515. *A Simple Molecular-orbital Treatment of the Hammett ρσ-Equation : Inductive Constants of the Common Substituents.*

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A simple perturbation treatment of the Hückel molecular-orbital method is applied to the σ-constants of the Hammett ρσ equation. A series of inductive constants is deduced for the common substituents.

SEVERAL authors [1-5] have discussed the Hammett ρσ equation [6] in terms of the simple Hückel molecular-orbital method. Jaffe [1] has derived the σ-constants of the common monatomic substituents (hydroxy, amino and the halogens; the word " monatomic " is used in this connexion to denote substituents contributing one atomic orbital), solving the secular equations for all values of the heteroatom parameters; a comparison of the results with experiment allows the selection of a unique set of parameters for the heteroatoms. This method is perhaps more precise than that used here,[*] but it suffers from certain disadvantages : no comparison with the familiar inductive and mesomeric effects of the resonance theory is possible, and the extension of the method in its present form to more complex substituents (nitro, etc.) would require the acquisition of a large amount of experimental data; further, a complex substituent would have several parameters, and, if it is possible to assign only two parameters, an inductive and a mesomeric, to all substituents, the position is enormously simplified. Jaffe [3] has also discussed the σ-values of the heterocyclic nitrogen atom, using a perturbation method.

In the present paper, a different approach from that used by Jaffe [1-3] is adopted, the perturbation method being applied to the common substituents. The above-mentioned difficulties are then avoided, and interesting information concerning the inductive power of these substituents is obtained. That such an approach has real meaning is suggested by the fact that σ-constants are additive.[8]

Method.—The isolated-molecule approximation [9] is used, although discussions of the chemical reactivity of mesomeric systems are more reliable when the localisation method,[9] with its sound theoretical basis in the transition-state theory,[10] is used. The more precise method meets with difficulties, however. Sixma [4] has used such an approach but here, the side chain, the reaction centre, must be incorporated into the basic model to which the calculations are applied. This results in a multiplicity of models and does not emphasise the most important point of the Hammett ρσ equation, that the σ-constants are independent of the structure of the side chain. If the treatment is to be kept as general as possible, the isolated-molecule approximation is required, together with Hammett's original assumption that the substituents act by virtue of their ability to modify the charges at the *meta-* and *para-*positions in the benzene ring.

The relevant conclusions which follow from the application of perturbation methods to the Hückel method are well known.[11, 12] To evaluate the mesomeric effect, the hetero-atoms of the substituent are replaced by carbon atoms and the effect of this idealised

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* Perturbation methods are not invariably less accurate than the full solution of the secular equations since the self-consistency of the latter method is lost when heteroatoms having coulomb integrals differing from that of carbon are included.[7]

[1] Jaffe, *J. Chem. Phys.*, 1952, **20**, 279.
[2] *Idem, ibid.*, p. 778.
[3] *Idem, ibid.*, p. 1554.
[4] Sixma, *Rec. Trav. chim.*, 1953, **72**, 673.
[5] Sandorfy, *Bull. Soc. chim.*, 1949, **16**, 615.
[6] Hammett, " Physical Organic Chemistry," McGraw Hill, New York, 1940, chapter 7.
[7] Coulson and Dewar, *Discuss. Faraday Soc.*, 1947, **2**, 54.
[8] Jaffe, *Chem. Rev.*, 1953, **53**, 191.
[9] Brown, *Quart. Rev.*, 1952, **6**, 63.
[10] Dewar, *J. Amer. Chem. Soc.*, 1952, **74**, 3355.
[11] Jaffe, *ibid.*, 1955, **77**, 274.
[12] Coulson and Longuet-Higgins, *Proc. Roy. Soc.*, 1947, *A*, **191**, 39; 1948, *A*, **192**, 16.

substituent on the charge distribution in the benzene ring is calculated.[12, 13, 14] The majority of the substituents listed by Hammett [6] and by Jaffe [8] may be classified according to the number of atomic orbitals—0, 1, 2, or 3 *—which they contribute to the mesomeric system. In no case does the mesomeric effect alter the charge at the *meta*-position and in only one case, the monatomic substituents, does it affect the charge at the *para*-position.† This distinction leads us to separate the substituents into two groups, those contributing 0, 2 or 3 atomic orbitals to the mesomeric system (class a) and those contributing 1 atomic orbital (class b). Table 1 and 2 present the data thus arranged, all taken from Jaffe [8] with the exception of that for the SR_2^+ which is from ref. 15.

TABLE 1. *Class a.*

Substituent	NR_3^+	SR_2^+	NO_2	CN	SO_2Me *	SOMe *
σ_m	+0·95	+1·0	+0·71	+0·68	+0·65	+0·55
σ_p	+0·86	+1·0	+0·78	+0·63	+0·75	+0·57

Substituent	CF_3	COR	CO_2R	CO_2^-	Alkyl
σ_m	+0·41	+0·35	+0·35	+0·1	−0·05
σ_p	+0·55	+0·26—0·5	+0·26	+0·13	−0·15

* The structure of these substituents is relatively complex (Koch, *J.*, 1949, 408; Koch and Moffitt, *Trans. Faraday Soc.*, 1951, **47**, 7; Barnard, Fabian, and Koch, *J.*, 1949, 2442) but their mesomeric effect seems to be of no importance here and they are included in Table 1.

TABLE 2. *Class b.*

Substituent	NR_2	OR	Cl, Br, I
σ_m	−0·25	+0·1	+0·35
σ_p	−0·6	−0·3	+0·25

Within the limits of accuracy of the perturbation treatment, then, both the σ_m and the σ_p constants of the class (a) substituents originate in the inductive effect of these groups. This effect is usually [3] represented as :

$$\sigma_r = \gamma(q_r - 1) = \delta\alpha_a \cdot \gamma \cdot \sum_s \pi_{rs} \cdot \varepsilon^n \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where γ is a proportionality constant between the σ-constant and charge (q_r), carbon atom a of the benzene ring carries the substituent, $\delta\alpha_a$ is the change in the coulomb integral of this carbon atom resulting from the introduction of the substituent, π_{rs} is the mutual atom polarisability of atoms r and s, n is the number of bonds between atoms a and s, and ε is a constant. A relation between σ_m and σ_p is required in order to derive a value of ε and hence of the $\delta\alpha$-values of the substituents. Such a relation is apparent from Tables 1 and 2, namely, that the σ_m- and σ_p-constants are equal to within the precision of the Hammett equation itself, for substituents of class (a). There is no significant drift in either direction, and this equality does not hold for substituents of class (b).

Combination of this equality with equation (1) and the π_{rs} values [16] ($\pi_{11} = +43/108$, $\pi_{12} = -17/108$, $\pi_{13} = +1/108$, $\pi_{14} = -11/108$) gives a cubic in ε :

$$\varepsilon^3 - 0·65\varepsilon^2 + 0·25\varepsilon - 0·1 = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

(terms in ε^4 and higher powers have been neglected in the expansion of equation 1). Equation (2) has one real root at +0·53. This value of ε is rather higher than that (0·33)

* Attached to the benzene ring by the central, not by the terminal atom.
† The absence of a mesomeric effect in the *para*-position to the CN and CO groups follows [11] from the fact that their parent hydrocarbon is an even alternant—styrene—and, in both benzene and styrene, the charge at the *para*-position is unity. The NO_2 and CO_2R groups have as their parent hydrocarbon the 2-phenylallyl carbanion and here the non-bonding molecular orbital is confined to the terminal atoms of the allyl portion of the molecule. The charge at the *para*-position of the benzene ring is thus unity both in the substituted and in the unsubstituted molecules and the mesomeric effect vanishes.

[13] Pullman and Pullman, " Les Theories Electroniques de la Chimie Organique," Masson et Cie, Paris, 1952, chapter 10.
[14] Longuet-Higgins, *J. Chem. Phys.*, 1950, **18**, 265.
[15] Bordwell and Boutan, *J. Amer. Chem. Soc.*, 1956, **78**, 87.
[16] Wheland and Pauling, *ibid.*, 1935, **57**, 2086.

used by Jaffe [1] but is in line with that suggested by Branch and Calvin [17] and by Dewar,[18] *i.e.*, 0·4—0·5. The earlier value of 0·1, derived by Wheland and Pauling [16] from a perturbation treatment of electrophilic substitution in pyridine, seems much too small.

In order to obtain values for the $\delta\alpha$'s in terms of β,* the proportionality constant γ must be considered. Jaffe's value [2] of γ ($-15\cdot5$) is based on a value of 0·33 for ϵ and it is not clear how the former should be modified now that ϵ is taken as 0·53. Rather than report the $\delta\alpha$'s as ratios, the value of $-15\cdot5$ has been used for γ but the numerical magnitude of the results must be accepted with reservation. The point is not of great importance since the ratios of the $\delta\alpha$'s, which are independent of γ, are our primary concern. Hence

$$\delta\alpha_a = 1\cdot0\sigma_m = 1\cdot0\sigma_p \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

for class (a) substituents and the values of α are numerically equal, when expressed in units of β, to the σ-constants. Average values of the $\delta\alpha$'s are reported in Table 3, together with Branch and Calvin's I values.[17] The latter are discussed below. Values [19] for the SMe

TABLE 3.

Substituent	NR_3^+	SR_2^+	NO_2	CN	SO_2Me	SOMe	CF_3	COR	CO_2R	CO_2^-	Alkyl
$\delta\alpha_a$	+0·9	+1·0	+0·75	+0·7	+0·65	+0·55	+0·45	+0·3—0·4	+0·45	+0·1	−0·1
I	+13·6	+15·7	+12·1	+10	—	—	—	+5	+6·5	−1·9	—

group fit the generalisation less well ($\sigma_m = +0\cdot15$, $\sigma_p = 0\cdot0$), but here, as with the alkyl group, the inductive effect is not large and small mesomeric effects, not revealed by the perturbation treatment, may be of comparable importance.

The order of inductive constants ($\delta\alpha$'s) given in Table 3 agrees well with general expectation. The positively charged trialkylammonium and dialkylsulphonium ions have the largest inductive constants of all groups, while the nitro- and the cyano-group have the largest constants of the uncharged groups. At the opposite extreme, the alkyl group is alone in having a small electron-repelling effect, while the negative charge of the carboxyanion is sufficient to reduce the electron-attracting effect of the alkoxycarbonyl group markedly. The sulphone and sulphoxide groups are interesting, the second oxygen atom increasing the electron-attracting power of the group by 0·1β.

The monatomic substituents remain for discussion. Although they exhibit a mesomeric effect in the *para*-position, the *meta*-position is not affected mesomerically, so that the inductive constants of the groups may be obtained from the σ_m-values as before. The results are presented in Table 4. The $\delta\alpha$ values are not in agreement with general expectation. The latter is derived from the belief that the coulomb integral is closely related to

TABLE 4.

Substituent	NR_2	OR	Cl, Br, I
$\delta\alpha_a$ ($= \sigma_m$)	−0·25	+0·1	+0·35
($\sigma_p - \sigma_m$)	−0·35	−0·4	−0·1

the electronegativity of the heteroatoms. Unfortunately, difficulties related to the nature of the Hückel Hamiltonian prevent a precise description of the coulomb integral and it is becoming increasingly clear that this simple relation is inadequate. Bassett, Penfold, and Brown [20] recently suggested that the position of the heteroatom in the mesomeric system is of greater importance than has hitherto been realised : an example will clarify the point. Consider the nitrogen atoms in pyridine and in aniline. The isoelectronic hydrocarbons are benzene and the benzyl anion. When one of the benzene carbon atoms is replaced by

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* β is the standard carbon–carbon bond resonance integral. Overlap is neglected.

[17] Branch and Calvin, " The Theory of Organic Chemistry," New York, Prentice-Hall, 1941, chapter 6.

[18] Dewar, *J.*, 1950, 2329.

[19] Bordwell and Cooper, *J. Amer. Chem. Soc.*, 1952, **74**, 1058.

[20] Bassett, Penfold, and Brown, *Chem. and Ind.*, 1956. 892.

the nitrogen atom to form pyridine, the nitrogen atom is taking over a place of unit charge, while, when the nitrogen atom replaces the carbon atom of the methylene group of the benzyl anion to form aniline, it is taking over a place carrying a large fraction of a unit of negative charge in excess of that on the carbon atom of benzene. The overall result is that the nitrogen atom of aniline, instead of being weakly electron-attracting as is the nitrogen atom of pyridine, becomes weakly electron-repelling. Jaffe [1] reached the same conclusion. The more strongly electron-attracting oxygen atom is effectively neutralised by this positional effect, and the strongly electron-attracting halogens are reduced until they are weakly electron-attracting. The difference between the σ_p- and σ_m-constants of the monatomic substituents (Table 4) should then represent the mesomeric effect at the *para*-position of these substituents. It is unlikely that much significance is to be attached to the magnitude of these ($\sigma_p - \sigma_m$) factors, but it is encouraging that they are of the correct sign and in a reasonable order, the nitrogen and oxygen atoms conjugating with the ring more strongly than the halogen atoms.

Branch and Calvin [17] developed a similar series of inductive constants (I) from acid strengths. Their I values are reproduced in Table 3 and there is good agreement in both order and relative magnitude with the present series.

The inductive constants developed in this paper go some way towards putting the qualitative ideas of the resonance theory on a quantitative basis. Some instances of the utility of the series have come to the author's notice. In particular, the high inductive constants of the nitro- and the cyano-group suggest the explanation of some observations in the literature. Sixma [4] found that a treatment of σ-constants, which proved satisfactory for all other substituents, failed with these groups and he attributed this to their large inductive effects. In a molecular-orbital investigation of the directive effects of substituents on the phenyl radical addition to, or substitution in, the substituted benzene ring,[21] a reaction which is entirely governed by the mesomeric effects of most substituents, the two substituents which deviate from the calculations are the nitro- and the cyano-group. Evidently their inductive effects are sufficiently large to be comparable with their mesomeric effects.

Another situation in which the large inductive constants of these groups are evident is the pyrolysis of substituted benzyl bromides reported by Leight, Sehon, and Szwarc.[22]

TABLE 5.

Substituent	Me			Cl			NO₂		CN	
Position	o	m	p	o	m	p	m	p	m	p
$-\delta D$ (kcal./mole)	2·0	0	1·4	0·9	0·1	0·4	2·1	1·1	1·4	0·7

The bottom row of Table 5 indicates the decrease in activation energy ($-\delta D$) resulting from the introduction of the substituents into the benzene ring in the reaction, $Ph \cdot CH_2Br \longrightarrow Ph \cdot CH_2 \cdot + Br \cdot$. With methyl and chloro-substituents, the familiar mesomeric effects of these groups are evident; the *ortho*-substituent is the strongest activator, the *para*-substituent is less activating, and the *meta*-substituent has little or no effect on the reaction rate. Nitro- and cyano-groups exhibit a different behaviour and it seems that their inductive effects are large enough to compete with their mesomeric effects.

[21] Peters, unpublished work.
[22] Szwarc, Leigh, and Sehon, *J. Chem. Phys.*, 1951, **19**, 657; Leigh, Sehon, and Szwarc, *Proc. Roy. Soc.*, 1951, *A*, **209**, 97.

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