637. The Transmission of Polar Effects through Aromatic Systems. Part III.* Hammett σ-Constants.

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The rates of alkaline hydrolysis of ethyl phenylacetate and nine monosubstituted derivatives in aqueous acetone at 25° have been measured. The results support the theory of van Bekkum, Verkade, and Wepster that mesomeric *para*-interaction between substituent and functional centre may affect the σ-value of a substituent. Variations in σ-values arising from the polar effect of the substituent on the resonance interaction of the functional centre with the aromatic nucleus are noted. An improved method of obtaining σ-values is proposed in which use is made only of those reaction series where resonance interaction between the functional centre and the aromatic ring is precluded.

IN a recent re-examination of the Hammett equation, van Bekkum, Verkade, and Wepster[1] pointed out that the σ-value attributed to a *para*-substituent depends on the variation in the mesomeric *para*-interaction between the substituent and the functional centre in different reactions. This gives rise to a multiplicity of σ-values which depend on the reactions from which they are derived. One set of values, σ^n, applies when there is no mesomeric *para*-interaction.

To confirm this theory we have examined the rates of alkaline hydrolysis of substituted phenylacetic esters. In these compounds, no resonance interaction can occur between the substituent and the functional centre because of the insulation provided by the intervening methylene group. As a result of these experiments, we have modified the treatment used by van Bekkum, Verkade, and Wepster, on the basis of which a new set of σ-values has been derived.

TABLE 1. *Rate constants* (l. mole^{-1} sec.$^{-1}$) *for the alkaline hydrolysis of ethyl phenylacetates at* 25°.

Subst. ...	H	*m*-Me	*p*-Me	*p*-OMe	*p*-F	*p*-Cl	*p*-Br	*p*-COMe	*m*-NO_2	*p*-NO_2
10^2k	4·40	3·58	3·18	3·93	6·96	9·71	10·10	13·0	18·4	26·2

RESULTS AND DISCUSSION

Second-order rate constants for the alkaline hydrolysis of ethyl phenylacetate and nine monosubstituted ethyl phenylacetates are recorded in Table 1. Using Jaffé's statistical methods,[2] we have obtained the correlation coefficient (r) and the standard deviation (s) for the correlations of our hydrolysis rates with the σ-values compiled by McDaniel and Brown[3] (from the strengths of substituted benzoic acids) and the σ^n-values of van Bekkum, Verkade, and Wepster. The less satisfactory correlation with σ-values ($r = 0·957$; $s = 0·101$) than with σ^n-values ($r = 0·983$; $s = 0·063$) arises principally because of the deviations of the points for *p*-halogen and *p*-methoxyl. For example, the rates of hydrolysis indicate that the *p*-Me group is more strongly electron-releasing than *p*-OMe. This is consistent with the σ^n-values of the groups (—0·129 and —0·111 respectively[1]) but not with the σ-values[3] (—0·170 and —0·268), the more negative σ-value of *p*-OMe arising from its conjugation with the carboxyl group in *p*-anisic acid. Thus our results are in agreement with the theory of van Bekkum, Verkade, and Wepster.[1]

However, the annexed plot of log (k/k_0) against σ^n-values, for our hydrolyses, reveals that the points for our three substituents of greatest electron-attracting power (*m*-NO_2,

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* Part II, *J.*, 1961, 2938.

[1] van Bekkum, Verkade, and Wepster, *Rec. Trav. chim.*, 1959, **78**, 815.

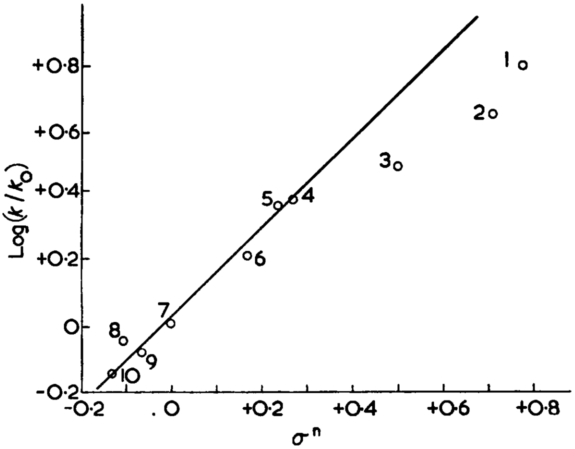
[2] Jaffé, *Chem. Rev.*, 1953, **53**, 191.

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

p-NO$_2$, and *p*-COMe) lie considerably below the best straight line for the other seven compounds. These deviations are not due to entropy effects since the pre-exponential factors for the hydrolysis of ethyl phenylacetate and its *m*- and *p*-nitro-derivatives are constant (Table 2) (cf. Leffler [4]).

Our results give good correlation with those from the alkaline hydrolysis of substituted benzyl acetates,[5] from the alkaline hydrolysis of ethyl phenylacetates in aqueous ethanol,[6] and from the *N*-chlorination of *N*-benzylacetamides.[7] These reaction series are similar to ours in that mesomeric *para*-interaction is prevented by the methylene group. Further, as with our results, the points for the *m*- and *p*-NO$_2$ substituents are abnormal, the deviations being in the same direction as in ours.* These similarities suggest a weakness in the method by which the σ^n-values for the *m*-NO$_2$, *p*-NO$_2$, and *p*-COMe groups were derived.

van Bekkum, Verkade, and Wepster assumed that the σ^n-values of *meta*-substituents, and of *p*-NO$_2$ and *p*-COMe substituents (derived from reactions in which no resonance interaction occurs between these groups and the functional centre), are the same as their well-established σ-values.[1] But this assumption neglects one other type of interaction: namely, the polar effect of the substituent on the resonance interaction of the functional centre with the aromatic nucleus. Two of the reactions used by these workers for deriving the σ^n-values of *p*-NO$_2$ and *p*-COMe groups were the ionisations of the *para*-substituted benzoic acids and the *para*-substituted phenylacetic acids. Now, in the equilibrium of benzoic acid with its anion, there is evidence that the conjugation of the carboxyl group with the benzene ring, represented by the contribution of structure (I) to the molecule, is responsible for stabilising the acid by about 1 kcal. mole^{-1} more than the corresponding conjugation in the benzoate ion, represented by the contribution of structure (II).[8]



Plot of log (k/k_0) *against* σ^n*-values of substituents in ethyl phenylacetate.*

1, *p*-NO$_2$. 2, *m*-NO$_2$. 3, *p*-COMe. 4, *p*-Br. 5, *p*-Cl. 6, *p*-F. 7, H. 8, *p*-OMe. 9, *m*-Me. 10, *p*-Me.

TABLE 2. *The pre-exponential factor.*

Subst.	H	*m*-NO$_2$	*p*-NO$_2$	Subst.	H	*m*-NO$_2$	*p*-NO$_2$
10^2k (25°) ...	4·40	18·5	26·2	10^2k (55°) ...	23·6	86·5	124
10^2k (40°) ...	10·4	42·0	59·1	$\log_{10} PZ$	6·6	6·7	6·6

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* The *p*-COMe substituent was not studied in any of these reactions, nor was the *m*-NO$_2$ substituent studied by Watkinson and his collaborators.[6]

[4] Leffler, *J. Org. Chem.*, 1955, **20**, 1202.

[5] Tommila and Hinshelwood, *J.*, 1938, 1801; Tommila, *Ann. Acad. Sci. Fennicae*, 1942, **59**, *A*, No. 4.

[6] J. G. Watkinson, personal communication.

[7] Williams, *J.*, 1930, 37.

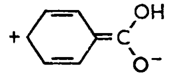
[8] Taft in " Steric Effects in Organic Chemistry," ed. M. S. Newman, John Wiley and Sons, Inc., New York, 1956, p. 581.

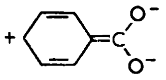
A polar *para*-substituent in benzoic acid will affect the contribution of forms (I) and (II) to their respective hybrids. For example, an electron-attracting group will decrease their contributions and thereby reduce the difference in their importance, corresponding to an acid-strengthening effect, but this cannot occur in *para*-substituted phenylacetic acids, where there is no interaction between the carboxyl group and the aromatic ring. Therefore, we expect that the σ-values of *p*-NO_2 and *p*-COMe groups calculated from the strengths of the benzoic acids will be larger than those calculated from the strengths of the phenylacetic acids or from reactions on other systems with insulating methylene groups. This is confirmed by our results. The same argument applies in principle to *meta*-substituents, though presumably to a smaller extent, for the effect of the substituent on the resonance interactions represented by forms (I) and (II) has to be relayed through a carbon atom. Possibly this is why it is only for the strongly electron-attracting nitro-group that a deviation is observed for a *meta*-substituent.

The corollary to this argument is that the resonance interaction of a group of $+M$ type with the benzene ring should be enhanced by an electron-attracting substituent. Evidence for this has been adduced by Wepster [9] from measurements of the basic strengths of substituted dimethylanilines.

According to these arguments, the σ-value of a *para*-substituent derived from a reaction series in which the functional centre is conjugated with the aromatic ring, should differ from its σ^n-value because of the effect of this substituent on the conjugation. It may also differ because of direct conjugation between functional centre and substituent. van Bekkum, Verkade, and Wepster have taken account only of the latter effect in their treatment; we wish to emphasise that the former may make a significant difference to the σ-values derived from a particular reaction series.

(I)





(II)

We propose a new scale of σ-values, based on reaction series in which the functional centre is insulated from the benzene ring. We have examined the rather small number of reactions which satisfy this criterion for the derivation of new σ-values and have chosen only those for which data referring to five or more substituents are available and which have ρ-values greater than 0·5. σ-Values have been derived only for substituents which have been studied in at least three of the reactions.

The hydrolyses reported in this paper were initially chosen as the basis for the new σ-values, this reaction being assigned the value $\rho = 1$. ρ-Values for five reaction series and σ-values for nine substituents were then obtained, by using the method employed by Jaffé in compiling Hammett σ-constants.[2] A plot of these σ-values against σ^n-values was linear except for the points for the *m*- and *p*-NO_2 groups. This probably indicates that it is only strongly polar groups which significantly affect the conjugation of a second substituent with the aromatic nucleus. The slope of the regression line obtained by including all values except for the *m*- and *p*-NO_2 groups was used to relate our new σ-constants to the σ^n-scale, and the revised values are set out in Table 3. The new σ has been designated σ_G because, since it is a polarisation parameter which refers to the *ground-state* electron distribution, it has the same basis as the σ_G-constant derived from a recent treatment of electrophilic aromatic substitution.[10]

TABLE 3. *Values of* σ^n *and* σ_G.

Subst.	*p*-Me	*m*-Me	*p*-OMe	*p*-F	*p*-Cl	*p*-Br	*m*-Cl	*m*-NO_2	*p*-NO_2
σ^n	−0·129	−0·069	−0·111	+0·168	0·238	0·265	0·373	0·710	0·778
σ_G	−0·129	−0·105	−0·097	+0·143	0·256	0·281	0·334	0·576	0·708

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[9] Wepster, *Rec. Trav. chim.*, 1956, **75**, 1473.

[10] Knowles, Norman, and Radda, *J.*, 1960, 4885.

TABLE 4. *Reactions from which* σ_G *and* ρ *were obtained.*

Reaction	Solvent	Temp.	ρ	s	r	n	Ref.
Ar·CH_2·CO_2Et + OH^-	60% Me_2CO	25°	1·069	0·029	0·996	8	
Ar·CH_2·CO_2Et + OH^-	85·4% EtOH	24·8	1·168	0·021	0·998	5	6
Ar·CH_2·CO_2H (pK_a)	H_2O	25	0·612	0·027	0·989	8	11
Ar·CH_2·OAc + OH^-	56% Me_2CO	25	0·894	0·019	0·998	8	5
Ar·CH_2·NHAc + Cl_2	40% AcOH	18	−1·256	0·049	0·987	5	7

The reactions from which σ_G-values were obtained are shown in Table 4 together with the corresponding reaction constant, ρ, the standard deviation, s, the correlation coefficient, r, and the number, n, of substituents used in the derivation.

EXPERIMENTAL

Materials.—Substituted phenylacetic acids were prepared, where necessary, by methods reported in the literature and were converted into their ethyl esters by the Fischer–Speier method. Liquid esters were purified by fractional distillation, and solid esters by repeated recrystallisations from light petroleum (b. p. of various ranges). The physical data and references to the preparation of these compounds are shown in Table 5. M. p.s are recorded for two of the esters which were previously reported as liquids.

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Solvent.—" AnalaR " acetone was dried (K_2CO_3) and fractionally distilled. It was diluted with freshly boiled, distilled water to give a mixture containing 60% (v/v) of acetone. Rate measurements carried out with " AnalaR " acetone which had not been purified in this way gave identical results.

TABLE 5. *Phenylacetic acids and their ethyl esters.*

	Acid		Ethyl ester			
Subst.	M. p.	Ref.	M. p.	Ref.	B. p.°/mm.	Ref.
H					227/758	12
m-Me	62°	13			122—123/18	14
m-NO_2	118—120	15	11·5—12·5°	*a*	127—135/0·25	16
p-Me	94	13			134—135/25	17
p-OMe	85—86	18			143—144/11	19
p-F	84·5	20	34	*b*	128—130/31	21
p-Cl			33—33·5	22		
p-Br			31—31·5	23		
p-COMe			62—63	24		
p-NO_2			63	25		

[a,b] M. p.s not previously reported. [a] Found: C, 57·1; H, 5·2; N, 7·2. Calc. for $C_{10}H_{11}NO_4$: C, 57·4; H, 5·3; N, 6·7%. [b] Found: C, 66·1; H, 6·3. Calc. for $C_{10}H_{11}FO_2$: C, 66·0; H, 6·1%.

Rate Measurements.—The procedure followed was essentially that described previously by Tommila and Hinshelwood.[5] Atmospheric carbon dioxide was excluded from standard alkali solutions with Carbosorb guard tubes, and these solutions were restandardised frequently. Initial concentrations of alkali and ester were equal (*ca.* 0·01M), and the extent of hydrolysis

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[11] Dippy and Williams, *J.*, 1934, 161 and 1888; Baker, Dippy, and Page, *J.*, 1937, 1774; Dippy and Page, *J.*, 1938, 357.
[12] Perkin, *J.*, 1896, **69**, 1175.
[13] Radziszewski and Wispek, *Ber.*, 1885, **18**, 1280.
[14] Senkowski, *Monatsh.*, 1888, **9**, 855.
[15] de Boer and Backer, *Rec. Trav. chim.*, 1954, **73**, 229.
[16] Muenzen, Cerecedo, and Sherwin, *J. Biol. Chem.*, 1926, **68**, 504.
[17] Claus and Kroseberg, *Ber.*, 1887, **20**, 2051.
[18] King and McMillan, *J. Amer. Chem. Soc.*, 1946, **68**, 2335.
[19] Cain, Simonsen, and Smith, *J.*, 1913, **103**, 1036.
[20] Dippy and Williams, *J.*, 1934, 1466.
[21] Corse, Jones, Soper, Whitehead, and Behrens, *J. Amer. Chem. Soc.*, 1948, **70**, 2837.
[22] Mehner, *J. prakt. Chem.*, 1900, **62**, 565.
[23] Wislicenus and Grützner, *Ber.*, 1909, **42**, 1933.
[24] Papa, Schwenk, and Klinsberg, *J. Amer. Chem. Soc.*, 1946, **68**, 2133.
[25] Maxwell, *Ber.*, 1879, **12**, 1767.

was studied from approximately 10 to 80% of completion. Each reaction obeyed second-order kinetics. The results recorded in Table 1 are the averages of at least two runs in each case, rate coefficients from different runs agreeing to within ±2%.

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