.$^{-1}$)	k_t * (l. mole^{-1} min.$^{-1}$)	Subst.	k_2^a (l. mole^{-1} min.$^{-1}$)	k_t * (l. mole^{-1} min.$^{-1}$)	Subst.	k_2^a (l. mole^{-1} min.$^{-1}$)	k_t * (l. mole^{-1} min.$^{-1}$)
H	1·08	0·666	*o*-Cl	5·20	3·31	*o*-Et	1·13	0·724
o-Me	0·971	0·624	*m*-Cl	2·44	1·46	*p*-Et	0·784	0·455
m-Me	1·01	0·626	*p*-Cl	1·88	1·12	*o*-Pr^i	1·60	1·05
p-Me	0·888	0·515	2,6-Cl$_2$	27·4	17·7	*p*-Pr^i	0·901	0·523
o-F	2·71	1·64	*o*-Br	6·39	4·06	*o*-Bu^t	2·81	1·85
p-F	1·305	0·780	*o*-I	6·66	4·24	*p*-Bu^t	0·833	0·483
			p-I	1·82	1·09			

* Corrected for reaction with ethanol, acid concn. being 0·01M. The values of k_2^a and k_t are judged to be accurate to ±2% or better.

The value for *o*-isopropylbenzoic acid relates to a sample containing a few per cent of the *meta*- and *para*-isomers. Calculation shows that the rate coefficient for the pure material would probably be 3—4% higher than the value quoted above. This difference is unimportant to our discussion of log k_t. Roberts, McElhill, and Armstrong (*J. Amer. Chem. Soc.*, 1949, **71**, 2923) give k_2^a = 1·88 l. mole^{-1} min.$^{-1}$ for *p*-bromobenzoic acid (cf. p. 1828).

The effect of *o*-alkyl substitution upon the rate of esterification is striking, methyl substitution causing a decrease as expected on polar grounds, but alkyl substitution by the groups Et, Pr^i, or Bu^t noticeably increases the rate of reaction. Eaborn and Taylor's work [14] on the rate of detritiation of alkyl-substituted tritiobenzenes indicates that in this reaction, at least, methyl and t-butyl groups exert their polar influences equally from the *ortho*- and *para*-positions. This, together with the fact that the accepted polarity of alkyl groups is small, indicates that the considerable increases in rate are due to a steric effect.

It is highly probable that the secondary steric effect which facilitates the ionisation in water of *ortho*-substituted benzoic acids [15] is responsible. Conjugation between the carboxyl group and the benzene ring in the undissociated acid is considered to be stronger than similar conjugation of the carboxylate group in the ion. Such conjugation requires coplanarity between the carboxyl group and the benzene ring for maximum interaction, and bulky *ortho*-substituents, by disturbing this coplanarity and consequently decreasing the conjugation, will decrease the electron density in the carboxyl group and thus facilitate esterification with diazodiphenylmethane. The magnitude of such an effect increases sharply as the series Me to Bu^t is traversed. Models indicate that the plane of the carboxyl group of *o*-t-butylbenzoic acid is at approximately 90° to that of the benzene ring, and it seems reasonable to suggest that the conjugation discussed above is almost completely destroyed in this case.

A linear relationship is observed between log k_t and Taft steric parameters, E_s, for the β-methyl-substituted ethyl series, R = $[CH_3]CH_2$, $[CH_3{\cdot}CH_2]CH_2$, $[(CH_3)_2CH]CH_2$, and $[(CH_3)_3C]CH_2$.[16] This is illustrated in Fig. 1. The existence of such a relationship implies that steric effects upon log k_t can be related to the steric effects of groups measured in other circumstances, in this case the acid-catalysed hydrolysis of the ester $R{\cdot}CO_2R'$ or the acid-catalysed esterification of $R{\cdot}CO_2H$. This supports the conclusion that the

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[14] Eaborn and Taylor, *J.*, 1961, 247.

[15] Dippy, Hughes, and Laxton, *J.*, 1954, 1470.

[16] Ref. 1, p. 601.

accelerating effect of *o*-alkyl substituents can be accounted for in terms of a varying steric effect, with an approximately constant polar effect, throughout the series Me to Bu^t.

Consideration of the structure of the related systems reveals a stereochemical analogy. In both the aliphatic and the aromatic system the alkyl group and the carboxylic group are linked to a common residue, $-CH_2-$ and $-C_6H_4-$, respectively. This implies a degree of rigidity in both systems and it is suggested that the interactions of the analogous alkyl substituents with the carboxylic group should be related. The analogy is demonstrated pictorially in Fig. 2.

Polar and Steric Effects of Halogen Substituents.—*p*-Chloro-, -bromo-, and -iodo-substituents facilitate the esterification with diazodiphenylmethane to almost the same extent.

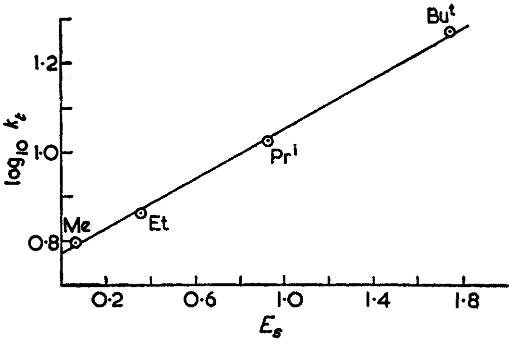
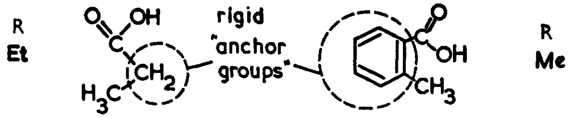


FIG. 1. Relation between log k_t and Taft steric parameters for β-methyl-substituted ethyl groups. For E_s values (from acid hydrolysis rates) R in $R{\cdot}CO_2R'$ = Et, Pr^n, Bu^i, or neopentyl. For log k_t values R in o-$R{\cdot}C_6H_4{\cdot}CO_2H$ = Me, Et, Pr^i, or Bu^t.

FIG. 2. Left, aliphatic system. Right, aromatic system.



The *p*-fluoro-compound, however, is less reactive, probably because of the increased mesomeric component of the polar effect of the substituent.

ortho-Halogen-substitution causes a remarkable increase in the rate of esterification. For all substituents the *ortho*-substituted acid is more reactive than the *para*-substituted compound, the reactivities increasing in the order, o-F $\ll$ o-Cl $<$ o-Br $\approx$ o-I. Such a phenomenon can be explained in three ways: either the secondary steric effect discussed above is alone the cause of the phenomenon, or, if there is no steric effect, the polar effect of the halogens is greater from the *ortho*- than from the *para*-position, or a combination of both these effects is facilitating the reaction.

The relationship shown in Fig. 1 provides a method of estimating the possible effect of steric interaction upon log k_t in the *o*-halogen-substituted series. Values of E_s for the group $X{\cdot}CH_2$ where X = F, Cl, Br, or I, are presented by Taft [16] and may be used to obtain from Fig. 1 the increment in log k_t (Δ log k_t), that would result from the interaction of *o*-halogen substituents with the carboxyl group. An estimate can also be made by comparing E_s values (for benzoate hydrolysis) for the *o*-halogens, with those of the *o*-alkyl groups featured in Fig. 1, *e.g.*, Br is of similar E_s to Me, so it is assumed that the secondary steric effect observed is the same for both; hence (Δ log $k_t)_2$ may be estimated from Fig. 1. A combination of the two estimates gives a reasonable assessment which is summarised in Table 4.

TABLE 4.

X	1	2	3	4	5	6
F	−0·24	+0·066	Negligible	0·00	+0·03	5·23
Cl	−0·24	+0·066	Slightly >Me	+0·02	+0·04	2·86
Br	−0·27	+0·074	~Me	+0·03	+0·05	3·21
I	−0·37	+0·104	Slightly >Et	+0·07	+0·09	3·34

1, E_s for $X{\cdot}CH_2-$. 2, (Δ log $k_t)_1$. 3, Qualitative estimate of secondary steric effect. 4, (Δ log $k_t)_2$. 5, Average value of Δ log k_t. 6, [log (k_o/k_u) − Δ log k_t]/log (k_p/k_u).

The quantity [log (k_o/k_u) − Δ log k_t]/log (k_p/k_u), where the subscripts *o*, *p*, and *u* distinguish the true rate coefficients for the *ortho-*, *para-*, and unsubstituted acid, respectively, is therefore a measure of the relative effects of *o-* and *p*-halogen substituents.

It seems clear that the secondary steric influence on the reaction between *o*-halogenobenzoic acids and diazodiphenylmethane is slight, and, if the allowances made for this effect are valid, that halogens exert a greater polar influence from the *ortho-* than from the *para*-position. A factor of about 3·0 ± 0·3 for Cl, Br, I, and about 5·0 for F, is indicated in column 6 of Table 4.

There is evidence in the literature of other reaction systems in which the polar effect of the halogens is greater from a position *ortho-* to the reaction centre than from the *para*-position. Mather and Shorter[10] have studied the reactions of chloro-substituted benzoyl chlorides with aniline in benzene and have found that the *o*-chloro-substituent exerts a polar influence 3·8 times that of the corresponding *para*-substituent. A related study by Stubbs and Hinshelwood,[17] with the chloro-substituents in the aniline molecule, has demonstrated a similar ratio of 3·2.

The dissociation constants of isomeric halogeno-anilinium ions and -phenols[18] provide further evidence of the increased polar effects from the *ortho*-position. This is illustrated in Table 5. No secondary steric effect is caused by *ortho*-substituents in these cases.

TABLE 5.

	log (K_o/K_u)/log (K_p/K_u), 30% ethanol, 25°	
Subst.	Subst. phenol	Subst. anilinium ion
F	3·00	7·69
Cl	2·45	3·07
Br	2·17	2·76
I	1·74	2·76

Any primary steric effect in *ortho*-substituted phenols hinders ionisation, probably because of inhibition of solvation of the ion; thus *o*-cresol is a slightly weaker acid than *p*-cresol.[19] For the anilinium ions any primary steric effect would be acid-strengthening and hence this may be partly responsible for the enhanced strength of the *ortho*-substituted compounds. These effects are small, however, and the main factor influencing the relative dissociation constants must be an increased polar effect from the *ortho*-position.

Smith and Larson[20] have demonstrated a linear relation between the pK_a values, in water at 25°, of *meta-* and *para*-substituted benzoic acids and of the analogous pyridinium ions. Brown and McDaniel[21] have suggested that, for *ortho*-substituents, deviations from such a relation arise because of steric effects operating in the benzoic acid system only. It is possible therefore to obtain from Smith and Larson's plot "corrected" Hammett sigma constants (σ_o) for *ortho*-substituents. These are listed in Table 6, in comparison with the corresponding *para*-values (σ_p).

TABLE 6.

Subst.	σ_o	σ_p	σ_o/σ_p
F	+0·92	+0·062	14·8
Cl	+0·74	+0·227	3·26
Br	+0·69	+0·232	2·97
I	+0·63	+0·276	2·28
Me	−0·13	−0·170	0·76

With the exception of fluorine the factor of about 3·0 is again evident for *ortho*-halogen substituents, and it is of interest that the polar effect of methyl is only slightly different from the two positions.

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[17] Stubbs and Hinshelwood, *J.*, 1949, S 71.

[18] Bennett, Brooks, and Glasstone, *J.*, 1935, 1821.

[19] Herington and Kynaston, *Trans. Faraday Soc.*, 1957, **53**, 138.

[20] Smith and Larson, *J. Amer. Chem. Soc.*, 1960, **82**, 99.

[21] Brown and McDaniel, *J. Amer. Chem. Soc.*, 1955, **77**, 3756.

If, as an alternative, it is assumed that polar effects are the same from the *ortho*- and the *para*-positions,[1] then the greater reactivity of the *ortho*-substituted compounds must be due entirely to the secondary steric effect, and the quantity $\log (k_o/k_u) - \log (k_p/k_u)$ will be a measure of such an effect. It is reasonable to assume that the *ortho*-t-butyl substituent completely destroys any conjugation between the carboxyl group and the benzene ring. It can be concluded from Table 7 therefore that the secondary steric effect is a maximal when the substituents are Bu^t, Br, or I, that F and Cl exert a considerable secondary steric effect, and that Cl is intermediate in bulk between Pr^i and Bu^t. Some of these conclusions are not readily acceptable in view of established ideas about the relative sizes of the groups in question. Further, the rate coefficient for 2,6-dichlorobenzoic acid may be calculated from that for *o*-chlorobenzoic acid on an additive basis; $\log (k/k_u)_{o\text{-Cl}} = 0{\cdot}696$, $\log (k/k_u)_{2,6\text{-Cl}_2} = 1{\cdot}426$. This would not be possible if in *o*-chlorobenzoic acid the chlorine atom was causing an almost maximal secondary steric effect.

TABLE 7.

Substituent	Me	Et	Pr^i	Bu^t	F	Cl	Br	I
$\log (k_o/k_u) - \log (k_p/k_u)$ ...	+0·084	+0·202	+0·303	+0·584	+0·322	+0·470	+0·559	+0·590

Thus the kinetic results are best accommodated in an explanation that demands a greater polar effect from an *ortho*-halogen substituent than from the corresponding para-substituent.

Jenkins [22] has calculated for halogenobenzenes the electrostatic potential (ψ) at carbon atoms *ortho-*, *meta-*, or *para-* to the substituent. Table 8 lists ratios, ψ_o/ψ_p for the halogens.

TABLE 8.

Substituent	F	Cl	Br	I
ψ_o/ψ_p	2·71	2·73	2·82	2·71

The factor of about 2·7 is comparable with that of about 3·0 obtained from kinetic and equilibrium studies. It must be noted, however, that in calculating these parameters Jenkins made the simplifying assumption that the value of the dielectric constant involved was the same for all the isomers and could therefore be neglected for purposes of comparison. In spite of this, the approximate correspondence of the reactivity ratios and the ratios of electrostatic potentials suggests that the main influence of halogeno-substituents on reactivity is by the direct field effect.[23]

Roberts and Moreland [24] have shown further that the π-electron system of the benzene ring plays little or no part in transmitting the polar effects of halogen substituents. This would not be the case if such effects were transmitted by the " non-classical " inductive mechanism proposed by Everard and Sutton,[25] which demands the participation of the π-electron system, or by the " classical " inductive mechanism which involves the polarisability of the system.

The larger polar effect of halogens from the *ortho*-position may possibly be due to a decreased mesomeric component of the polar effect. This would effectively increase the resultant polar influence of the halogens. There is some evidence that *ortho*-mesomeric interactions are smaller than the corresponding *para*-interactions in that *ortho*- are less stable than *para*-quinones. The maximum increase in polarity caused by such an effect can be estimated from the Hammett σ-values for the halogens. In the absence of any proximity effects and with the mesomeric component of the polarity of the halogen

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[22] Jenkins, *J.*, 1939, 640, 1137, 1780.

[23] Ingold, " Structure and Mechanism in Organic Chemistry," Bell and Sons Ltd., London, 1953, p. 60.

[24] Roberts and Moreland, *J. Amer. Chem. Soc.*, 1953, **75**, 2167.

[25] Everard and Sutton, *J.*, 1951, 2821.

inhibited we should expect σ_{meta} to be applicable for the *ortho*-position. However, for chlorine $\sigma_{meta}/\sigma_{para} = 0{\cdot}373/0{\cdot}238 = 1{\cdot}57$. The observed factor of about 3·0 is not therefore explained in these terms.

The Relation between Acid Dissociation in Water and the Rate of Esterification in Ethanol.—The uncertainly in slope of the lines shown in Fig. 3 is such that they can be regarded as parallel. Corresponding points on the two lines are horizontally separated by a distance represented by about 0·4 pK_a unit. The parallelism suggests that the apparent secondary steric effect of all *ortho*-substituents, except Bu^t, but including F, is greater in acid dissociation than in esterification by a constant amount corresponding to 0·4 pK_a unit.

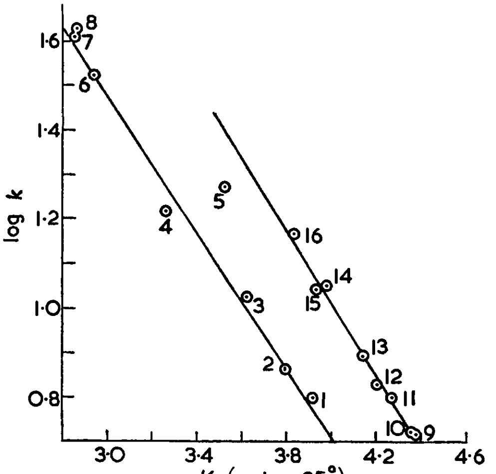


Fig. 3. Relation between pK_a for water at 25° and log k for reaction with diazodiphenylmethane in ethanol at 30° for a series of substituted benzoic acids.

Substituents: 1, *o*-Me. 2, *o*-Et. 3, *o*-Pr^i. 4, *o*-F. 5, *o*-Bu^t. 6, *o*-Cl. 7, *o*-Br. 8, *o*-I. 9, *p*-Me. 10, *p*-Pr^i. 11, *m*-Me. 12, H. 13, *p*-F. 14, *p*-Cl. 15, *p*-I. 16, *m*-Cl.

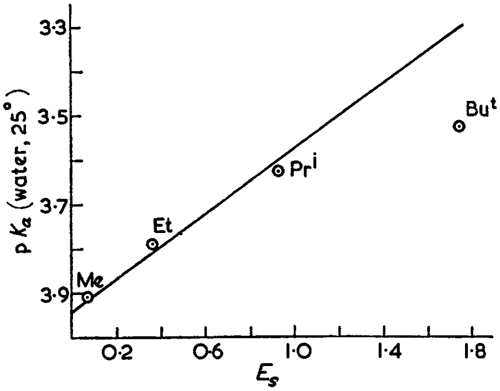


Fig. 4. Relation between pK_a for water at 25° of a series of acids *o*-R·C_6H_4·CO_2H (R = Me, Et, Pr^i, or Bu^t), and Taft steric parameters, E_s (E_s values as for Fig. 1).

The point for 2,6-dichlorobenzoic acid is displaced by about 0·4 pK_a unit from the line relating to the *ortho*-substituents, and about 0·8 pK_a unit from the corresponding plot for *meta*- and *para*-substituents. It appears, therefore, that benzoic acids in water are strengthened by about 0·4 pK_a unit by the introduction of any *ortho*-substituent irrespective of its bulk or polarity (cf. p. 1832).

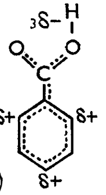
Two further conclusions can be drawn from the parallelism. (i) The relative susceptibility of the two systems to polar effects is not influenced by the position of the substituents, *i.e.*, the Hammett ρ value is the same for the *ortho*-, *meta*-, and *para*-positions. (ii) The relative susceptibility of the two systems to variations in electron-density at the reaction centre is the same whether such changes are produced by a secondary steric effect or by the polar effect of a substituent.

The Relation between pK_a *and Steric Parameters for Other Systems.*—In Fig. 4 the points for Me, Et, Pr^i, but not Bu^t, lie on or near a straight line of slope +0·273. This is smaller by a factor of 0·8 than the slope of the line shown in Fig. 1 (+0·357). Such a factor is equal to the relative susceptibility to polar effects of the acid dissociation in water, and the esterification in ethanol, *i.e.*, the ratio of Hammett ρ-values for the two reaction systems.

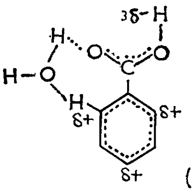
This is strong evidence that for *o*-toluic, *o*-ethylbenzoic, and *o*-isopropylbenzoic acid, acid strengthening is the result of a secondary steric effect.

The point for *o*-t-butylbenzoic acid does not lie on the line in Fig. 4, although it does fit the log k_t–E_s relation (Fig. 1). It is reasonable to assume, therefore, that the dissociation of *o*-t-butylbenzoic acid in water is hindered by an effect opposing the secondary steric effect. This is probably the steric inhibition of solvation of the anion, which hinders dissociation. If the plot in Fig. 4 is extrapolated to $E_s = 0$, a pK_a value of 3·94 is obtained. This value should represent the strength of an *o*-alkyl-substituted benzoic acid uninfluenced by a secondary steric effect, and should therefore be near that of *p*-toluic acid. In fact the pK_a of *p*-toluic acid is 4·37, which indicates that the strength of *o*-alkyl-substituted acids is enhanced by about 0·4 pK_a unit by the mere presence of a substituent (see p. 1831). It is to be noted that in Fig. 1, when $E_s = 0$, log $k_t = 0{\cdot}765$, which is comparable with 0·712 for log k_t for *p*-Me. This indicates that there is no similar anomaly in the effect of *ortho*-substitution on the reactivity of the acids in pure ethanol.

It is unlikely that the initial decrement in the pK_a value will be the same for all *ortho*-substituents, including fluorine, unless the conjugation between the carboxyl group and the benzene ring is completely destroyed by the small substituents. This cannot be so, as acid strengths continue to increase with the increasing bulk of the substituents. Also, the additivity of the effect of *ortho*-substitution, observed for the dissociation of 2,6-dichlorobenzoic acid,[10] cannot be explained on the basis of a maximum inhibition of mesomerism by this substituent. It appears possible therefore that a hitherto unrecognised factor influences the acidity of benzoic acids in water, a factor that involves the positions *ortho* to the carboxylic function. A tentative suggestion as to the nature of this factor can be advanced. If the resonance hybrid for benzoic acid is represented as (II), then it is possible that solvation of this molecule may include solvation by water bridges, *e.g.*,



(III)



(IV)

(IV), which by encouraging the tendency of the molecule to assume a planar configuration will stabilise the hybrid and thus hinder acid dissociation. Substitution at the *ortho*-positions will destroy this solvation, consequently lessening the stability of the planar hybrid and thus facilitating acid dissociation. Conjugation between the carboxylate group and the benzene ring in the anion is probably not significant,[26] and only effects on the acid itself can therefore modify acid dissociation.

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[26] Ref. 23, p. 744.