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STRUCTURE AND REACTIVITY OF ORGANIC COMPOUNDS (QUANTITATIVE LAWS)

V. A. Pal'm

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I. INTRODUCTION

Several quantitative relations have recently been discovered between the reactivities of organic compounds and their structures, and also the nature of the solvent. Analogous quantitative relations exist also between certain physical parameters and the structure or the properties of the solvent. These are not just disconnected, purely empirical relations, but form a single unified whole such that it is not unreasonable to discuss whether we are not dealing here with a basis for an extremely general quantitative theory in this field.

This recalls the idea put forward by a committee report of the Chemical Sciences Section of the Academy of Sciences of the USSR[1]: "The problem of reactivity must be posed as a problem of the *quantitative* study of chemical changes in various systems . . . . The whole of the immense accumulation of experimental results in organic chemistry relating to the problem of reactivity must be examined critically and analysed carefully from this point of view".

This task, of course, cannot be completed in a single paper. Our objective is more limited — to discuss, as far as possible systematically, what are in our opinion the most important successes achieved in developing a quantitative theory of the dependence of the reactivities of organic compounds on their structures and on the nature of the solvent.

It then proves possible to consider most of the existing data from a single point of view, because many of the quantitative relations are based on the rule of the linear relationship between changes in free energy (LFE). This rule, first employed by Brønsted[2] and by Hammett[3,4] on a comparatively restricted scale, can now be regarded as a very general empirical relationship.

The present review does not claim to cover completely all the results available, this applying in particular to section XX, written in collaboration with E. S. Rudakov. We are unable to examine the problems of a quantitative theory of the influence of the solvent on reactivity and other properties with the necessary breadth of view. We can only point out the necessity for a separate detailed review of this problem.

Qualitative aspects of the dependence of reactivity and other properties of organic compounds on their structure will not be considered separately here, but the reader can obtain useful information from the well-known monographs[5-9] and the committee report of the Chemical Sciences Section of the Academy of Sciences of the USSR[1]. We need consider here only a few problems of terminology. The term "resonance", adopted in several original papers, is replaced by "conjugation". In the present state of our knowledge it appears useful to distinguish two forms of conjugation — non-polar and polar. The former refers to what may be called (from a purely formal point of view, of course) a "homolytic" mechanism of interaction between π electrons. Non-polar conjugation takes place, for example, in butadiene, benzene, etc. Polar conjugation represents a "heterolytic" mechanism of interaction between π-electron pairs and atoms, and occurs for example in aniline, nitrobenzene, the carboxyl group, etc.

Substituents having electron-donor properties when polar conjugation occurs are said to be substituents of +C type, the corresponding electron-accepting substituents representing the -C type. The latter must contain an atom possessing either complete or partial co-ordination unsaturation. Examples are the boron atom in the $B(CH_3)_2$ group (complete co-ordination unsaturation) and atoms linked by a π bond to more electronegative atoms such as carbon in the carbonyl group, etc. (partial co-ordination unsaturation).

II. THE LINEAR FREE ENERGY (LFE) RELATIONSHIP

Let us first examine the concept of the reaction series[4,10]. This represents a single type of chemical reaction which a series of compounds X_i—Y can undergo, Y being a reactive centre which is the same for a given series (the part of the molecule which changes as a result of the given reaction), and X_i being some substituent. It is understood that the conditions under which the reaction occurs (temperature, solvent, etc.) remain the same.

If the centre, type, and conditions of the reaction are regarded as variables, a set of reaction series is obtained which in principle embraces all possible organic reactions. The substituent X_i is the variable in each of these series.

In a particular reaction series, the reagent (b_i) and the solvent (s_i) may also serve as variables. In such cases we obtain the following sets of reaction series

$$a + b_i \rightarrow \text{reaction products},$$

$$\text{starting materials} \xrightarrow{s_i} \text{reaction products}.$$

In the case of a given reaction series, a quantitative measure of reactivity is either the free energy of the reaction ΔF_i if equilibrium is being considered, or the free energy of activation $\Delta F_{\neq i}$ if reaction velocity is being considered.

From thermodynamics[11] and the theory of the activated state[12] it is known that

$$\Delta F = -2.303RT \log K$$

and

$$\Delta F_{\neq} = -2.303RT \log k - 2.303RT \log \frac{kT}{n},$$

where K is the equilibrium constant and k the rate constant.

A measure of change in free energy which is convenient from a chemical point of view is thus the logarithm of the equilibrium constant or the rate constant $\log k$.

The LFE is satisfied if a linear relation exists between values of $\log k_i$ for the various reaction series in any of the above three sets:

$$(\log k_i)_m = \alpha + \beta(\log k_i)_n, \qquad (2.1)$$

where m and n denote the reaction series, and α and β are constants.

If k_0 represents the equilibrium or rate constant for some reaction of a given series chosen as standard (standard x_0, a_0, or s_0), the following general expression is obtained for LFE:

$$(\log k_i/k_0)_m = \text{const.}(\log k_i/k_0)_n. \qquad (2.2)$$

The quantity $\log k_i/k_0$ is a measure of the change in free energy of the reaction or of activation on passing from the standard to the i-th reaction in a given reaction series.

An example of the application of the LFE rule in the form (2.1) is Brønsted's law of catalysis, which can be written as follows:

$$\log k = \text{const.} + \beta \log K,$$

where k is the catalytic rate constant for some acid (or base) in a reaction subject to general acid (or base) catalysis, and K is the acid (or basic) dissociation constant of the given acid (or base).

The LFE rule in the form (2.2) was used extensively by Hammett[3,4] to correlate the reactivities of *meta* and *para* derivatives of benzene. Assuming that the constant $\rho \equiv 1$ for the reaction series (dissociation of substituted benzoic acids in water at 25°) selected as the standard of comparison, he gave the relation (2.2) in the following form:

$$\log k_i/k_0 = \rho\sigma_i, \qquad (2.3)$$

where $\sigma_i \equiv \log k_i/k_0$, and k_i and k_0 are the dissociation constants of the substituted and the unsubstituted benzoic acids respectively.

The relation (2.3) is known as Hammett's equation. Its field of application is quite restricted (*meta*- and *para*-substituted derivatives of benzene). As will be shown below, the LFE rule in the form (2.1) or (2.2) is only a particular case of a more general law.

III. EFFECT OF STRUCTURAL FACTORS ON REACTIVITY. FUNDAMENTAL PRINCIPLES

The general problem of the dependence of reactivity on structure was discussed by Hammett[4]. The principles

which he introduced have been further developed and received further practical application mainly in the work of Taft[10] and others. These principles are as follows.

Since the magnitude of the equilibrium or rate constant is determined by the *change* in free energy during a reaction or an activation, not all the factors influencing the free energies of the starting materials and of the final reaction products or activated complexes will influence the reactivity as well. Such an effect is observed only if the changes produced in the free energies of the starting materials are not equal to those for the final reaction products or the activated complex. If this is not the case, these changes will cancel out, and will have no effect on the magnitude of ΔF or $\Delta F_{\neq}$.

If, following the theory of the activated state, activated complexes are regarded as analogous to ordinary molecules, calculation of the effect of structural factors on reaction velocity should not differ in principle from the corresponding calculation in the case of equilibrium.

Another important fact is that changes in ΔF or $\Delta F_{\neq}$ produced by different structural factors are mutually independent, and the total change in free energy can be regarded as produced by simple addition of the individual changes[10]. The independence and the additivity of these quantities result from the fact that the changes produced in the magnitude of ΔF by the different structural factors may be treated as small perturbations in the free energies of the reactants and of the final reaction products or activated complexes[10].

Consequently the total change in the free energy of reaction or activation may be expanded into a series of terms representing the different structural factors which affect the reactivity:

$$\log k/k_0 = P + H + G + \psi + S, \qquad (3.1)$$

where k and k_0 are equilibrium or rate constants for the given and the standard compound respectively, and P = $= -\Delta\Delta F_p/2.303RT$, etc.; the structural factors are denoted by P = inductive effect, H = hyperconjugation, G = = polar conjugation, ψ = non-polar conjugation, and S = = steric effects.

Eqn. (3.1) contains no terms corresponding to anchimeric assistance, the field effect, or the effect of an intramolecular hydrogen bond, since few examples are yet available of a quantitative calculation of the influence of these factors on reactivity.

Comparison of (3.1) with (2.2) suggests that the LFE principle really applies, not to the quantity $\log k_i/k_0$, but to the individual terms on the right-hand side of (3.1), *e.g.* to P. If this is so, the successful application of LFE in the form of relations of the type (2.1) or (2.2) indicates that all the remaining terms on the right-hand side of (3.1) are small, with the exception of one or two, which are linked together if only by a very roughly linear relationship. It follows from this that the range of application of the LFE principle may be wider than the limits of application of relations of the type (2.1) and (2.2).

IV. INDUCTIVE CONSTANTS OF SUBSTITUENTS

Several attempts have been made at a quantitative assessment of the influence of the inductive effect of substituents on the reactivity of organic compounds[13-16]. Up to the present the appropriate σ^* constants, introduced by Taft[17], for the various substituents have had the greatest practical application.

On the basis of Ingold's conclusion[18] that conjugation and the steric factor for a substituent X_i in esters (X_i–COOR) have the same effect on the rates of both alkaline and acid hydrolysis, Taft[17] made a quantitative determination of the inductive effect:

$$P_i = (\log k_i/k_0)_B - (\log k_i/k_0)_A, \qquad (4.1)$$

where the subscripts B and A denote alkaline and acid hydrolysis respectively.

Values of P were employed by Taft to construct a quantitative scale of so-called aliphatic polar constants σ^* for different substituents. Values of σ^* are obtained by dividing P by 2.48,[10] the factor 2.48^{-1} being introduced in order to bring the scale of σ^* into line with that of the Hammett constant σ. The methyl group was selected as standard substituent, so that $\sigma^*_{CH_3} \equiv 0$.

Since electronegative substituents accelerate the alkaline hydrolysis of esters, the more electronegative substituents are characterised by more positive values of σ^*, and conversely. As the choice of standard substituents is arbitrary, the numerical values of σ^* and even their sign depend on the standard selected. However, the difference between the values of σ^* for any given pair of substituents is independent of the choice of standard for comparison.

Two simple laws — those of additivity and of the damping of the inductive effect — hold for the dependence of σ^* on the structure of the substituent[10]. The additivity rule can be written as follows:

$$\sigma^*_{(X_1X_2X_3C)} = \sigma^*_{(X_1CH_2)} + \sigma^*_{(X_2CH_2)} + \sigma^*_{(X_2CH_2)} \qquad (4.2)$$

In most cases the additivity rule is obeyed very exactly, but if X_1, X_2, and X_3 are strongly electronegative substituents, such as chloro or fluoro, departures from additivity occur, especially on introduction of a third substituent.

According to the law of the damping of the inductive effect, introduction of carbon (the CH_2 group) between a substituent X and the reactive centre diminishes the influence of the inductive effect of the former on the latter by a factor of 2.8 if X is an electronegative substituent:

$$\sigma^*_{(XCH_2)} = (1/2.78)\sigma^*_{(X)} \pm 0.005. \qquad (4.3)$$

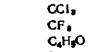
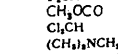
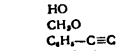
However, if X is hydrogen or a saturated hydrocarbon radical, then

$$\sigma^*_{(XCH_2)} = -0.100 + (1/4.90)\sigma^*_{(X)} \pm 0.01. \qquad (4.4)$$

The factor 2.8 in Eqn. (4.3) is not quite universal. For example, McGowan[15] points out that insertion of a CH_2 group between a substituent and the reactive centre decreases the influence of the inductive effect on the change in free energy to only half.

The inductive constants of substituents are complicated quantities giving a measure of the combined effect of the following factors — the electronegativity of the first atom of the substituent X, the hybridisation of the valency orbitals of this atom, the polar conjugation or polarisation of the π bonds within the substituent X, the field effect in the direction of the σ bonds joining the substituent with the reactive centre (especially if one of the atoms of the substituent other than the first carries a unit charge), the electron density on the first atom (especially if this atom possesses a complete unit charge), and the electronegativity of atoms which are more remote from the reactive centre[10,19]. It

TABLE 1. Taft's polar (inductive) constants σ^*.

Substituent	σ^*	Ref.	Substituent	σ^*	Ref.
$(CH_3)_3N^+$	+5.3	*	$CH_3-CO-CH_2$	+0.60	10
NO_2	+3.9	*	C_6H_5	+0.600	10
CH_3SO_2	+3.7	*	$HOCH_2$	+0.555	10
CN	+3.6	*	CH_3OCH_2	+0.520	10
F	+3.1	*	$O_2N(CH_2)_2$	+0.50	10
Cl	+2.9	*	H	+0.490	10
COOH	+2.9	*	$C_6H_5CH=CH$	+0.410	10
Br	+2.8	*	$(C_6H_5)_2CH$	+0.405	10
CCl_3	+2.65	10	$Cl(CH_2)_2$	+0.385	10
CF_3	+2.6	*	$CH_3CH=CH$	+0.360	10
C_6H_5O	+2.38	10	$CF_3(CH_2)_2$	+0.32	10
I	+2.36	*	$NC(CH_2)_2$	+0.30	24
F_2CH	+2.05	10	$C_6H_5CH_2$	+0.215	10
CH_3OCO	+2.00	10	$CH_3CH=CH-CH_2$	+0.13	10
Cl_2CH	+1.940	10	$CF_3(CH_2)_3$	+0.12	10
$(CH_3)_3NCH_2^+$	+1.90	10	$C_2H_5(CH_3)CH$	+0.11	10
$O_2N-CH=CH$	+1.704	10		+0.11	25
CH_3CO	+1.65	10			
HO	+1.55	*	$C_6H_5(CH_2)_2$	+0.080	10
CH_3O	+1.45	*	$NC(CH_2)_4$	+0.06	24
$C_6H_5-C\equiv C$	+1.35	10	$C_6H_5(C_6H_5)CH$	+0.04	10
$R-C\equiv C$	+1.30	20	$C_6H_5(CH_2)_3$	+0.02	10
$CH_3SO_2CH_2$	+1.32	10	CH_3	+0.000	10
$NCCH_2$	+1.300	10		−0.06	10
$Cl_2C-CH=CH$	+1.188	10			
FCH_2	+1.10	10	$CN(CH_2)_3$	−0.06	24
$HOOCCH_2$	+1.05	*	C_2H_5	−0.100	10
$ClCH_2$	+1.05	10	$n-C_3H_7$	−0.115	10
$HOOC-CH=CH$	+1.012	21	$n-C_4H_9$	−0.125	10
$BrCH_2$	+1.000	10	$n-C_5H_{11}$	−0.130	10
CF_3CH_2	+0.92	10	Cyclohexyl	−0.15	10
$Cl-CH=CH_2$	+0.900	21	$(CH_3)_3C-CH_2$	−0.165	10
$Cl_2CH-CH=CH_2$	+0.882	21		−0.18	25
	+0.86	22			
$C_6H_5OCH_2$	+0.850	10	$(CH_3)_2CH$	−0.190	10
ICH_2	+0.85	10	Cyclopentyl	−0.200	10
$N\equiv C-(CH_2)_3$	+0.80	24	$C_6H_5(CH_2)CH$	−0.210	10
$C_6H_5(OH)CH$	+0.765	10	$(C_2H_5)_2CH$	−0.225	10
$CH_2=CH$**	+0.653	21		−0.24	25
	+0.70	22		−0.26	25
	+0.67	22	$(CH_3)_3SiCH_2$	−0.26	10
			$(CH_3)_3C-(CH_2)CH$	−0.28	10
			$(CH_3)_3C$	−0.300	10

* Calculated from the formula: $\sigma^*_{(X)} = 2.8\sigma^*_{XCH_2}$.

** The value +0.653 for the substituent CH_2:CH is evidently rather too high. If σ^* is calculated for this substituent by combining the rules of damping and additivity of the inductive effect, a value of +0.40 is obtained.

is the combined effect of these factors which in the classical electronic theory has been termed the inductive effect of the substituent.

Values of σ^* for different substituents are given in Table 1, from which it can be seen that the sequence of the substituents according to decreasing values of σ^* is the same as that indicated by qualitative ideas about the inductive effect[6,7,9].

V. GENERAL APPLICABILITY OF INDUCTIVE CONSTANTS OF SUBSTITUENTS

At the end of section III it was noted that the simplest form of LFE, as represented by the Hammett equation, is to be expected when all terms on the right-hand side of Eqn. (3.1), other than the first, can be neglected. When only the inductive effect is responsible for the change in reactivity, the following relation[26] holds:

$$\log k/k_0 = \rho^*\sigma^*, \quad (5.1)$$

or, if the reactive centre is linked with several substituents,

$$\log k/k_0 = \rho^*\Sigma\sigma^*, \quad (5.2)$$

where k and k_0 are rate or equilibrium constants for compounds X−Y and X_0−Y respectively, σ^* is the inductive constant of the substituent X, and ρ^* is a constant representing sensitivity to the inductive effect in the given reaction series. The summation in Eqn. (5.2) covers values of σ^* for all substituents combined with the reactive centre.

The expression (5.1) can be termed "Taft's special equation", since it takes account only of the inductive effect. With reaction series in which the terms other than P on the right-hand side of Eqn. (3.1) are not small, Taft's special equation is written in the form[26]

$$P = \rho^*\sigma^*. \quad (5.3)$$

Taft and his collaborators[26-32], as well as several other workers[16,20-22,33-39] have shown that Eqns. (5.1)−(5.3) are applicable to a great variety of reaction series. Positive values of ρ^* are characteristic of reactions facilitated by electronegative substituents. Negative values of ρ^* are found when electronegative substituents tend to inhibit the reaction.

It must be stressed that the same values of σ^* characterise the effects of substituents on the reactivities of organic compounds in a very great variety of chemical processes, and also give a quantitative measure of their effect on several physical constants of organic compounds. Among these are the infra-red absorption frequencies corresponding to the stretching vibrations of several groups[10,25,26,39,40], the infra-red absorption coefficients of aliphatic alcohols[41], and dipole moments[10,26].

From the above facts Taft concludes that the σ^* values are universal parameters characteristic of the corresponding substituents alone, and are independent of the structure of the rest of the molecule or of the chemical or physical properties under consideration. The laws of the dependence of σ^* on the structure of the substituent indicate that we are dealing with a quantitative expression of the phenomenon which has been termed the inductive effect[10,26]. The general applicability of relation (5.3), and especially the validity of Eqns. (5.1) and (5.2), make it possible to determine values of σ^* from a great variety of reaction series. In principle, the actual origin of the σ^* determinations is immaterial and does not affect their magnitude. The values of σ^* for various substituents given in Table 1 were obtained from various reaction series. In the case of substituents whose σ^* values can be calculated from several reaction series, mean values are quoted.

The extremely important problem of the application of Taft's equation to reactions involving heterogeneous catalysis has not yet been discussed in the literature. If data for the dehydrogenation of the alcohols X_1X_2CHOH are treated[42] in the appropriate manner, $\rho^*\Sigma\sigma^*$ correlation is maintained satisfactorily only for five out of eight alcohols. The observed deviations cannot be ascribed to the steric effect.

It can now be regarded as established that the quantities σ^* are only roughly of general applicability. Apparently this is true especially of compounds in which the reactive centre is separated from the substituent by an atom not of carbon but of some other element, silicon for example[16].

VI. STERIC CONSTANTS OF SUBSTITUENTS FROM KINETIC DATA ON THE ACID HYDROLYSIS OF ESTERS

It was pointed out in section IV that, in the acid hydrolysis of esters, $P \simeq 0$ or, what is equivalent, $\rho^* \simeq 0$. Consequently, the quantity $(\log k/k_0)_A$ depends on the steric factor and on conjugation. In the case of esters of α,β-unsaturated carboxylic acids, non-polar conjugation also is absent, and the reactivity will then depend only on the steric factor and on hyperconjugation. Neglecting the latter too, Taft[17,10] utilised data on the kinetics of the acid hydrolysis of esters in order to construct a quantitative scale of steric constants of substituents, on the assumption that

$$(\log k/k_0)_A \equiv S \equiv E_S . \qquad (6.1)$$

The methyl group was chosen as standard substituent, so that $E_{S(CH_3)} \equiv 0$. Since activation of an ester involves the conversion of the carbon of the carbonyl group from the second to the first valency state, it is accompanied by a "contraction" of the substituents. As a result of this, bulky radicals retard the reaction, and values of E_S are negative for all substituents larger than the methyl group.

The laws governing the dependence of E_S on the structure of the substituents have nothing in common with those operating in the case of the inductive constants of the substituents. At the same time, the character of these laws confirms the steric nature of the E_S values.

It is interesting that substituents have a rather greater effect on E_S when introduced into the β than into the α position. Substitution in the γ position has practically no effect on E_S. It must also be stressed that the additivity rule, valid in the case of the inductive constants σ^*, cannot be applied to the steric constants of substituents. Introduction of a second and a third substituent into the α or β position has a far greater effect on the magnitude of E_S than has introduction of the first substituent[10].

Taft and his coworkers[10,17,31,32] have shown that the quantities E_S are not only characteristic of the corresponding substituents in the acid hydrolysis of esters. In the case of some other reaction series, for which $\rho^* \simeq 0$, the following relation is observed:

$$\log k/k_0 = \delta E_S , \qquad (6.2)$$

where δ is a constant representing sensitivity to the steric effect of the substituent in the given reaction series.

In some cases in which the inductive effect cannot be ignored, the following relation holds[17,32]:

$$\log k/k_0 = \rho^*\sigma^* + \delta E_S . \qquad (6.3)$$

Eqns. (6.2) and (6.3) are essentially examples of the application of the LFE rule to the steric term on the right-hand side of (3.1):

$$S = \delta E_S . \qquad (6.4)$$

The question of the generality and limits of applicability of Eqn. (6.4) cannot yet be regarded as solved, because of the inadequacy of the experimental data available. A relation of type (6.2) does not hold for the acid hydrolysis of thiolacetates $CH_3-CO.S-X$.[10] In some cases the inapplicability of Eqn. (6.4) may be due to additional steric effects, such as steric hindrance to conjugation, as in the alkaline hydrolysis of anilides[43].

Steric effects in the hydrolysis of ketals are discussed by Glasstone *et al.*[12]

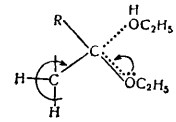
Although few quantitative data are yet available on the steric effects of substituents on reactivity, some important conclusions can nevertheless be drawn. On the one hand, it can be accepted as proved that the LFE rule is applicable to the steric term of (3.1) if the reaction series under consideration are analogous with respect to the steric changes occurring about the reactive centre during the reaction or activation. On the other hand, there is apparently no universal scale of steric constants of substituents analogous to that of the σ^* values. It is possible that calculation of the steric effects of substituents in different types of reaction series may require the use of a definite set of steric constants for each substituent.

The influence of steric factors on reactivity may be regarded as the net effect of two factors — steric strain and steric hindrance to movement[10,44].

Another approach to a quantitative treatment of the steric effect is given by De la Mare *et al.*[45] The values of E_S are shown to include, besides the steric effect, the so-called "ponderal" effect (effect of a change in mass of the substituent on the vibration frequencies and the partition function).

VII. QUANTITATIVE CALCULATION OF THE HYPERCONJUGATION EFFECT

Kreevoy and Taft[28] have shown that change in the hyperconjugation of the substituents with the reactive centre during activation or reaction in the acid hydrolysis of acetals and ketals leads to considerable departures from a relation of type (5.1) or (5.2). In an actual case of this reaction, hyperconjugation is absent in the original acetals and ketals, but arises in the activated state owing to the appearance of a carbon atom showing partial co-ordination unsaturation in the carbonyl group which is formed†:



The hyperconjugation component in (3.1) was shown[28] to be the sum of quantities representing the hyperconjugation of the individual C–H bonds with the reactive centre:

$$H = (\Delta n)h , \qquad (7.1)$$

where h is a parameter characteristic of the given reaction series and $\Delta n = n - n_0$, n being the number of C–H bonds involved in hyperconjugation in the given substituents, and n_0 the corresponding quantity for the standard substituents. The methyl group, for which $n = 3$, was chosen as standard.

† The mechanism of the acid hydrolysis of acetals and ketals is discussed by Kreevoy and Taft[46].

The rates of acid hydrolysis of acetals and ketals are correlated by the equation[28]:

$$\log k/k_0 = \rho^*\Sigma\sigma^* + (\Delta n)h. \qquad (7.2)$$

The relation (7.1) describes quantitatively the effect of hyperconjugation on reactivity for several other series of reactions as well — the hydrogenation of aldehydes and ketones[26], the hydrogenation of *trans*-substituted ethylenes[26], etc.

Developing these ideas further, Taft and Lewis[47] concluded that more accurate results can be obtained by also taking into account the part played by C–C bonds (α-carbon atoms) in hyperconjugation. The hyperconjugation term can then be represented by

$$H = n_H h_H + n_C h_C, \qquad (7.3)$$

where n_H and n_C are the numbers of C–H and C–C bonds respectively, taking part in the hyperconjugation. In this case hydrogen was chosen as standard substituent ($n_H = n = 0$). The ratio h_H/h_C is 1.3 ± 0.1 for *p*-alkyl substituents in benzene derivatives, and ~2.5 in aliphatic compounds, independently of the reaction series.

An attempt has been made[48,49] to calculate h_H and h_C by the method of molecular orbitals, hyperconjugation being regarded, by analogy with anchimeric assistance (see section XV), as the result of the "overlapping" of an *s* orbital of hydrogen by a π orbital of the second carbon atom in $H-C^1-C^2$, *i.e.* as resulting from the presence of an "α-hydrogen" bond. Semi-quantitative agreement with the experimental data was obtained.

Consideration of hyperconjugation from this point of view leads to the conclusion that this phenomenon (the Baker–Nathan effect) is not to be classed with those combined under the term conjugation.

The problem of steric hindrance to hyperconjugation is considered by Jaffe and Roberts[50].

VIII. QUANTITATIVE CALCULATION OF CONJUGATION BETWEEN π BONDS

If compounds containing α,β-unsaturated substituents are included in reaction series in which a correlation of the type (7.2) is applicable, Eqn. (3.1) becomes[30]

$$\Delta\Delta F \text{ (or } \Delta\Delta H) = \rho^*\Sigma\sigma^* + (\Delta n)h + \Delta\Delta E_\psi. \qquad (8.1)$$

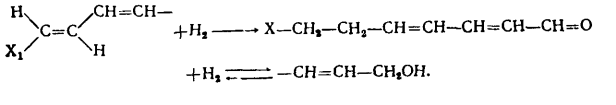
Hence the energy of conjugation $\Delta\Delta E_\psi$ can be calculated by means of the formula:

$$\Delta\Delta E_\psi = \Delta\Delta F \text{ (or } \Delta\Delta H) - \rho^*\Sigma\sigma^* - (\Delta n)h. \qquad (8.2)$$

If the experimental data relate to reaction velocities (*e.g.* in the acid hydrolysis of acetals and ketals), the free energy of conjugation is calculated from the equation[30]:

$$\Delta\Delta F_\psi = -2.303RT[\log k/k_0 - \rho^*\Sigma\sigma^* - (\Delta n)h]. \qquad (8.3)$$

Kreevoy and Taft[30] calculated values of $\Delta\Delta E_\psi$ for a series of *trans*-substituted ethylenes and unsaturated aldehydes starting from the heats and the free energies of equilibrium respectively. Both these reaction series are distinguished by the absence from the final reaction product of the conjugation present in the initial molecule:



Kreevoy and Taft[30] also give values of $\Delta\Delta F_\psi$ for the acid hydrolysis of acetals and ketals. Kreevoy[20] calculated values of $\Delta\Delta F_\psi$ for conjugated substituted acetylenes from the heats of hydrogenation of these compounds.

In all these cases[20,30] the energy of conjugation of the π bond (forming part of a double or a triple bond) with some system of π bonds (in the simplest case with a double bond) remains constant in a given reaction series, within the limits of accidental fluctuations, which seldom exceed ±1 kcal. Furthermore, the conjugation of two $\rangle C=C\langle$ bonds is energetically equivalent to that between $\rangle C=C\langle$ and $\rangle C=O$ bonds. Only non-polar conjugation is present in the former case, but in the latter polar conjugation is present also, since the carbonyl group is a -C type of substituent. From the equality of the energies of conjugation in the two cases it follows that the polar conjugation component is small compared with the energy of non-polar conjugation. It can therefore be stated that the quantities considered in this section relate to non-polar conjugation.

The conjugation energy is additive in the sense that the value of $\Delta\Delta E_\psi$ is approximately twice as great for compounds in which a given double or triple bond is conjugated with two systems of π bonds as for singly conjugated systems.

Taft and Kreevoy emphasise[30] that the so-called "experimental resonance energies" quoted by Wheland[51] were obtained without allowing for the inductive effect. Neglect of this factor leads to such large errors that the data obtained in this way are of no practical value.

The good agreement with experimental data of the conjugation energies calculated by the molecular-orbital method must be specially emphasised[30].

The changes in the energy of conjugation of the carboxyl group with the benzene nucleus during formation of the activated complex in the catalytic decomposition of diphenyldiazomethane by benzoic acid[52] and in the dissociation of benzoic acid[26] are ~0.5 kcal. In both cases the change in conjugation energy is associated with the conversion of carboxyl into a carboxylate anion. In this process the valency state of the carbonyl carbon remains unchanged, and the non-polar conjugation is obviously maintained. However, the capacity of the carboxyl group for polar conjugation must be greatly diminished by the appearance of a negative charge on the group. Thus there are grounds for ascribing the above 0.5 kcal to a decrease in (or the disappearance of) the polar conjugation of the carbonyl group with the benzene nucleus. This supports the above conclusion that the energy of non-polar conjugation of a polar double bond of the type $\rangle C=O$ with a π-electron system is considerably greater than the energy of the corresponding polar conjugation.

The general conclusion is that the energy of non-polar conjugation of a double bond with a system of π bonds varies between 5 and 7 kcal. A value of 6 kcal can be used for rough calculations.

The value of the parameter h for the hydrolysis of esters was estimated from the empirical rule that the energy of hyperconjugation is about one-tenth of the energy of conjugation[30]. The resulting value of h = 0.5 kcal mole^{-1} indicates that the steric constants of substituents contain an appreciable hyperconjugation term of $0.35\Delta n$. In the case of hydrogen, for example, E_S = +1.24, Δn = -3, and

$0.35\Delta n = +1.05$. Consequently, the so-called "steric" constant of hydrogen is mainly of the nature of hyperconjugation.

IX. POLAR EFFECTS OF NUCLEAR SUBSTITUENTS ON THE REACTIVITY OF AROMATIC COMPOUNDS. HAMMETT'S EQUATION

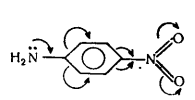
A detailed review of existing data on the use, accuracy, and limits of applicability of Hammett's equation was published by Jaffe[53] in 1953. This paper contained valuable standard data in the shape of values of ρ and of $\log K_0$ for 218 reaction series. In the present section only a few of the main points discussed by this author will be considered, since many ideas in this field have been considerably improved in the ensuing period of rapid development of the underlying theory.

As stated above, Hammett's equation served as a model for many other attempts at applying LFE to organic reactions. This was because this equation, like Eqn. (5.1), is the most simple form in which LFE is satisfied, when there is no need to expand $\Delta\Delta F$ into its components. This is also omitted with Taft's special equation, since this equation applies only to reaction series in which all factors other than the inductive effect can be neglected. Such is not the case with Hammett's equation, however. Right from the start it was clear that the effect of polar conjugation cannot be neglected in this case, at least with *para*-substituted benzene derivatives. Thus Hammett's equation describes the combined effect of two factors — the inductive effect and polar conjugation[41]. The analysis of problems associated with the application of Hammett's equation is therefore more complicated.

As already noted in section II, Hammett's equation is

$$\log k/k_0 = \rho\sigma. \qquad (9.1)$$

Originally only one set of constants σ, based on the dissociation constants of the substituted benzoic acids, was used for the substituents (standard reaction series, $\rho = 1$). Values of the σ constants were determined for many different substituents and were used to calculate values of ρ for a large number of reaction series[4,53]. In some cases Eqn. (9.1) fitted the experimental data with great accuracy (Fig. 1), but there were also examples of departures from the equation (Fig. 2), which were sometimes considerable (Fig. 3). Thus values of σ for such substituents as NO_2, COOH, CHO, CN, $COCH_3$, etc., determined from the dissociation constants of the benzoic acids, cannot be used to study the acid dissociation of *meta*- and *para*-substituted phenols or the basic dissociation constants of *meta*- and *para*-substituted anilines[4,54-56]. Since all these substituents possess considerable negative polar conjugation effects, the above phenomenon was explained in terms of direct conjugation between a -C type of substituent and a +C type of reactive centre[4].



New, so-called "dualistic" values σ^- of the constants for *para*-substituents of -C type were introduced for reaction series in which this type of conjugation is present‡.

‡ The symbol σ_p* was employed formerly[4,43,53] instead of σ^-.

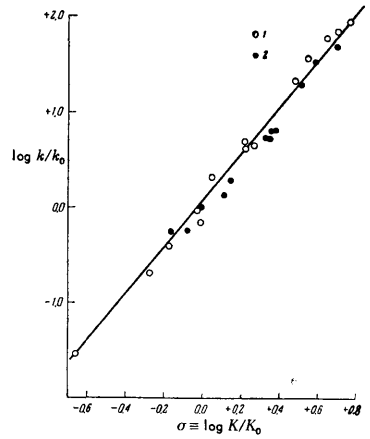


Fig. 1. Linear dependence of values of $\log k/k_0$ for the alkaline hydrolysis of *meta*- and *para*-substituted ethyl benzoates in 60% aqueous acetone at 25° on Hammett σ values determined from the dissociation constants of the benzoic acids: 1) *meta*-substituents; 2) *para*-substituents.

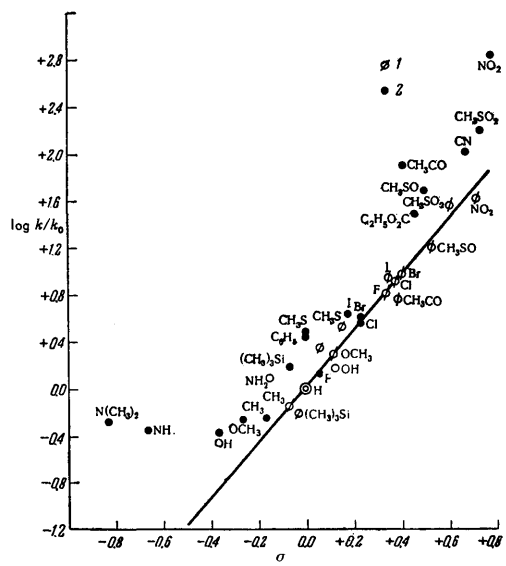


Fig. 2. Departures from Hammett's equation for the acid dissociation of *meta*- and *para*-substituted phenols at 25°: 1) *meta*-substituents; 2) *para*-substituents.

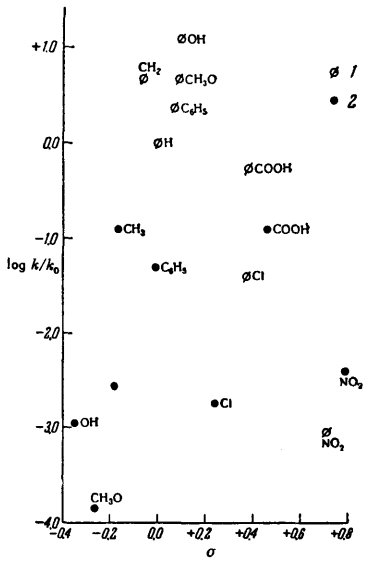
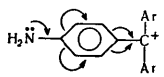


Fig. 3. Failure of the Hammett equation for the decomposition of *meta*- and *para*-substituted benzenediazonium chlorides in water at 29°: 1) *meta*-substituents; 2) *para*-substituents.

A comparable situation arises if a +C type of substituent enters into direct polar conjugation with a -C type of reactive centre. An example is provided by reactions in which triarylcarbonium ions either take part or are formed:



New constants σ^+, taking account of the ability of a given substituent to enter into direct polar conjugation with a -C type of reactive centre, were introduced[57-65] for such reaction series. Since the -C type includes also the carboxyl group, which is directly combined with the benzene nucleus in substituted benzoic acids, and can enter into direct conjugation with a +C type of substituent, the "normal" σ values for *para*-substituents of this type have in fact already made some allowance for their capacity for direct polar conjugation[57-66].

Since direct polar conjugation always intensifies the polarisation of the reactive centre produced by the substituent, $\sigma^- > \sigma$ and $\sigma^+ < \sigma$.

If the reactive centre can undergo direct polar conjugation with both +C and -C substituents, σ^+ constants are employed with the first type, and σ^- with the second[67].

The interrelationships between the quantities σ and σ^- were also analysed by the molecular-orbital method. The changes in electron density in the *meta* positions are proportional to the corresponding values of σ. Changes in the energy of localisation in the *meta* positions are proportional to the values of σ, and those in the *para* position to values of σ^-.[68]

The values of σ, σ^+, and σ^- do not remain constant if different reaction series are used to determine them. Consequently the substituent constants in Hammett's equation are not completely general parameters. For example, the value of σ^- calculated for CH_3SO_2 from data for the dissociation of substituted anilinium ions is +0.98, whereas the value calculated from data for the dissociation of phenols[55] is +1.13, etc. It is for this reason that it has been necessary to introduce σ^+ constants for some reaction series. Thus the "normal" σ values for substituents of +C type, determined from the dissociation constants of benzoic acids, are by definition also constants of σ^+ type. Therefore values of σ calculated for +C substituents from experimental data for reaction series in which the reactive centre is of +C type or is separated from the benzene nucleus by a saturated side-chain, have considerably larger positive values than the "normal" σ values[57].

The values of σ can change within wide limits on passing from one reaction series to another, even in the absence of direct conjugation of the substituent with the reactive centre[57].

The dependence of the reaction constant ρ on the nature of the reaction, the structure of the reagent, and the solvent is of no less interest. This constant has positive values for all reactions facilitated by electronegative substituents. Reactions favoured by electron-donating substituents are characterised by negative values of ρ. The numerical value of ρ measures the "sensitivity" of a given reaction to polar effects, and the ability of the atomic grouping linking the benzene nucleus with the reactive centre to transmit the polar effects of the nuclear substituents. The insertion of a group of atoms Z between the aromatic nucleus and the reactive centre results in a diminution in ρ, which may be expressed quantitatively by a factor π' independent of the nature of the reactive centre and of the reaction and the conditions under which it occurs[53,70,71]. Values of π' calculated by the molecular-orbital method[53] agree with the experimental results, as can be seen from the data below.

Z	π' expt.	π' calc.	Z	π' expt.	π' calc.
$-CH_2$	0.410∓0.084	—	—N=N—	0.145∓0.015	0.136
$-CH_2-CH_2$	0.206∓0.009	—	—CH=CH—CO	0.035	—0.010
—CH=CH—	0.508∓0.038	0.683		— —	—0.013
	0.303∓0.040	0.177		0.25	—

In the case of reaction series representing the dissociation of acids in which the functional acid group is directly linked to a benzene nucleus, the magnitude of ρ depends on the polarisability of the central atom [*e.g.* in $B(OH)_2$] of the functional group. The value of ρ increases with the ionic refraction of the ion obtained by filling the valency shell of this atom to complete its octet[53,72].

Jaffe, on the basis of his statistical investigation covering 336 reaction series[73], concluded that $\rho_m = \rho_p$. This result is not surprising, since the values of σ_{meta} and σ_{para} which he employed had been calculated on the assumption that $\rho_{meta} = \rho_{para}$. The result obtained by Jaffe therefore bears no relation to the actual constants representing sensitivity to the polar effects of substituents in the *meta* and

para positions of the benzene nucleus. Hine[74] in considering this problem rules out the postulate that the two sensitivity constants are equal, and concludes that ρ_m and ρ_p should differ appreciably. This is quite understandable in view of the rapid damping of the influence of the inductive effect as the distance between substituent and reactive centre increases.

There are several examples of empirical relations linking ρ for a given reaction with the composition of a mixed solvent[75] or with the dielectric constant of the medium[76].

As regards the range of applicability of Hammett's equation, it covers a great variety of reaction series, both heterolytic and homolytic[53].

Hammett's equation allows several physical properties of substituted aromatic and heterocyclic compounds to be correlated, for example the infra-red absorption frequencies corresponding to some stretching vibrations[53,77-83].

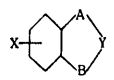
A few additivity rules are important in practice[53]. If a benzene nucleus contains more than one substituent in the *meta* and *para* positions, or if several benzene nuclei are linked symmetrically with the reactive centre, the following relation can be employed:

$$\log k/k_0 = \rho\Sigma\sigma. \qquad (9.2)$$

If several benzene nuclei are linked unsymmetrically with the reactive centre,

$$\log k/k_0 = \Sigma\rho\sigma. \qquad (9.3)$$

In the case of compounds of the type



the following formula can be used[84]:

$$\log k/k_0 = \rho_1\sigma_m + \rho_2\sigma_p. \qquad (9.4)$$

Since values of σ_p measure the combined influence of the inductive effect and polar conjugation, they can also be used with the corresponding unsaturated aliphatic systems. The acidity of *trans*-3-substituted acrylic acids is represented by the usual Hammett equation[85]. The inductive constants of substituents of the type *trans*-X−CH=CH− are related to values of σ_p for X by the following relation[86]:

$$\sigma^* = 0.60 + 1.60\sigma_p. \qquad (9.5)$$

Application of Hammett's equation to heterocyclic compounds is of very great interest and has several aspects. Examples are known of the usual Hammett $\sigma-\rho$ correlation when the heteroatom is the reactive centre, as with the basic dissociation constants of 3- and 4-substituted pyridines and the corresponding oxides[87]. On the other hand, replacement of a =CH− group in the benzene nucleus by =N−, $\overset{\backslash}{\underset{/}{N}}\rightarrow O$, and $\overset{\backslash}{\underset{/}{NH^+}}$ groups can be regarded as analogous to the replacement of hydrogen in the *meta* or *para* position, and appropriate values of σ_3 and σ_4 can be assigned to these groups[87-89]. There are indications, however, that the values of σ_3 and σ_4 for =N− do not remain constant on passing from one reaction series to another[90].

A Hammett type of equation

$$\log k/k_0 = \rho\sigma, \qquad (9.6)$$

where σ represents the logarithm of the ratio of the dissociation constants of substituted and unsubstituted carboxylic acids of a given series, is applicable to several substituted derivatives of thiophen, furan, thiazole, and pyridine. In the case of thiophen and furan derivatives ρ has about the same value as with benzene derivatives (with the exception of one reaction series), but this does not apply to thiazole and pyridine derivatives[91].

In these cases the Hammett equation does not imply proportionality between the quantities $\log k/k_0$ and σ determined from the dissociation constants of substituted benzoic acids. Therefore the values of σ in (9.6) are not necessarily equal to the Hammett σ constant [*i.e.* not when ρ in (9.6) is not equal to ρ in the Hammett equation for the benzene series]. Relations like (9.6) and cases of LFE in general are often combined under the general term "Hammett equation". Such a broad interpretation of this term and the identification of the Hammett equation with the LFE principle are hardly desirable at the present time.

The Hammett equation, like the Taft equation, can be successfully employed in the study of reaction mechanisms[4,10,53,72,92-95].

Values of the constants σ, σ^-, and σ^+ for various substituents are given in Table 2.

TABLE 2. Hammett constants for various substituents.

Values quoted from Jaffe[53] calculated by statistical averaging of data for all reaction series for which experimental results were available by 1953; values from McDaniel and Brown[96] obtained from the dissociation constants of substituted benzoic acids or from data for reaction series for which ρ had been determined by the use of values of σ calculated from the dissociation constants of benzoic acids; and individual values quoted by other authors from data on some reaction series for which the value of ρ was known.

Substituent	σ_m			σ_p			σ^-	σ^+	
	ref. 53	ref. 96	other refs.	ref. 53	ref. 96	other refs.		*meta*	*para*
CH_3	−0.069	−0.069		−0.170	−0.170	from −0.080[95] to −0.170		−0.066[65]	−0.311[65]
C_2H_5	−0.043	−0.07		−0.151	−0.151			−0.064[65]	−0.295[65]
C_3H_7	—	—		−0.126	—				
$CH(CH_3)_2$	—	—		−0.151	−0.151			−0.060[65]	−0.280[65]

TABLE 2 (contd.)

Substituent	σ_m			σ_p			σ^-	σ^+	
	ref. 53	ref. 96	other refs.	ref. 53	ref. 96	other refs.		*meta*	*para*
C_4H_9	—	—		−0.161	—				
$CH_2CH(CH_3)_2$	—	—		−0.115	—				
$CH(CH_3)C_2H_5$	—	—		−0.123					
$C(CH_3)_3$	−0.120	−0.10		−0.197	−0.197			−0.059[65]	−0.256[65]
$(CH_3)_2CH(CH_2)_2$	—	—		−0.225	—				
$C(CH_3)_2C_6H_5$	—	—		−0.190					
CF_3	+0.415	+0.43		+0.551	+0.54			+0.520[62]	+0.612[62]
CCl_3	—	—	+0.407[21]	—	—	+0.454[21]		—	—
CH_2Cl	—	—	—	+0.184	—	—	—	+0.14[65]	+0.01[65]
$CHCl_2$	—	—	+0.185[21]	—	—	+0.212[21]		—	—
CH_2CN	—	—	—	+0.007	—			—	—
CH_2CH_2COOH	−0.027	—		−0.066	—			—	—
OH	−0.002	+0.121		−0.357	−0.37			—	−0.92[65]
CCH_3	+0.115	+0.115		−0.268	−0.268	−0.361[98]		+0.047[65]	−0.778[65]
OC_3H_7	+0.150	+0.1		−0.250	−0.24			—	—
CC_2H_7	—	+0.1		−0.268	−0.25			—	—
$OCH(CH_3)_2$	—	+0.1		−0.286	−0.45			—	—
OC_4H_9	—	+0.1		−0.320	−0.32			—	—
OC_5H_{11}	—	+0.1		−0.340	−0.34			—	—
$O(CH_2)_2CH(CH_3)_2$	—	—		−0.265	—			—	—
$CCH_2C_6H_5$	—	—		−0.415	—			—	—
OC_6H_5	—	+0.252		−0.028	−0.320			—	−0.5[65]
O⁻	−0.708	—		−0.519				—	—
$OCOCH_3$	—	+0.39		—	+0.31			—	—
NH_2	−0.161	−0.16		−0.660	−0.66			−0.16[65]	−1.3[65]
$NHCH_3$	−0.302	—		−0.592	−0.84				
NHC_6H_5	−0.240	—		—					
NHC_4H_9	−0.344	—		—					
$N(CH_3)_2$	−0.211	—		−0.600	−0.83			—	−1.7[65]
$NHCOCH_3$	—	+0.21		−0.015	0.00				−0.6[65]
$NHCOC_6H_5$	+0.217	—		+0.078					−0.6[65]
$NHNH_2$	−0.020	—		−0.550					
NHOH	−0.044	—		−0.339					
NH_3^+	+0.634	—		—					
$NH_2CH_3^+$	+0.958	—		—					
$NH_2C_2H_5^+$	+0.958	—		—					
$N(CH_3)_3^+$	+0.904	+0.88	+0.67[64]	+0.859	+0.82	0.66—1.11[64]	—	+0.359[65]	+0.408[65]
			+1.02						
N_2^+	—	—	+1.7[99]	—	—	+1.8 ±0.5[99]			
COOH	+0.355	(+0.37)		+0.265	(+0.45)		+0.728[53]	+0.322[62]	+0.421[62]
$COOCH_3$	+0.315	—	—	—	—	+0.436[100]	+0.636[53]	+0.368[62]	+0.489[62]
$COOC_2H_5$	+0.398	+0.37		+0.522	+0.45		+0.678[53]	+0.366[62]	+0.482[62]
$COOC_4H_9$	—	—		—			+0.674[53]		
$COOCH_2C_6H_5$	—	—					+0.667[53]		
$CONH_2$	+0.280	—		—			+0.627[53]		
CHO	+0.355	—	+0.382[101]	+0.216			+0.126[53]		
$COCH_3$	+0.306	+0.376	+0.306[101]	+0.516	+0.502		+0.874[53]		
COC_6H_5	—	—		+0.459			—		
CN	+0.678	+0.56	+0.52[101]	+0.628	+0.660	+0.65[101]	+1.000[53]	+0.562[62]	+0.659[62]
COO⁻	+0.104	−0.1		+0.132	0.0	—	—	−0.028[65]	−0.023[65]
$C_2H_5OCOCH_2$	—	—		—	—	—	—	−0.01[65]	−0.164[65]
NO_2	+0.710	+0.710		+0.778	+0.778	—	+1.270[53]	+0.710[62]	+0.790[62]
NO	—	—		+0.123					
F	+0.337	+0.337		+0.062	+0.062			+0.352[65]	−0.073[65]
Cl	+0.373	+0.373		+0.227	+0.227			+0.399[65]	−0.114[65]
Br	+0.391	+0.391		+0.232	+0.232			+0.405[65]	+0.150[65]
I	+0.352	+0.352		+0.276	+0.18	+0.27[102]		+0.359[65]	+0.135[65]
IO_2	(+0.70)	+0.70		(+0.76)	+0.76				
SCH_3	+0.144	+0.15		−0.047	0.0			+0.158[65]	−0.604[65]
$SOCH_3$	+0.551	+0.52		+0.567	+0.49	+0.73[103]			
SO_2CH_3	+0.647	+0.60	+0.56[101]	+0.728	+0.72	+0.68[101]	+1.049[53]		
SCN	—	—		+0.699	+0.52				
SeCN	—			+0.664					
$B(OH)_2$	+0.006			+0.454					
$Si(CH_3)_3$	−0.121			−0.072	−0.07			+0.011[65]	+0.021[65]
$Si(C_2H_5)_3$	—	—		—	0.0				
$CH_2Si(CH_3)_3$	—	−0.16		—	−0.21				
C_6H_5	+0.218	+0.06		+0.009	−0.01			+0.109[65]	−0.179[65]
$N{=}N{-}C_6H_5$	—			+0.640	—				
$C_6H_5N{=}NC_6H_5$	—			—	—		+1.088[53]		
$CH{=}CH{-}C_6H_5$	+0.141				—		+0.619[53]		
AsO_3H^-	—			−0.019	−0.02		—		
PO_3H^-	+0.228	+0.2		+0.238	+0.26		—		
SO_2	—			+0.381	—		—		
SO_2NH_2	—	+0.46	+0.55[101]	+0.621	+0.57	+0.62[101]	+0.94[101]		
SO_3^-	—	+0.05	+0.31[101]	—	+0.09	+0.37[101]	+0.58[101]		
3,4-$(CH_2)_3$	—			−0.259	—				
3,4-$(CH_2)_4$	—			−0.477	—				
3,4-(CH)$_4$	—	—		+0.170	+0.042				−0.135[65]
3,4-CH_2O_2	—			−0.159					
$Ge(CH_3)_3$	—	—		—	−0.0				
$Ge(C_2H_5)_3$	—	—		—	−0.0				
$Sn(CH_3)_3$	—	—		—	−0.0				
$Sn(C_2H_5)_3$	—	—		—	−0.0				
$ScCH_3$	—	+0.1		—	+0.0				
SC_6H_5	—	—		—	+0.03				
$SCH(CH_3)_2$	—	—		—	+0.07				
SH	—	+0.25		—	+0.15				
$SCOCH_3$	—	+0.34		—	+0.44				
$S(CH_3)_2^+$	—	+1.0		—	+0.90				
$2\text{-}CH_3C_6H_3$	—	—	—	—	—	−0.016			
$2\text{-}HOC_6H_4$	—	—	—	—	—	+0.003			
$2\text{-}CH_3OC_6H_4$	—	—	—	—	—	+0.012			
$2\text{-}ClC_6H_4$	—	—	—	—	—	+0.047			
$HC{\equiv}C$-	—	—	—	—	—	+0.281			
$CH_3C{\equiv}C$—	—	—	—	—	—	+0.087			
$CH_2CH{=}CH$—	—	—	—	—	—	−0.043			
$\gg N^+H$	—	—	+2.1[87]	—	—	+2.3[87]	4.0[87]		
$\gg NO^+H$	—	—	+2.3[87]	—	—	—	3.9[87]		

X. POLAR AND STERIC CONSTANTS OF *ortho*-SUBSTITUENTS

The Hammett equation is usually inapplicable to *ortho*-substituted benzene derivatives[53], the "anomalous" behaviour of these compounds being known as the "*ortho* effect". The anomaly is ascribed to steric effects, including steric hindrance to conjugation between the reactive centre and the aromatic nucleus, the field effect, and intramolecular hydrogen bonding[53,72].

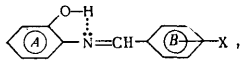
Taft[10,17,26] attempted to discuss *ortho*-substituted benzene derivatives by analogy with aliphatic compounds. He calculated the polar constants σ_o^* for *ortho*-substituents from data on the rates of alkaline and acid hydrolysis of *ortho*-substituted benzoates by means of Eqn.(4.1), hydrogen being taken as standard substituent. The "aromatic" polar constants σ_o^* thus obtained for the substituents were analogous in physical significance to the Hammett σ constants, since they represent the combined influence of an inductive effect and polar conjugation. They will therefore be denoted, in what follows, by σ_o. The values of σ_o for different substituents are similar in magnitude to the Hammett σ_p constants.

Several reaction series are known in which the steric effect of *ortho*-substituents on the reactive centre is insignificant, and the Hammett–Taft equation[10,17,26] is applicable:

$$\log k/k_0 = \rho_o\sigma_o. \qquad (10.1)$$

The quantity ρ_o is usually close to ρ in the Hammett equation for the given reaction series, but this is not always the case[10]. Eqn. (10.1) cannot be applied with *ortho*-substituents which can form an intramolecular hydrogen bond with the reactive centre[10].

Values of the polar constants for *ortho*-substituents were determined also by Baker and Shulgin[77] from a study of the changes in infra-red absorption frequency of a hydroxyl group forming an intramolecular hydrogen bond in Schiff bases of the type



produced by substitution in nucleus *B*. In this case there is good agreement with the Hammett equation $\Delta\nu = \rho\sigma$. These workers calculated values of σ_o for the *ortho*-substituents by substituting in this equation the value of ρ obtained from data for *meta*- and *para*-substituents. In view of the considerable distance of the *B* ring from the hydrogen bond, the resulting values of σ_o should represent only the combination of inductive effect and polar conjugation, if the component due to the field effect is disregarded. Except for the nitro group, values of σ_o determined in this way differ little from Taft's σ_o^*.

Apparently because of the superimposition of the field effect, the Taft and Baker–Shulgin σ_o constants are not so generally applicable as the Hammett σ values. As an example, although the infra-red absorption frequencies for the carboxyl group in *ortho*-substituted benzoic acids, acetanilides, and several other benzene derivatives vary in the same direction as the Taft σ_o values, this variation is not linear[104].

With fourteen reaction series involving compounds of the type $o\text{-X-C}_6\text{H}_4\text{-Z-Y}$, where Z is an "isolating" chain consisting of two or more atoms (Z = $-CH=CH-$, $-CH_2-CH_2-$, $-O-CH_2-$, etc.), Charton[105] has shown that the Hammett equation can be applied in the form (10.1), and Hammett's σ_p can be used instead of σ_o values. From this he concludes that the failure of Hammett's equation to hold for *ortho*-substituted benzene derivatives is in general a consequence of steric interaction between the substituent and the reactive centre, or else of the formation of a hydrogen bond between them.

Introduction of a substituent into the *ortho* position does not disturb the Hammett $\sigma-\rho$ correlations for a given series of *meta*- and *para*-substituted compounds[54,106]. It follows that *meta*- and *para*-substituents do not affect the magnitude of the *ortho* effect.

Values of "aromatic" steric constants have been calculated for several substituents from data on the kinetics of the acid hydrolysis of *ortho*-substituted benzoates[17,10]. One example is known of the application of the LFE principle to values of E_S for *ortho*-substituents[10].

E_S values for *ortho*-substituents vary in the same sense as the van der Waals radii of the substituents[10].

XI. PROBLEM OF THE QUANTITATIVE SEPARATION OF INDUCTIVE AND POLAR CONJUGATIVE EFFECTS

As noted above, the Hammett σ values characterise the combined influence of the inductive effect and the polar conjugation inherent in a given substituent. This is the reason for the fundamental inaccuracy of the Hammett equation. Numerous attempts have therefore been made to determine quantitatively the several effects of these factors. Various approaches may be made to this problem.

Roberts and Moreland[107] and later Taft[10] tried to evaluate the inductive term in the Hammett σ values. The former used model compounds in the shape of 4-substituted bicyclo[2,2,2]octane-1-carboxylic acids and their ethyl esters. Three reaction series involving these compounds exhibit LFE behaviour as represented by the Hammett equation:

$$\log k/k_0 = \rho_I\sigma_I, \qquad (11.1)$$

where $\sigma_I = [\log(k/k_0)]/1.464$, k and k_0 being the dissociation constants of the 4-substituted and the unsubstituted bicyclo[2,2,2]octane-1-carboxylic acids respectively in 50 vol.% ethanol at 25°, and 1.464 being the value of ρ in the Hammett equation for the dissociation of substituted benzoic acids in 50% ethanol at 25°. Values of ρ_I in Eqn. (11.1) are similar to those of ρ in the Hammett equation for the corresponding reaction series. The above workers therefore concluded that values of σ_I are practically equal to the inductive component in the Hammett σ constants for the appropriate substituents.

Taft[111] has shown that the quantity $\sigma_{I(X)}/\sigma^*_{(X-CH_2)}$ has a constant value of +0.450 for different substituents. It follows that the σ_I and σ^* scales of inductive effects are fundamentally equivalent, and that values of σ_I can be obtained from the corresponding values of σ^* by means of the formula:

$$\sigma_{I(X)} = 0.450\sigma^*_{(X-CH_2)}. \qquad (11.2)$$

The inductive components in the σ values can be found also by determining the Hammett constants for groups whose conjugation with the benzene nucleus is completely

destroyed by steric hindrance[10,108-110]. The results obtained agree with the σ_I values.

The σ_I values have been used to separate the inductive and resonance (polar conjugation) components in the Hammett equation. Values of σ_I are given in Table 3.

Taft[111] notes that values of σ_I (and hence σ^*), Branch and Calvin's[14] inductive constants I_a, and Pauling's[5] electronegativities agree well with the Periodic Table.

It is further assumed that the effects of *meta*- and *para*-substituents on the reactivity and other properties of aromatic compounds should theoretically be represented by the following equations[112,114,118]:

$$\log k_p/k_0 = \rho_I^p \sigma_I + C_p, \qquad (11.3)$$

$$\log k_m/k_0 = \rho_I^m \sigma_I + C_m, \qquad (11.4)$$

where C_p and C_m represent the effects of polar conjugation for a given substituent in the *meta* and *para* positions respectively. Although there is no direct conjugation of a substituent with the *meta* position of the benzene nucleus, polar conjugation has nevertheless an indirect influence on such positions too[107,118]. The nature of this effect will be clear if it is assumed that charges induced in the *ortho* and *para* positions by polar conjugation cause like charges to appear in the *meta* positions owing to electrostatic repulsion or attraction of electrons along σ bonds (secondary inductive effect).

It has been suggested[114] that C_p and C_m should be divided into factors analogous to ρ_I and σ_I (application of LFE principle): $C_p = \rho_c^p \sigma_c$ and $C_m = \rho_c^m \sigma_c$. Eqns. (11.3) and (11.4) can then be rewritten as follows:

$$\log k_p/k_0 = \rho_I^p \sigma_I + \rho_c^p \sigma_c, \qquad (11.5)$$

$$\log k_m/k_0 = \rho_I^m \sigma_I + \rho_c^m \sigma_c. \qquad (11.6)$$

If $\rho_I^p = \rho_c^p = \rho$, the quantities ρ_I^m/ρ and ρ_I^p/ρ are constant for all reaction series, and σ_c is a universal constant for a given substituent, Eqns. (11.5) and (11.6) reduce to the Hammett equation:

$$\log k_p/k_0 = \rho\sigma_p \text{ and } \log k_m/k_0 = \rho\sigma_m,$$

where $\sigma_p = \sigma_I + \sigma_c$ and $\sigma_m = \dfrac{\rho_I^m \sigma_I + \rho_c^m \sigma_c}{\rho}$.

The above restrictions are necessary for the Hammett equation to be applicable. Clearly, this condition is not always observed, and consequently the Hammett equation is in principle not exact.

If $\rho_I^p = \rho_C^p = \rho$, then $\sigma_I + \sigma_C = \sigma_p$, and values of σ_C can be calculated from the formula[107,112,114]

$$\sigma_C = \sigma_p - \sigma_I. \qquad (11.7)$$

The quantities σ_C^- and σ_C^+, characterising the direct conjugation between a reactive centre and a substituent of type -C and +C respectively, are determined in a similar manner[114]:

$$\sigma_C^- = \sigma_p^- - \sigma_I, \qquad (11.8)$$

$$\sigma_C^+ = \sigma_p^+ - \sigma_I. \qquad (11.9)$$

Values of σ_C, σ_C^-, and σ_C^+ are given in Table 3.

Among examples of the practical application of these quantities, the chemical shifts in nuclear magnetic resonance for ^{19}F in *meta*- and *para*-substituted fluorobenzenes are well represented by the equations:

$$\delta_{^{19}F}^p = \rho_I \sigma_I + \rho_C \sigma_C, \qquad (11.10)$$

TABLE 3. Aromatic polar substituent constants: σ°, σ_I, σ_C°, σ_C, σ_C^-, σ_C^+, $\Delta\sigma_C^+$.

Substituent	σ° [111] meta	σ° [111] para	σ_I [118]	σ_C° [112]	σ_C [114]	σ_C^- [111]	σ_C^+ [115]	$\Delta\sigma_C^+$ [116]
H	(0.00)	(0.00)	(0.00)	(0.00)	(0.00)	(0.00)	(0.00)	(0.00)
CH_3	−0.07	−0.15	−0.05	−0.10	−0.13	—	−0.26	−0.131
C_2H_5	—	—	−0.05	—	—	—	—	−0.141
$(CH_3)_2CH$	—	—	—	—	—	—	—	−0.125
$(CH_3)_3C$	—	—	−0.07	—	—	—	—	−0.053
$(CH_3)_3Si$	—	—	−0.12	—	+0.11	—	−0.07	
C_6H_5	—	0,00[113]	+0.10	−0.10	−0.09	—	−0.22	−0.200
$C_6H_5CH_2$	—	—	+0.04	—	—	—	—	—
CH_2Cl	—	—	+0.17	—	—	—	(−0.11)	—
CF_3	—	—	+0.41	—	+0.14	—	—	—
F	+0.35	+0.17	+0.52	−0.35	−0.44	—	−0.57	−0.130
Cl	+0.37	+0.27	+0.47	−0.20	−0.24	—	−0.36	−0.106
Br	+0.38	+0.26	+0.45	−0.19	−0.22	—	−0.30	−0.081
I	+0.35	+0.27	+0.39	−0.12	−0.10	—	−0.25	−0.144
OH	+0.04[c]	−0.13[c]	+0.25	−0.37[a]	−0.50	—	(−1.07)	−0.56
	+0.13[a]	−0.12[a]		−0.41[b]			−0.99	−0.496
OCH_3	+0.06[b]	−0.16[b]	+0.25	−0.41[b]	−0.50	—	—	−0.494
C_6H_5	—	−0.123*	—	—	—	—	—	−0.51
OC_6H_5	—		+0.38	—	−0.41	—	—	—
OCF_3	—	—	+0.48	—	−0.11	—	—	—
SH	—	—	+0.25	—	—	—	—	—
SCH_3	—	—	+0.25	—	−0.24	—	—	—
SC_6H_5	—	−0.025*	—	—	—	—	—	—
SCF_3	—	—	+0.43	—	−0.05	—	—	—
$COCH_3$	+0.34	+0.46[d]	+0.28	+0.18[d]	+0.25	+0.60	—	—
		+0.40[c]		+0.12[c]				
COOH,COOR	+0.36	+0.46[d]	+0.30	+0.16[d]	+0.20	+0.36	—	—
COO^-	+0.08*	+0.08*	—	—	—	—	—	—
CN	+0.62	+0.69[d]	+0.58	+0.11[d]	+0.07	+0.41	—	—
		+0.63[c]		+0.05[c]				
NH_2	−0.14	−0.38	+0.10	−0.48	−0.76	—	−1.31	−1.00
$NHCH_3$	−0.22*	−0.42*	—	—	—	—	—	—
NHC_2H_5	−0.18*	—	—	—	—	—	—	—
NHC_4H_9	−0.24*	—	—	—	—	—	—	—
$N(CH_3)_2$	−0.15	−0.44	+0.10	−0.54	—	—	(−1.89)	−0.74
$NH—NH_2$	+0.02*	−0.40	—	—	—	—	—	—
$NH_3(CH_3)^+$	+1.00*	—	—	—	—	—	—	—
$NH_4(C_2H_5)^+$	+1.00*	—	—	—	—	—	—	—
$NH(CH_3)_2^+$	—	1.00*	—	—	—	—	—	—
$N(CH_3)_3^+$	—	—	+0.86	0.00	—	—	—	—
$NH(COCH_3)$	—	+0,03[113]	+0.28	−0.25	—	—	—	−0.58
NO_2	+0.70	+0.82[d]	+0.63	+0.19[d]	+0.15	+0.64	—	—
		+0.73[c]		+0.10[c]				
$SOCH_3$	—	—	+0.52	—	—	—	—	—
SO_2CH_3	—	—	+0.59	—	+0.14	+0.46	—	—
SO_2NH_2	—	+0.62	—	—	—	—	—	—
SO_2CF_3	—	—	+0.84**	—	+0.19**	—	—	—

* Calculated from Eqn. (14.2).

** Taken from ref. 117.

[a] Values only for pure aqueous solutions.

[b] Values for non-hydroxylic solvents and for most mixtures of water with organic solvents.

[c] Values only for non-hydroxylic solvents.

[d] Values for aqueous solutions and most mixtures of water with organic solvents.

$$\delta_{^{19}F}^m = \rho_I \sigma_I, \qquad (11.11)$$

where $\rho_I \neq \rho_C$. A similar relation holds also for chemical shifts in nuclear magnetic resonance for H in substituted benzenes[95]. Values of σ^- have been used also to correlate rates of acid dissociation of substituted methanes in water[119]. For the use of σ_C^- and σ_C^+ in the correlation of dipole moments, see section XIX. The quantities σ_I and σ_C may perhaps be related by[120]: $\sigma_I = 0.570 + 0.603\sigma_C$.

Taft *et al.*[113,118] tried to determine the inductive component by eliminating C_p and C_m from Eqns. (11.3) and (11.4). They assumed at first, following Roberts and Moreland[107], that $\rho_C^p = \alpha = 0.33$. It was also assumed[112] that, in the case of direct conjugation between a *para*-substituent and the reactive centre, $\alpha = 0.1$. Roberts and Jaffe[121] then demonstrated that α is not a universal constant for all reaction series. This was allowed for by Taft and Lewis[118], who calculated values of α for 88 reaction series. By eliminating C from the equations

$$\log k_p/k_0 = \rho_I\sigma_I + C, \qquad (11.12)$$

$$\log k_m/k_0 = \rho_I\sigma_I + \alpha C, \qquad (11.13)$$

they obtained the following relationship

$$\log k_m/k_0 - \alpha \log k_p/k_0 = (1 - \alpha)\rho_I\sigma_I. \qquad (11.14)$$

In the derivation of (11.14) it is assumed that $\rho_I^p = \rho_I^m$. This is not altogether obvious.

In all cases examined a quite good linear dependence of the left-hand side of (11.14) on σ_I was found[118]. This was regarded as yet a further proof of the general applicability of the inductive constants of the substituents.

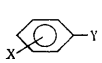
The differences $\log k/k_0 - \rho_I\sigma_I$ were used to calculate values of C_m and C_p, and, on the assumption that $\rho_C = \rho_I$, also σ_C^m and σ_C^p. The values of σ_C^p obtained for the same substituents from data for different reaction series were found to fluctuate extremely widely, and in several cases even changed their sign[118].

Moreover, it can be shown that the quantity α is not even roughly constant in a single reaction series. Division of Eqn. (11.14) by σ_I yields

$$(1/\sigma_I) \log k_m/k_0 = (1 - \alpha)\rho_I + \alpha(1/\sigma_I) \log k_p/k_0. \qquad (11.15)$$

Thus, if α is constant, the quantity $\sigma_I^{-1} \log k_m/k_0$ should vary linearly with $\sigma_I^{-1} \log k_p/k_0$. A check carried out here has shown that in most cases no such linear dependence exists. Consequently the values of C_p and C_m given by Taft and Lewis[118] cannot be accepted as correct, although it is stated there that σ_C^p values are universal constants.

In principle the problem of determining the magnitude of the influence of the inductive effect and of polar conjugation can be approached from two directions[111]. If Y is regarded as the reactive centre in compounds of the type



the interaction of the substituent $X.C_6H_4$ with Y along the Ar–Y bond results from superposition of the inductive effect of this substituent and the conjugation between it and the reactive centre Y. In such a case C_6H_5 is regarded as the standard substituent. Consequently the Hammett σ constants are parameters characterising the inductive effects of $X.C_6H_4$ substituents. Since the σ values are determined from the dissociation constants of substituted benzoic acids, they already contain, in the case of X substituents of +C type, some component due to conjugation between $X.C_6H_4$ and Y. As a result, the scale of Hammett σ values is not altogether suitable for quantitative examination of the problem.

In this case all departures from the Hammett equation must be ascribed to some quantity ψ which is a measure of the polar conjugation between $X.C_6H_4$ and Y. The task of making the Hammett equation more exact then reduces to finding the dependence of ψ on the structure of the $X.C_6H_4$ substituent and on the specific character of the reaction series.

Another possible approach is to take the



group as the reactive centre. We must now consider the interaction of substituent X with this reaction centre along the X–Ar bond. This interaction is made up of the following three factors: (1) the inductive effect of the substituent X, (2) the polar conjugation of substituent X with the aromatic nucleus, leading to a corresponding charge distribution at the different positions in the nucleus, and (3) direct polar conjugation between the substituent X and the reactive centre Y. The problem is reduced to finding the dependence of quantities characterising these factors on the structure of the X substituents and the nature of the reaction series.

It is easily observed that these two approaches are not mutually contradictory. The inductive effect of the $X.C_6H_4$ substituent can be equated to the overall effect of factors 1 and 2, and the polar conjugation between $X.C_6H_4$ and Y should be equivalent to the direct conjugation between X and Y (factor 3), since conjugation between Y and the benzene nucleus is excluded from consideration by taking phenyl as the standard substituent.

We have already seen that the second approach to a solution of the problem involves considerable difficulties. In addition, the σ_I values are only an approximate measure of the inductive effect in the case of the standard reaction series, since the bicyclo[2,2,2]octane ring is not exactly equivalent to the benzene ring in its ability to transmit the inductive effect, and also since the individual deviations from the relationship (11.2) are quite large[10].

The feasibility of solving the problem by the first method was examined by Taft *et al.*[113,118] and also by Wepster *et al.*[66] Taft's starting point was that, if conjugation cannot occur between the reactive centre and the benzene ring or especially the substituent, the constants for the substituents will definitely contain no component representing the effect of polar conjugation with the reactive centre. The corresponding new constants for the substituents are denoted by σ^0 and are normalised in such a way that the scale of the Hammett σ values is maintained. This is easily done, since with substituents of +C type, especially in the *meta* position, $\sigma^0 = \sigma$. Then for some arbitrary reaction series the Hammett equation can be modified as follows:

$$\log k_p/k_0 = \rho\sigma_p^0 + \Delta C_p, \qquad (11.16)$$

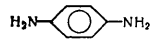
$$\log k_m/k_0 = \rho\sigma_m^0. \qquad (11.17)$$

The quantity ΔC_p in Eqn. (11.16) represents direct polar conjugation and polarisation interaction between the substituent and the reactive centre, and can be readily found by substituting in (11.16) the appropriate experimental data and the value of ρ obtained from data for *meta*-substituted compounds and those *para*-substituted compounds in which there is no direct interaction between the substituent and the reactive centre[111–113].

Values are also given for $\sigma_C^0 = \sigma_p^0 - \sigma_I$, it being noted[111,113] that $\sigma_C^0 = 2\sigma_C^m$, where σ_C^m is the mean value of $\sigma_m - \sigma_I$. Owing to the inaccuracies noted above, produced in bringing the σ_I values to the same scale as the σ values, the values thus obtained for σ_C^0 cannot be regarded as completely reliable.

Furthermore, with several substituents the magnitude of σ^0 depends on the type of solvent[66].

In principle, Wepster[66] starts from the same premises as Taft. However, the "normal" values (*i.e.* free from any component for polar conjugation with the reactive centre) which he obtained for σ^n are not equal to Taft's σ^0 values. The calculation of σ^n was also based on such reaction series as the dissociation of phenols and anilinium ions (in the case of +C substituents). This leads to distortions owing to the so-called saturation effect[66] in compounds of the type



Here the polar conjugation of both amino groups with the aromatic nucleus is less intense than, for example, in aniline. As a consequence, greater positive values of σ^p are obtained for +C substituents compared with the corresponding σ^0 values.

Yukawa and Tsuno[116] made a detailed investigation of the divergence of the experimental data from the Brown–Okamoto modification of the Hammett equation:

$$\log k/k_0 = \rho\sigma^+, \qquad (11.18)$$

where σ^+ are electrophilic constants of the substituents[65,122]. They concluded that, when the number of series examined is sufficient, the relation (11.18) often leads to considerable differences between calculated and experimental values of the constants for *para*-substituents.

Yukawa and Tsuno[116,123] also showed that the differences $\sigma_p^+ - \sigma_p$ determined from data for different reaction series (*A* and *B*) are proportional to one another:

$$(\sigma_A^+ - \sigma) = r(\sigma_B^+ - \sigma), \qquad (11.19)$$

where σ is the Hammett constant for the substituent, determined from data on the dissociation of substituted benzoic acids.

Taking the solvolysis of *meta*- and *para*-substituted α,α-dimethylbenzyl chlorides in 98% aqueous acetone at 25° as the standard reaction series ($r = 1$), these workers introduced a new scale of $\Delta\sigma_C^+$ values measuring the ability of +C substituents to undergo direct polar conjugation with a -C type of reactive centre:

$$\Delta\sigma_C^+ = \sigma^+ - \sigma, \qquad (11.20)$$

where the σ^+ are the Brown–Okamoto electrophilic constants of the substituents[65,122].

The modified Hammett equation is then obtained in the following form:

$$\log k_p/k_0 = \rho(\sigma + r\Delta\sigma_C^+), \qquad (11.21)$$

where ρ and r are parameters characteristic of the reaction series, and σ and $\Delta\sigma_C^+$ are characteristic of a given substituent.

The relations (11.19) and (11.21) are obtained by application of the LFE principle to the direct conjugation of substituents with the reactive centre.

Values of $\Delta\sigma_C^+$ for various substituents are given in Table 3.

Yukawa and Tsuno made a statistical test of Eqn. (11.21) for 35 reaction series. Good results were obtained in all cases, and the accuracy of correlation was considerably greater when the Yukawa–Tsuno equation was used than with Eqn. (11.18).

An attempt has also been made to separate the inductive effect from polar conjugation by calculations based on the method of molecular orbitals[124].

XII. GENERALISATION OF THE CONCEPT OF POLAR CONSTANTS OF SUBSTITUENTS

Hine[74,86,124] demonstrated that when a Hammett type of equation holds for equilibrium we have

$$\rho = \tau(\sigma_{Y_2} - \sigma_{Y_1}), \qquad (12.1)$$

where τ is a universal constant depending on the structure of the "skeleton" of the molecule, to which the substituent and the reactive centre are joined, and σ_{Y_1} and σ_{Y_2} are the polar constants of the substituent with the reactive centre in its initial and final states respectively.

Hine also showed[124] that relation (12.1), as well as the Hammett and Taft equations, can be derived on the assumption that the free energy of the polar interaction of any pair of substituents X and Y is proportional to the product of quantities termed the polar constants of the substituents, σ_X and σ_Y:

$$F_{X,Y} = \tau\sigma_X\sigma_Y. \qquad (12.2)$$

Hine examined specifically various reaction series involving *meta*- or *para*-substituted benzene derivatives, including some involving direct polar conjugation between the reaction centre and the substituent. The free energy of direct conjugation between the latter is regarded as analogous to ordinary polar interaction, and the capacity of substituents for polar conjugation is characterised by appropriate constants σ^C. The final equation is

$$\log k/k_0 = \tau[\sigma_X(\sigma_{Y_2} - \sigma_{Y_1}) + \sigma_X^C\sigma_{Y_1}^C - \sigma_X^C\sigma_{Y_2}^C]. \qquad (12.3)$$

In the derivation it is also assumed that τ does not depend on whether "ordinary" polar interaction or direct conjugation between X and Y is being considered. By definition, the products $\sigma_X^C\sigma_Y^C$ vanish if σ_X^C and σ_Y^C have the same sign, since there can be no polar conjugation between two substituents of type +C (or -C).

In the case of an equilibrium, σ_{Y_2} in (12.3) relates to the reaction centre in the product of the reaction. If k/k_0 is a ratio of velocity constants, σ_{Y_2} then represents the state of the reaction centre in the activated complex. Therefore the σ_{Y_2} values cannot be defined here in the usual way, since a reaction centre in an activated state cannot fill the role of substituent in some other reaction series. Eqn.(12.3) was therefore modified as follows for application to reaction velocities:

$$\log k/k_0 = \rho\sigma_X + \rho^C\sigma_X^C, \qquad (12.4)$$

where $\rho = \tau(\sigma_{Y_1} - \sigma_{Y_2})$ and $\rho^C = \tau(\sigma_{Y_1}^C - \sigma_{Y_2}^C)$.

Hine gives values which he has calculated for σ_m, σ_p, and σ_p^C for several substituents, τ_m and τ_p for aqueous solutions at 25°, and ρ_m, ρ_p, and ρ^C for some reaction series. The quantity τ is normalised on the basis that $\tau(\sigma_{COOH} - \sigma_{COO^-}) \equiv 1$ for *meta*- and *para*-substituted benzoic acids.

Eqns. (12.1) and (12.4) enable σ_{Y_2} to be calculated for a reaction centre in an activated state, which is important for the investigation of reaction mechanisms.

The definition of the polar constants of substituents in Eqn. (12.2) is more general than those given earlier. Both substituent and reactive centre are regarded from the same

point of view. In deriving the formulae, Hine notes their similarity to Kirkwood's formula[13] for the free energy of interaction between two dipoles. This may perhaps provide a theoretical basis for applying the LFE principle in cases of polar interaction, which would be of fundamental importance.

XIII. USE OF THE LFE PRINCIPLE TO OBTAIN SPECIAL CORRELATION EQUATIONS HAVING A LIMITED RANGE OF APPLICATION

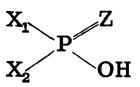
Section XI has confirmed that the Hammett equation is a purely empirical relationship in the sense that the inductive effect and the effect of polar conjugation are not separated, and only those cases are covered (though, of course, they are numerous) in which the conditions indicated in section XI are satisfied, albeit very roughly. However, this defect (from the viewpoint of a more rigorous theory) of the Hammett equation is offset by an important practical advantage, since it is possible with this equation to apply the LFE principle to the gross ΔF values, in spite of the fact that several factors are influencing the reactivity at the same time. In general, the existence of the Hammett equation indicates the possibility of making an overall quantitative allowance for the effect of several factors when either the substituents possess in some sense similar structural features (*meta*- and *para*-substituted phenyls) or else similar reaction series are being considered. In this respect the Hammett equation can be regarded as an example of the use of the LFE principle to obtain an approximate correlation equation having a limited range of application. In this sense the Hammett equation does not form an exception, and has several analogues. Some examples will be given below.

Taft's equation[125] for the hydrolysis of esters $X_1.COOX_2$ or o-$X_3.C_6H_4.COOX_2$ and the esterification of the corresponding acids by the alcohols X_2OH:

$$\log k/k_0 = fA, \qquad (13.1)$$

where k and k_0 are rate constants for the given ester and the standard ester (acid or alcohol) respectively (methyl being the standard substituent), A is a constant for the substituent X depending on whether it is in positions 1, 2, or 3 and on the type of catalysis (acid or alkaline), and f is a parameter characteristic of the reaction series (only one X substituent varies in the given series). The constant A is an approximate measure of the overall effect of the inductive and the steric factors of the X substituents.

Kabachnik's equation[126-128] for the dissociation constants of substituted phosphinic acids of the type



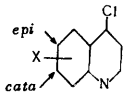
where X_1 and X_2 are substituents, and Z is an atom of oxygen or sulphur. This equation is of the form

$$\log k/k_0 = \rho_\Phi \Sigma\sigma_\Phi. \qquad (13.2)$$

The σ_Φ values are characteristic of the substituents X_1 and X_2, and ρ_Φ of the reaction series§. Hydrogen is selected as standard substituent, and the standard reaction series is the dissociation of X_1X_2POOH acids in water at 25°.

The σ_Φ values may be a quantitative measure of the joint influence of the inductive effect and the field effect (see section XIV).

Hammett equation for quinoline derivatives. Baciocchi *et al.*[129] have shown that the basic dissociation constants K_a of 6- and 7-substituted 4-chloroquinolines



and the rate constants k_2 of the nucleophilic replacement of chlorine in these compounds by reaction with CH_3O^- in methanol at 75° are related by the formula:

$$\log k_2 = 1.02 \log K_a + 0.12. \qquad (13.3)$$

Since the basic dissociation constants of β- and γ-substituted pyridines are represented by a Hammett equation having "normal" σ values[130], the Hammett σ_{epi} and σ_{cata} were calculated from the known value of ρ.

Rate constants for the formation of semicarbazones k_{sem} and oximes k_{ox} from various ketones are related as follows[131]:

$$\log k_{sem} = a + b \log k_{ox}. \qquad (13.4)$$

Zahradnik's correlation scheme[132,133] establishes proportionality between values of $\log k/k_0$ for the following reaction series: (1) X.NCS + OH → X.NH.CO.S$^-$ in water containing 2% of dioxan; (2) the same reaction in alcohol and water (50% by volume); (3) X.NCS + n-$C_4H_9NH_2$ → → X.NH.CS.NH.C_4H_9 in water containing 2% of dioxan; and (4) CH_3.NCS + X.NH_2 → CH_3.NH.CS.NH.X in 50% alcohol.

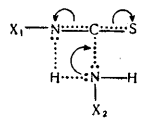
With these reactions, proportionality between $\log k/k_0$ and Taft's σ^* is observed only with a few substituents[133], although the steric factor is absent.

Salomaa's correlation scheme[134] establishes proportionality between values of $\log k/k_0$ for the following reaction series: (1) rate of the acid hydrolysis of dialkoxymethanes $CH_2(OX)_2$ in 0.13 M aqueous HCl; (2) rate of the ethanolysis of alkoxymethyl chlorides $XOCH_2Cl$ in absolute ethanol; (3) this reaction in 53.5% ethanol; and (4) rate of the acid hydrolysis of alkoxymethyl acetates CH_3COOCH_2OX and alkoxymethyl formates $HCOOCH_2OX$ in 0.1–0.15 M aqueous HCl. The steric factor is also absent from these reactions. Correlation with the Taft σ^* values gives a poor result, since the point for X = $ClCH_2CH_2$ falls markedly out of line, this being the only substituent with $\sigma^* > 0$ for which experimental data exist. Salomaa therefore introduced new polar constants for the substituents: $\bar{\sigma}^* \equiv \equiv \log k/k_0 = (2.76 \pm 0.36)\sigma^*$, where k and k_0 relate to reaction series 3.

These last two correlation schemes are apparently of the same type. In both cases the substituent X is linked with the reactive centre *via* a heteroatom possessing a lone pair of electrons and therefore capable of polar conjugation both with the reactive centre and with the substituent X if the latter has a suitable structure. It is significant that the reactivity of amines X.NH_2 in Zahradnik's reactions correlates not with Taft's inductive constants for the X substituents but with values of $\log k/k_0$ for Zahradnik's

§ The symbols σ and ρ in the original have been replaced by σ_Φ and ρ_Φ to avoid confusion with Hammett's σ and ρ.

reaction series (1). This suggests that the two nitrogen atoms in the activated complex occupy analogous positions:



Zahradnik's $\log k/k_0$ and Salomaa's σ^* values form quantitative measures of the inductive effect and the capacity for polar conjugation, with a -C type of reactive centre, of $X-\ddot{N}<$ and $X-\ddot{\underset{\cdot\cdot}{O}}-$ substituents respectively. The intensity of transmission of the inductive effect through the nitrogen and oxygen atoms may vary with the nature of the substituent X.

Relation between partial rate and selectivity factors. With electrophilic substitution reactions in the benzene nucleus, the following relation has been shown to exist between the partial rate and the selectivity factors[135,136]

$$\log pf = b \log Sf, \qquad (13.5)$$

where $S_f = pf/mf$ is the selectivity factor, pf and mf being the relative rates of substitution in the *para* and *meta* positions respectively if the reaction velocity with unsubstituted benzene is taken as unity:

$$pf = k_p/k_0 \text{ and } mf = k_m/k_0.$$

The relation (13.5) is a direct consequence of the applicability of the Hammett equation to these reactions[137-140], since

$$\log pf = \sigma_p/\sigma_m \log mf \text{ or } \log pf = \sigma_p^+/\sigma_m \log mf,$$

and hence

$$b = \frac{\sigma_p}{\sigma_p - \sigma_m} \text{ or } b = \frac{\sigma_p^+}{\sigma_p^+ - \sigma_m^+}.$$

A more detailed review of this question will be found in the monograph by Shatenshtein[141].

Among other correlations having a limited range of application may be mentioned the linear relationship between the infra-red absorption frequencies of the carbonyl group in ketones and the half-wave potentials of the polarographic reduction of the latter[142], the relation between conformational equilibrium and dissociation constants in the case of cyclohexanecarboxylic acids[143], the linear relation between values of $\log K$ for the first and second instability constants of the chelate complexes of di-isobutylketone and acetylacetone with various metals[144], and the application of the LFE principle to the reactivity of *trans*-4-substituted-cyclohexanecarboxylic acids and the corresponding methyl esters[144].

XIV. THE PROBLEM OF CALCULATING THE FIELD EFFECT

By the field effect is meant electrostatic interaction between substituent and reactive centre occurring directly through space. It was pointed out in section IV that Taft's σ^* value may contain a term due to the field effect. Apparently partly for this reason, Taft himself terms these quantities aliphatic polar constants of the substituents, in contrast to the Hammett aromatic polar constants σ. However, he also argues that the orientation of the substituent X in space has no effect on the corresponding σ^* value, and hence that this quantity is not associated to any appreciable extent with the field effect[52].

On the other hand, Roberts and Carboni[145] concluded, from a study of the reactivity of substituted (with NO_2 and Cl) phenylpropiolic acids and their ethyl esters, that the field effect forms a considerable proportion of the Hammett σ values. These workers consider that, with a given substituent in the *meta* and *para* positions, internal compensation of the overall influence of the inductive effect and the field effect occurs, since in virtue of the latter effect a *para*-substituent strengthens the inductive effect, while a *meta*-substituent weakens it. In the *ortho* position the relative proportion contributed by each of the above factors varies from one reaction to another (depending, for example, on the distance between the reactive centre and the *ortho*-substituent), which is one of the causes of the "*ortho* effect". A similar view is held by Smith and Larson[146].

Since the literature contains few data on the quantitative separation of the inductive and field effects, Kabachnik's σ_Φ values (see section XIII) are, in the opinion of the present reviewer, of special interest. In the case of aromatic substituents $X.C_6H_4$, the σ_Φ values vary linearly with Taft's σ^0 (see Fig. 4):

$$\sigma_\Phi = -0.48 + 0.78\sigma^0. \qquad (14.1)$$

The linear dependence on the Hammett σ value is not nearly as good owing to positive deviations in the case of *C*-substituents. Thus in the case of aromatic substituents the σ_Φ values are equivalent to σ^0 constants and are a measure of the inductive effects of $X.C_6H_4$ substituents, hydrogen being chosen as the standard substituent. Since values

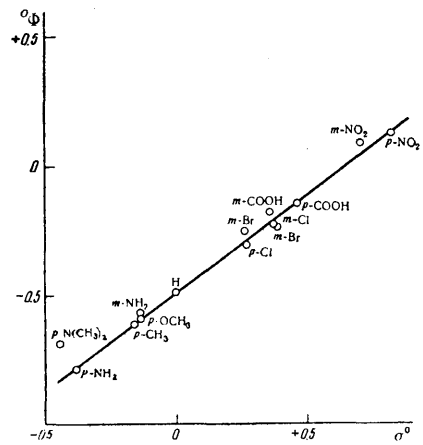


Fig. 4. Linear relation between Kabachnik's σ_Φ values and Taft's σ^0 values for *meta*- and *para*-substituted phenyl compounds.

of σ_Φ are known for a greater number of substituents than are the σ^0 constants, the former can be used to calculate the latter by means of the equation:

$$\sigma^0 = 1.28(\sigma_\Phi + 0.48). \qquad (14.2)$$

Conditions are more complicated with non-aromatic substituents. Values of σ_Φ for hydrogen and all hydrocarbon radicals are related to Taft's σ^* values by the formula (see Fig. 5):

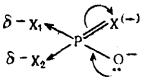
$$\sigma_\Phi = 0.965 + 1.97\sigma^*. \qquad (14.3)$$

Consequently the σ_Φ constants for these substituents also provide a measure of the inherent inductive effect of the latter. The points for all the remaining substituents (OH, CH_2OH, OCH_3, OC_6H_5, CH_2Cl, CH_2Br, CH_2I, $CHCl_2$, CCl_3, CF_3), however, give a poor fit on the straight line representing Eqn. (14.3) (see Fig. 5). The σ_Φ values for these substituents are considerably lower than would be expected from the corresponding σ^* values.

With the phenyl radical, and hence with all the remaining aromatic substituents, there is a marked discrepancy between the aliphatic (σ^*) and the aromatic (σ^0) scales of inductive effects, although the scales have been brought to a common basis. The slopes of the straight lines (14.1) and (14.3) also differ, by a factor of about 2.5, although they should be the same in view of the above identical basis for the σ^* and σ^0 values.

These deviations are of great interest. The possibility of direct conjugation with the reactive centre is excluded because relation (14.1) is obeyed well. Steric effects are also excluded, for otherwise relation (14.3) would not be satisfied for hydrocarbon radicals which have very different values of the steric constants E_S. Steric hindrance, and in most cases the actual nature of the substituents, also exclude the possibility of an intramolecular bond being formed. Among factors known to affect reactivity only the development of a field effect can be invoked to account for these deviations. It is also noteworthy that all substituents for which the σ_Φ values diverge from the "norm" are more electronegative than the methyl group.

In view of all the above, there are grounds for suggesting that these "abnormalities" are caused by electrostatic repulsion of electronegative substituents from negatively charged atoms of oxygen (or sulphur) in anions of acids of the class under consideration:



Such repulsion should act to decrease the stability of these anions, leading to a decrease in the dissociation constant of the acids and in the value of σ_Φ. This does in fact occur.

If this hypothesis is correct, Kabachnik's σ_Φ values are a measure of the combined inductive and field effects inherent in the substituents. Since the σ_Φ values for hydrogen and hydrocarbon radicals obey Eqn. (14.3) very exactly, it follows that no field effect is present with these substituents. Thus in these cases the σ_Φ values are a measure of the inductive effect alone, and Eqn. (14.3) can be used to calculate the inductive components σ_Φ^i in the σ_Φ values for all the remaining substituents. The component σ_Φ^F, due to the field effect, can be found by difference:

$$\sigma_\Phi^F = \sigma_\Phi - \sigma_\Phi^i = \sigma_\Phi + 0.965 - 1.97\sigma^*. \qquad (14.4)$$

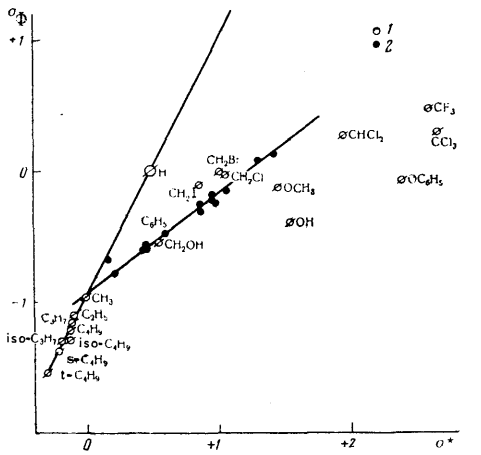


Fig. 5. Relation between Kabachnik's σ_Φ and Taft's σ^* values: ● *meta*- or *para*-substituted phenyl compounds.

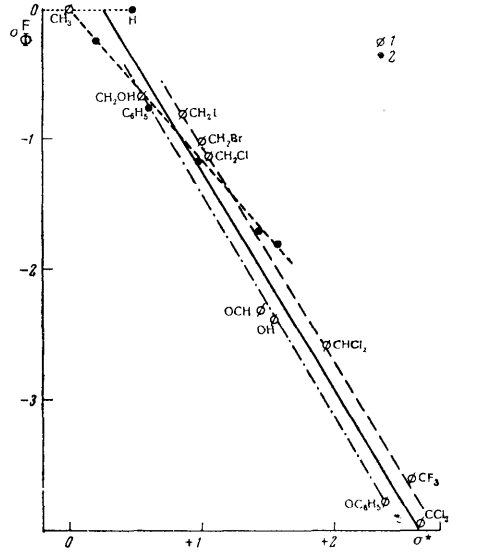


Fig. 6. Variation of the field effect component σ_Φ^F in Kabachnik's σ_Φ values with Taft's σ^* values: ● aromatic substituents.

In absolute magnitude σ_Φ^F is comparable with, and in several cases even greater than, σ_Φ^i.

Fig. 6 shows the variation of σ_Φ^F with Taft's σ^* values, the latter being calculated for aromatic substituents by means of the formula $\sigma^* = 0.600 + \sigma^0$. The first point of interest is the approximate linear relation between σ_Φ^F and σ^*:

$$\sigma_\Phi^F = (+0.40 - 1.63\sigma^*) \pm 0.25. \qquad (14.5)$$

Although all the σ_Φ^F values are grouped about this straight line (the continuous line in Fig. 6), it is obvious that the substituents can be divided into three separate groups — (1) mono-, di-, and tri-halogenated methyls, (2) oxygen-containing substituents (OH, OCH_3, OC_6H_5, and CH_2OH), and (3) aromatic substituents. Within each of these groups there is a very exact linear relation between σ_Φ^F and σ^* (broken lines in Fig. 6). The straight lines for the two groups of aliphatic substituents are parallel and their slope is 1.63, as in Eqn. (14.5). The slope for the aromatic substituents has a lower numerical value of 1.18, and also the line passes through the origin.

To these three groups of substituents should be added a fourth, comprising hydrogen and hydrocarbon radicals, for which σ_Φ^F is zero.

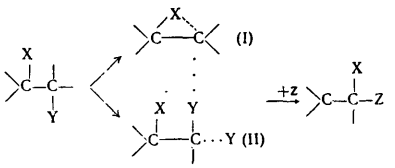
On the basis of the above, the following rules can be formulated as a working hypothesis, and can be usefully borne in mind in considering the problem of the field effect.

1. The influence of the field effect on reactivity may be comparable in magnitude with that of the inductive effect.
2. Hydrogen and hydrocarbon radicals do not interact with the reactive centre by the mechanism of the field effect.
3. The ability of substituents to interact with the reactive centre by the field effect mechanism can be measured quantitatively by Taft's σ^* or σ^0 values, or perhaps by other polar constants of the substituents. All substituents can then be divided into several groups each having its own linear relationship between field effect and σ^*, σ^0, etc.
4. In many cases, therefore, Taft's relations (5.1) and (5.3) and the Hammett equation can evidently take account also of the field effect.
5. These rules can yield far reaching conclusions. It follows from points 2 and 3 that Taft's σ^* values may be on different scales for hydrogen and hydrocarbon radicals on the one hand, and for all electronegative substituents on the other. Different laws are therefore to be expected for these two groups of substituents, as was noted in connection with the damping of the inductive effect (see section IV).

The conclusions reached in this section require to be checked against more extensive experimental results. However, the suggestion that the component due to the field effect can often make a very substantial contribution to the value of $\Delta\Delta F$ is evidently correct.

XV. ANCHIMERIC ASSISTANCE

The term anchimeric assistance¶ denotes the effect exerted on reaction velocity by a substituent X attached to an α-carbon atom relative to the reactive centre:



¶ The term "anchimeric assistance" is used in the American literature[98,124] and is translated into Russian as "immediate proximity effect".

Anchimeric assistance is observed if the activated complex has structure (I), but is absent from the activated complex (II). A qualitative and semi-quantitative theory of this effect was worked out by Winstein and his collaborators[147,148] and by others. The quantity L' is taken as a measure of this effect:

$$L' = RT \log k/k_c, \qquad (15.1)$$

where k and k_c are rate constants in the presence and in the absence respectively, of anchimeric assistance. Because no exact allowance is made for the inductive effect, estimates of L' given by Winstein are at best semi-quantitative and will not be considered here.

Streitwieser[149] investigated the kinetics of the solvolysis of a series of esters of p-bromobenzenesulphonic acid of the type $X_1X_2CH.O.SO_2.C_6H_4.Br$, *trans*-2-X-cyclohexyl-p-bromobenzenesulphonates, and tertiary alkyl halides. Taft's Eqn. (5.2) applies to all these reactions. Streitwieser was therefore able to determine the magnitude of L' by means of the formula:

$$L' = \log k/k_0 = \rho^*\Sigma\sigma^*. \qquad (15.2)$$

Since anchimeric assistance stabilises the activated complex, L' is always greater than zero. Substituents for which $L' = 0$ do not exhibit anchimeric assistance.

XVI. CORRELATION SCHEMES WITH A VARIABLE REACTIVE CENTRE

The correlation schemes considered so far have been characterised by the fact that only the substituent X in X–Y varied in a given reaction series, while the reaction centre P remained constant. The present section will give correlation equations for reaction series in which the reactive centre varies, while the structure of the substituent can also change. These correlation equations have also been obtained by the use of the LFE.

Formally the Grunwald–Winstein equation[150,151], which served in some sense as a prototype for relationships of analogous form, also belongs to this type. Since this equation represents in essence the dependence of reactivity on the nature of the solvent, it will be considered in section XX. Only cases of bimolecular interaction between reactants will be given here.

The Swain – Scott equation[152] relates to the S_N1 type of nucleophilic substitution reactions in the aliphatic series. A substrate S, capable of undergoing substitution, is attacked by the nucleophilic reagent N. The LFE principle is of the form:

$$\log k_{ij}/k_{ip} = S_i \log k_{0j}/k_{00}, \qquad (16.1)$$

where k_{ij} is the rate constant for reaction between S_i and N_j, k_{i0}, k_{0j}, and k_{00} have an analogous significance, S_0 and N_0 are the standard substrate and standard nucleophilic reagent respectively, and S_i is a constant characterising the sensitivity of the substrate to nucleophilic attack. Denoting $\log k_{0j}/k_{00}$ by n_j, we can write (16.1) as follows:

$$\log k_{ij}/k_{i0} = S_i n_j, \qquad (16.2)$$

where n_j is a constant characterising the nucleophilic character of reagent N_j relative to the standard N_0.

The Swain–Scott equation is not generally applicable, and the degree of nucleophilic character of a reagent N may change on passing from one group of substrates S to another[152].

Edwards' equation[153] for the S_N2 type of reaction evidently has a considerably wider range of application. It can also be used to calculate the equilibrium constants of reactions involving the formation of a new covalent bond. The equation is

$$\log k_{ij}/k_{i0} = \alpha E_n + \beta H, \quad (16.3)$$

where k_{ij} and k_{i0} are velocity or equilibrium constants for the given and the standard nucleophilic reagents respectively, E_n and H are the nucleophilic constant and the relative basic strength respectively of the attacking reagent (electron donor), and α and β are constants characteristic of the substrate.

Values of H are obtained from the basic strengths on the pK_a scale (K_a being the dissociation constant of the corresponding conjugate acid in water) by means of the formula

$$H = pK_a + 1.74, \quad (16.4)$$

where 1.74 is the value of pK_a for water.

Values of E_n are obtained from the oxidation potentials E_0 of the reagents N by means of the equation

$$E_n = E_0 + 2.60, \quad (16.5)$$

where 2.60 is the electrode potential of the cell†:

$$2H_2O \rightleftharpoons H_4O_2^{2+} + 2e.$$

Eqns. (16.4) and (16.5) mean that water is regarded as the standard nucleophilic reagent.

Eqn. (16.3) was used by Edwards[153] to correlate the rates of S_N2 reactions at a carbon atom, the rates of substitution reactions at a halogen atom, equilibrium in the formation of complex ions, solubility product, equilibrium in complex formation by iodine with various compounds, and several other reactions. All equilibria are regarded as the substitution of water, co-ordinated with the substrate, by reaction with the nucleophilic reagent.

The nature of E_n is discussed by Edwards[154]. The nucleophilic character of an electron donor depends on the polarisability of its reactive centre and on its basic strength:

$$E_n = aP + bH, \quad (16.6)$$

where $P \equiv \log R_\sim/R_{H_2O}$, $R_\sim$ and R_{H_2O} being the molar refractions of the reactive centre of the electron donor and of water respectively, H is given by Eqn. (16.4), $a = 3.60$, and $b = 0.0624$.

Differences between values of E_n calculated by means of Eqn. (16.6) for anions (F^-, Cl^-, Br^-, OH^-, I^-, and S^{2-}) and those obtained from electrode potentials do not exceed 0.06 E_n unit.

Eqn. (16.3) can therefore be transformed as follows:

$$\log k_{ij}/k_{i0} = AP + BH, \quad (16.7)$$

where $A = 3.60$ and $B = 0.0624\alpha + \beta$.

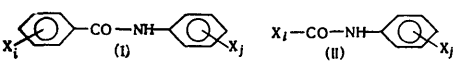
Substantial deviations from the Swain–Scott and Edwards equations are found in reactions between *p*-nitrophenyl acetate and nucleophilic reagents[155].

Exner – Horak equation[156,157]. These workers showed that the infra-red absorption frequency of the carbonyl group ν_{CO} in derivatives of carboxylic acids of the type R.CO.Y is given by the formula:

$$\nu_{CO} = kx + q, \quad (16.8)$$

where k is a constant characteristic of the substituent R, and x is constant for a given class of compounds. Change in the functional group Y in this case corresponds to a change in the reactive centre.

Exner[83] showed that, for compounds of types (I) and (II)



the values of k and x vary linearly with the Hammett σ and Taft σ^* constants of the substituents.

With compounds of type (I) the following relations hold:

$$k_i = k_0 + \rho_1\sigma_i^+, \quad (16.9)$$

$$x_j = x_0 + \rho_2\sigma_j, \quad (16.10)$$

In the case of compounds of type (II) x_j can be represented by Eqn. (16.10) and

$$k_i = k_0^* + \rho^*\sigma_i^*. \quad (16.11)$$

Hence with compounds of type (I)

$$\nu_{CO} = (q + k_0x_0) + x_0\rho_1, \quad \sigma_i^+ + k_0\rho_2\sigma_j + \rho_1\rho_2\sigma_i^+\sigma_j, \quad (16.12)$$

where $(q + k_0x_0) = 1678.2$; $x_0\rho_1 = 7.5$; $k_0\rho_2 = 15$; and $\rho_1\rho_2 = 0.7$.

In the case of compounds of type (II)

$$\nu_{CO} = (q + k_0^*x_0) + x_0\rho^*\sigma_i^* + k_0^*\rho_2\sigma_j + \rho^*\rho_2\sigma_i^*\sigma_j, \quad (16.13)$$

where $(q + k_0^*x_0) = 1697$; $x_0\rho^* = 39.1$; $k_0^*\rho_2 = 16.7$; and $\rho^*\rho_2 = 3.5$ (all frequencies in cm^{-1}).

If the quantity $q + k_0x_0$ is denoted by ν_{CO}^0, it becomes obvious that Eqns. (16.12) and (16.13) represent a particular case of the second solution of (16.12) for cross-correlations having $m = 2$ (see section XXII).

XVII. CORRELATION OF POLAROGRAPHIC HALF-WAVE POTENTIALS

Zuman[158-161] has recently shown that, for many series of organic compounds of the type X–Y (where X is the substituent and Y the electronically active group), the dependence of reactivity on structure is the same for heterogeneous electrode reactions as for homogeneous reactions. A measure of reactivity in this case is the half-wave potential $E_{\frac{1}{2}}$ of polarographic reduction or oxidation. With reversible and irreversible electrode processes $E_{\frac{1}{2}}$ is a measure of the free energy of reaction and of activation respectively.

The general form of the dependence of $\Delta E_{\frac{1}{2}} = E_{\frac{1}{2}} - E_0$ (where E_0 refers to the standard substituent) on structure is written as follows[160]

$$\Delta E_{\frac{1}{2}} = P + M + S. \quad (17.1)$$

Eqn. (17.1) is a particular case of the relation (3.1), where M represents the effect of various forms of conjugation. The quantity P can be represented by the usual relation $\rho\sigma$, $\rho_I\sigma_I$, or $\rho^*\sigma^*$ according to Hammett or Taft. This applies also to heterocyclic compounds[159,161].

† This quantity was estimated indirectly by Edwards, using his proposed method of correlation by means of Eqn. (16.3).

In the case of *para*-substituted benzene derivatives the quantity M can be roughly calculated by using the σ^+ or σ^- constants of the substituents.

The dependence of S on structure is given by the equation $S = SE_S$, where E_S represents Taft's steric constants (see section VI). With *meta*- and *para*-substituted benzene derivatives a linear relation is found[160] to exist between the values of E_0 for the unsubstituted benzene derivatives and the corresponding value of ρ, which enables values of $E_{\frac{1}{2}}$ for the substituted derivatives to be estimated from the value of E_0 alone.

These regularities, apart from their great theoretical importance, may serve as a basis for working out the least laborious, and yet reliable, methods for determining new values of constants for substituents.

With NH_2 and NH_3^+ it was necessary to introduce new "polarographic" values of the Hammett σ constants[160].

XVIII. USE OF THE LFE PRINCIPLE FOR RADICAL REACTIONS

A particular case of the LFE principle, known as the Polanyi–Evans rule[162], can be applied to radical reactions, thus establishing a linear relation between energy of activation and heat of reaction in a reaction series of the type

$$R\cdot + X_i Y \rightarrow \text{reaction products.}$$

Problems of the application of this rule have been examined in greater detail by Semenov[163].

Several aspects of the application of the LFE rule to reactions involving free radicals were investigated by Bamford *et al.*[164], who subdivided all radical reactions into the following three types:

1. Reactions involving transfer of an atom (or a group) at the same time as electron transfer:

$$R\cdot + XQ \rightarrow RX + Q,$$

where R· is a free radical, and X a hydrogen, halogen, etc. atom.

2. Reactions involving electron transfer alone (oxidation–reduction reactions):

$$R\cdot + M^{z+} \rightarrow R^+ + M^{(z-1)+},$$

$$R\cdot + M^{z-} \rightarrow R^- + M^{(z-1)-},$$

where M^z are any ions (metallic or otherwise).

3. Addition of a radical to a double bond:

$$R\cdot + \underset{|\ \ |}{C=C} \rightarrow R-\underset{|\ \ |}{C-C}\cdot .$$

If XQ is a hydrocarbon in reactions of class 1, only non-polar interaction takes place, and it is necessary to take into account only the non-polar reactivity of the radical R· and the reagent XQ, including the non-polar conjugation in R· and in Q. In all the remaining cases the polar component (induction effect and polar conjugation) also must be allowed for.

The non-polar reactivity of free radicals is characterised by the rate constant k_{3_1T} for their reaction with toluene at 60° (standard reaction series). The velocity constant k_{3_1HC} for reaction of a given radical with any other hydrocarbon can then be obtained by simple application of the LFE principle to the overall value $\Delta\Delta F$:

$$\log k_{3_1HC} = \log\gamma + b \log k_{3_1T}. \qquad (18.1)$$

Since $b = 1$ always, Eqn. (18.1) simplifies to

$$\log k_{3_1HC}/k_{3_1T} = \log\gamma \text{ or } k_{3_1HC} = \gamma k_{3_1T}. \qquad (18.2)$$

The relationships (18.1) and (18.2) can be regarded as a particular case of the correlation equation for a scheme involving a variable reactive centre. Each free radical is characterised by a k_{3_1T} value, and each hydrocarbon by $\log\gamma$, which is a measure of its non-polar reactivity. In most cases the accuracy of the correlation does not exceed ±20%, the maximum deviations resulting in an error not exceeding a factor of 3, whilst the range of variation of k_{3_1HC} exceeds a factor of 10^6.

When the polar component in the value of $\Delta\Delta F$ (induction effect and polar conjugation) must also be taken into account, the velocity constant k_3 for reactions of classes 1 and 3 is given by the formula

$$\log k_3 = \log k_{3_1T} + \alpha\sigma_p + \beta, \qquad (18.3)$$

where α and β are constants characteristic of the reagent attacked by the free radical, and σ_p is the Hammett *para* constant for the substituent in the free radical. Eqn. (18.1) is a particular case of (18.3) when $\alpha = 0$. Hence $\beta = \log\gamma$. Values of $\log k_{3_1T}$ are regarded as a measure of the energy of dissociation at the R–X bond, and β as a measure of the energy of dissociation at the Q–X bond.

Bamford's equation (18.3) confirms that the principle of the independence and the additivity of the individual components in $\Delta\Delta F$ and the LFE rule are valid also in radical reactions.

Reference must also be made to the equation of Levy and Szwarc[165]: $\log k_{ij} = n \log k_{0j}$, where i and j relate to the free radical and the hydrocarbon respectively (for details see ref. 166).

XIX. CORRELATION OF DIPOLE MOMENTS

The correlation of dipole moments by means of the various polar constants of substituents is of great theoretical value for an understanding of the physical meaning of these constants. Taft[10] managed to correlate the dipole moments of compounds of the type R–Y, where R is a hydrocarbon radical or hydrogen, by means of the equation $\mu - \mu_0 = \rho^*\Sigma\sigma^*$. Not altogether successful attempts were also made to correlate the dipole moments of aromatic compounds with the Hammett σ parameters[167,168]. As Exner[115] has shown, simple correlation of dipole moments with σ values is not justified, since the latter take into account only variation in charge (electron density) on the atom or group Y, whereas the dipole moment also depends to a considerable extent on the distance between charges of opposite sign. By allowing for the distance d between the charges, Exner[115] showed the possibility of a satisfactory linear correlation between the values of μ/d and Taft's σ^* constants for the substituents X in the series X–Cl, where X should not possess an appreciable internal dipole moment. He showed a similar correlation for μ/d and the corresponding σ_I in the series $X-CH_3$ and $X-C_6H_5$.

In the case of various aromatic compounds of the type $X-C_6H_5$, where X is any substituent, the component of the

dipole moment due to polar conjugation, μ_c, is connected with the constants of the substituents by the relation:

$$\mu_c/d_c = \rho\sigma_c^{+,-}. \quad (19.1)$$

The symbol $\sigma_c^{+,-}$ means that σ_c^+ values must be used in the case of +C substituents, and σ_c^- values in the case of -C substituents. Values of μ_c are given by the difference $\mu_c = \mu_{Ar} - \mu_{Alk}$, where the μ_{Ar} are the dipole moments of the $X-C_6H_5$ compounds, and the μ_{Alk} those of the $X-CH_3$ compounds.

Exner suggested the following general formula for the dependence of dipole moments on the polar constants of substituents:

$$\vec{\mu} = \vec{\mu}_0 + \rho_I\vec{d_I}\vec{\sigma_I} + \rho_c\vec{d_c}\sigma_c^{+,-}, \quad (19.2)$$

where d_I is the distance between the charges due to the inductive effect (usually the length of the X–Y bond) and d_c the distance between those due to polar conjugation.

Since the dipole moments of molecules are solely a function of the charge distribution in the latter, Exner's equations given in this chapter indicate that the σ^*, σ_I, σ_c^+, and σ_c^- values define quantitatively the ability of the corresponding substituents to acquire a negative or a positive charge. Hence these parameters have in fact the physical meaning which is ascribed to them.

XX. SOME QUANTITATIVE ASPECTS OF THE DEPENDENCE OF REACTIVITY ON THE NATURE OF THE SOLVENT

The preceding sections have discussed the dependence of the reactivity of organic compounds on their structure. The problem of the dependence of reactivity on the medium in which the reaction takes place is of no less importance, as was pointed out at an early date by Menshutkin[169,170].

The dependence of rates and equilibria on the nature of the solvent will be examined below only for reactions for which the mechanism is independent of the solvent. The problem is then reduced to finding the dependence of the activity coefficients of the activated complex (or reaction products) and of the initial compounds on the properties of the solvent. Only the appropriate activity coefficient ratios need to be known[12].

The influence of the solvent on the activity coefficient of a solute can be of two types. On the one hand, dissolved species interact with the electrostatic field of the surrounding solvent molecules, without preferential interaction with any of the latter (the field, of course, is produced mainly by the neighbouring solvent molecules, but this is not what is meant). Such interaction is termed a non-specific solvation effect, of which polar and non-polar types must be distinguished. The former is purely electrostatic in nature, and involves interaction of electric charges existing on polar solvent and solute molecules (dipole–dipole or ion–dipole interaction). The latter type is based on interaction of dispersion forces between non-polar components of the solution.

In addition to non-specific solvation there can also be specific interaction between solvent molecules and solute species — formation of hydrogen bonds, complex formation, unbalanced fluctuations in concentration of the components of a mixed solvent around solute species, etc.

The problem of the quantitative assessment of non-specific polar interaction between solvent and solute will be discussed below. The main results have been obtained for nucleophilic substitution reactions of type S_N1, and are based on the work of Ingold, Hughes, and their collaborators[171-175] on the mechanism of this class of reactions.

The Grunwald – Winstein activity postulate[150,151,176-178]. These workers found that the following form of the LFE rule can be applied to solvolysis reactions occurring by an S_N1 mechanism in different solvents:

$$\log k_{ij}/k_{i0} = m_i \log k_{0j}/k_{00}, \quad (20.1)$$

where k_{ij} is the velocity constant for solvolysis of the i-th solute in the j-th solvent, the subscripts 0 denoting the standard solute (t-butyl chloride) and the standard solvent (80% ethanol by volume), and m_i is a constant depending solely on the nature of the i-th solute. The value of $\log k_{0j}/k_{00}$ for t-butyl chloride is denoted by Y_j. Remembering that $k_{ij}/k_{i0} = \gamma_{ij}/\gamma_{\neq ij}$, where γ_{ij} and $\gamma_{\neq ij}$ are the activity coefficients of the i-th reactant and the corresponding activated complex respectively in the j-th solvent, and taking a solution in 80% ethanol as the standard state, we can write the Grunwald–Winstein equation as follows:

$$\log k_{ij}/k_{i0} = \log \gamma_{ij}/\gamma_{\neq ij} = m_i Y_j. \quad (20.2)$$

This relationship represents the so-called activity postulate, since it establishes the form of the dependence of the activity coefficient ratio on the nature of the solvent. This last is characterised by the parameter Y, termed the "ionising power" of the solvent. The reactant is characterised by the parameter m.

It is clear from the standard conditions that in 80% ethanol $Y \equiv 0$, and for t-butyl chloride $m = 1$. The value of Y for some one solvent other than the standard can be chosen arbitrarily.

Eqn. (20.2) is satisfied by the alkyl halides. The deviations observed in several cases, especially with alkyl fluorides and derivatives containing phenyl groups, were explained by the formation of hydrogen bonds with the solvent molecules and by the effect of "reassociation of ion pairs"[178]. Owing to this effect the true rate of ionisation by the S_N1 mechanism found from formula (20.2) is greater than the measured "titration" reaction velocity.

The choice of $(CH_3)_3CCl$ as basis for the scale of Y values is linked with Winstein and Grunwald's view that the solvolysis of this compound is truly unimolecular. In this case the "titration" velocity coincides with the rate of ionisation[172].

There is no definite relation between the Y values and the dielectric constants of the solvents[146].

Reference must be made to the work of Kosower[179-181], who showed that the quantity $Z = h\nu_{max}$, where ν_{max} is the absorption frequency for a solution of a very polar compound (*e.g.* pyridine oxide), varies linearly with the Y values for the corresponding solvents.

The activity postulate was used also to obtain the quantitative dependence of dissociation constants of acids on the nature of the solvent[182-184]. "Activity functions" Y_0 and Y_- were introduced. With the carboxylic type of acids (charge on conjugate base $Z = -1$)

$$pK_{AH}^S - pK_{AH}^0 = \log f_H^S + m_{A^-} - Y_-. \quad (20.3)$$

With acids of the type of substituted ammonium ions (charge on conjugate base $Z = 0$)

$$pK_{BH^+}^S - pK_{BH}^0 = \log f_H^S + m_B Y_0. \quad (20.4)$$

The symbols S and 0 indicate the given solvent and the standard solvent respectively, f_H^S is the degenerate activity coefficient of the proton in the given solvent, m_{A^-} and m_B are constants characteristic of the given acids, and Y_- and Y_0 are constants characteristic of the given solvent. It must be stressed that

$$\log\gamma_{A^-}/\gamma_{AH} = m_{A^-}Y_- \text{ and } \log\gamma_B/\gamma_{BH^+} = m_B Y_0. \quad (20.5)$$

In media to which Hammett's acidity function is applicable, both activity functions vanish:

$$Y_- = Y_0 = 0; \quad (20.6)$$

since water is selected as standard solvent, condition (20.6) is assumed for it.

The values of m_{A^-} for *meta*- and *para*-substituted benzoic acids, and of m_B for *meta*- and *para*-substituted anilines have been shown to be related linearly with the Hammett σ values[182,183]. From this were obtained the following relations between Hammett's ρ values and Y_0 and Y_-

$$\rho = \rho_0 + \beta_0 Y_0; \quad \rho = \rho_0 + \beta_- Y_-, \quad (20.7)$$

where ρ_0 is the value of ρ in the standard solvent (water), β_0 and β_- are constants having very similar numerical values for substituted benzoic acids and substituted anilines (+0.628 and -0.57 respectively).

Brownstein[185] showed that a somewhat modified Grunwald–Winstein equation was of wide application. His equation is

$$\log k_{ij}/k_{i0} \text{ (or } \nu_{ij} - \nu_{i0}) = S_j R_i, \quad (20.8)$$

where the k terms are velocity or equilibrium constants, the ν terms are ultra-violet or infra-red absorption frequencies, and i and j denote the compound and the solvent respectively. Absolute ethanol was selected as standard solvent ($R \equiv 0$), the standard compound being 1-methyl-4--methoxycarbonylpyridinium iodide (ultra-violet absorption $S \equiv 1$).

Swain's equation. In the opinion of Swain and his collaborators, a definite borderline cannot be drawn between S_N1 and S_N2 mechanisms[186-190]. They therefore regard Eqn. (20.2) as a particular case. With different types of reagents it would be necessary to introduce several scales of Y values for the same solvents[152,191]. A more general equation[152,192] containing four parameters is therefore proposed:

$$\log k/k_0 = Sn + S'e \quad (20.9)$$

or

$$\log k/k_0 = c_1 d_1 + c_2 d_2,$$

where k is the velocity constant of the reaction in the presence of the given nucleophilic (N) and electrophilic (E) reagents, k_0 is the rate constant in the presence of the standard nucleophilic (N_0) and electrophilic (E_0) reagents, n and e (d_1 and d_2) are constants measuring the nucleophilic character of N and the electrophilic character of E respectively, and S and S' (or c_1 and c_2) are constants representing, according to the authors' treatment, the "sensitivity" of the reagent to the action of nucleophilic and electrophilic reagents respectively. When Sn is constant,

$$\log k/k_0 = S'e, \quad (20.10)$$

and, assuming that $S' = m$ and $e = Y$, Eqn. (20.9) reduces to (20.2). If $S'e$ is constant (when, for example, water present in excess acts as the electrophilic reagent), Eqn.(20.9) reduces to (16.2).

Swain and Dittmer[193] proposed a special equation containing two parameters for the rates of solvolysis of organic chlorides or bromides:

$$\log k_{ij}/k_{i0} - \log k_{0j}/k_{00} = a_i b_j, \quad (20.11)$$

where the subscript i refers to the reagent, j to the solvent, and 0 to the standard reagent (methyl bromide) and the standard solvent (80% ethanol).

Swain's views on the S_N type of reaction mechanism, including the termolecular character of reactions previously assigned to the S_N class, have been critically analysed by Hughes and Ingold and their collaborators[194,195] and by Winstein *et al.*[178] These workers discovered errors in the experimental data quoted by Swain and in his treatment of the data, and on the basis of additional experimental results they showed several of his conclusions to be incorrect. Eqn. (20.9) is apparently a purely empirical formula, and no concrete physical meaning can be ascribed to the parameters on its right-hand side.

The problem of the interrelationship between the polarity of a solution and its dielectric constant was examined in greater detail by Rudakov[196]. He has shown that the dielectric constant D is not a universal measure of the polarity of a solvent. For this purpose he proposes another empirically defined quantity D_0, which is equal to D only in the case of alcohols and water.

Reference must also be made to correlation equations obtained in using the theory of regular solutions[197] to calculate activity coefficients.

McGowan's equation[198]. This is

$$\log f_2/f_1 = \log c_2/c_1 = k_M P, \quad (20.12)$$

where f_2 and f_1 are the activity coefficients of the solute in the immiscible solvents 2 and 1 respectively, the concentration ratio c_2/c_1 is equal to the partition coefficient of the solute between these solvents, k_M is a constant characteristic of the given pair of solvents, and P is the parachor of the solute, taken as a measure of its molecular volume. Eqn. (20.12) allows for the non-polar non-specific (dispersion) interaction between solvent and solute.

Deno and Berkheimer[199] tested Eqn. (20.12) with a number of compounds. The molar concentration of a given pure substance "in itself" was taken as c_1, while c_2 represented the concentration of a saturated solution of this substance in water. Eqn. (20.12) proved to be applicable to liquid aromatic and aliphatic, solid aromatic, and gaseous aliphatic hydrocarbons, as well as to halogenated aliphatic and aromatic hydrocarbons. With all these compounds and water as the second component, k_M had a value of ~ 0.0130 at 25°.

In the presence of some specific interaction between the solute and water (for example, a hydrogen bond), a term $E_A = E_H/2.3RT$, where E_H is the energy of the specific interaction, must be added to the right-hand side of Eqn.(20.12):

$$\log c_2/c_1 = k_M P + E_A. \quad (20.13)$$

The above value of k_M is retained. It is also found that E_A has an approximately constant value for compounds having the same functional group.

Eqn.(20.13) is applicable to ethers and esters, aldehydes and ketones (apart from the lower members), nitriles and nitro compounds[199]. With all these classes of compounds, it is apparently no longer possible to neglect the polar non-specific interaction: in this connection, the applicability of

Eqn. (20.13) with the value of k_M unchanged is not altogether easy to understand. Perhaps the term E_A roughly takes into account also the energy of polar interaction.

Rudakov's equation[200,201]. This worker gives fresh proofs that solvolysis of t-butyl chloride is a truly unimolecular reaction, and that its mechanism does not undergo substantial changes on passing from such a polar solvent as water to the gas phase. The influence of solvents on the velocity of this reaction (the change in rate on passing from water to the gas phase amounts to a factor of $10^{19.5\pm2}$) may be considered a result of polar non-specific interaction of the reagent and the activated complex with the solvent.

From the theory of regular solutions, the activity coefficient of a dissolved substance, *e.g.* $(CH_3)_3CCl$, can be expressed as follows[199,200]:

$$RT \ln\gamma_1 = V_1^{2/3}(\Pi_1 - \Pi_C)^2, \qquad (20.14)$$

$$\Pi_1 = E_1^{1/2}V_1^{-1/3}; \quad \Pi_C = E_C^{1/2}V_C^{-1/3},$$

where V_1 is the molar volume of the solute in the pure state, E_1 is the molar energy of the pure solvent, and V_C and E_C are the corresponding quantities for the dissolved substance.

The quantities Π_1 and Π_C are called polarity factors.

An expression analogous to (20.14) is assumed for the activated complex:

$$RT \ln\gamma_{\neq} = V_{\neq}^{2/3}(\Pi_{\neq} - \Pi_C)^2. \qquad (20.15)$$

Eqns. (20.14) and (20.15) give values of γ_1 and $\gamma_{\neq}$ referred to the corresponding pure liquids‡ as standard states. If a solution in some solvent is chosen as the standard state, the activity coefficients relative to this new standard are given by the following expressions:

$$2.3RT \log\gamma_1^0 = V_1^{2/3}[2\Pi_1(\Pi_0 - \Pi_C) + \Pi_C^2 - \Pi_0^2] \qquad (20.16)$$

and

$$2.3RT \log\gamma_{\neq}^0 = V_{\neq}^{2/3}[2\Pi_{\neq}(\Pi_0 - \Pi_C) + \Pi_C^2 - \Pi_0^2], \qquad (20.17)$$

where Π_0 is the polarity factor of the standard solvent.

In the case of a unimolecular reaction, the velocity constant k_C in an arbitrary solvent is connected with the velocity constant k_0 in the standard solvent by the relation[12]

$$k_C/k_0 = \gamma_1^0/\gamma_{\neq}^0. \qquad (20.18)$$

On substituting γ_1^0 and $\gamma_{\neq}^0$ from (20.16) and (20.17) in (20.18) and assuming that $V_1 = V_{\neq}$ (such equality is approximately true in the case of t-butyl chloride[200]), we have

$$\log k_C/k_0 = V_1^{2/3}/2.3RT(\Pi_{\neq} - \Pi_1)(\Pi_C - \Pi_0) \qquad (20.19)$$

Eqn. (20.19) represents in essence the Grunwald–Winstein equation (20.2) deduced theoretically: Y_C is given by the expression (20.19), and

$$m_i = V_i^{2/3}(\Pi_{\neq i} - \Pi_i)V^{2/3}(\Pi_{\neq} - \Pi_1)$$

if the subscript 1 refers to t-butyl chloride, and the subscript 0 to 80% ethanol.

If the gas phase is taken as the standard medium, the quantity Π_0 becomes zero. It follows from this that the polarity factor Π_C is the natural absolute measure of the intensity of polar interaction in a pure liquid.

‡ $\gamma_{\neq} = 1$ in a hypothetical liquid consisting entirely of activated complexes.

Using experimental rate constants for the solvolysis of t-butyl chloride, Rudakov calculated values of Π_C for various pure liquids and also values of Π_1 and Π for t-butyl chloride[200,201].

Values of Π_C for water and alcohols of general formula X–OH show very good linear dependence on Taft's σ^* values for the substituents X (see Fig. 7):

$$\Pi_C = 0.740 + 0.480\sigma^*. \qquad (20.20)$$

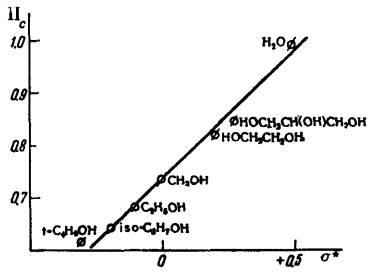


Fig. 7. Linear relation between Rudakov's polarity factors Π_C for alcohols X–OH and Taft's σ^* values for the substituents X.

This confirms the physical significance of the Π_C values as a measure of the capacity of a substance for polar non-specific interaction. It also gives grounds for hoping that the dependence of Π_C on the structure of the corresponding compounds can be considered on the basis of the principles which have been applied to the dependence of reactivity on structure, which is of great practical importance.

A universal scale for the effect of solvents on the electronic spectra of organic compounds has been given by Zhmyreva *et al.*[23]

XXI. FREE ENERGY AS THE SOLE UNIVERSAL MEASURE OF REACTIVITY

In the preceding sections the free energy ΔF of activation or reaction has been considered in nearly every case as the measure of reactivity. ΔF is a complicated quantity depending on the enthalpy ΔH and the entropy ΔS of activation or reaction: $\Delta F = \Delta H - T\Delta S$. Alternatively, ΔF can be regarded as a sum of terms representing the changes in potential energy (ΔEp) and in kinetic energy ($R \ln \Pi Q$) during activation or reaction.

The quantities ΔH and ΔS are in principle different in character, and should depend in different ways on the structure of the reactants.

Hammett himself[4] pointed out that the inductive effect and the various forms of conjugation should affect reactivity, producing corresponding changes in the energetic factor (energy of activation or heat of reaction). The experimental results, however, disproved this§[4]. Hammett attempted to find a way out by referring to the frequently observed empirical rule[4,202-204] of a linear relation between ΔH and ΔS. Recently[205] a theoretical basis has also been given to this rule in the case of condensed systems. Taft[10] suggests that this rule is widely applicable also in the aliphatic series.

However, data are now available suggesting that in many cases the changes in reactivity are caused mainly by changes in the entropy factor, the linear relation between ΔS and ΔH being absent[37,206,207]. The correlation equations of Taft and of Hammett remain applicable.

Ingold[7] and also Taft[10] consider that electronic effects influence the magnitude of $\Delta\Delta Ep$, which in most cases cannot be measured. Taft concludes that $\Delta\Delta F$ is a better measure of $\Delta\Delta Ep$ than is $\Delta\Delta H$.

The fact that the Arrhenius activation energy frequently has no definite physical meaning was pointed out as early as 1939 by Selivanova and Syrkin[208].

The factual material which has accumulated by now suggests strongly that it is to the free energies that the correlation equations examined above are applicable, as is postulated by the LFE principle, independently of how ΔH and ΔS vary individually, and of the relation existing between these quantities. It is impossible by considering ΔH and ΔS separately to obtain quantitative relations having such a wide range of application as has the LFE rule.

From the above it can be concluded that at the present time the only universal measure of reactivity which can serve as a basis for a quantitative theory in organic chemistry is the value of ΔF (in practice, $\log k$). This statement does not, of course, mean that determinations of energy of activation or enthalpy of reaction and entropy of activation or reaction are not of great importance. It is emphasised merely that, so far, it is impossible to base a quantitative theory on independent (or even interdependent) correlation schemes involving either only energetic or only entropic terms. In view of this, it must always be remembered that electronic "effects" are as much "entropic" as they are "energetic".

The above principles can evidently be extended to the theory of the dependence of reactivity on the nature of the solvent[209].

XXII. PRACTICAL EFFICIENCY OF LINEAR CORRELATION EQUATIONS

All the main correlation equations examined above can be written in the form

$$A_{ij} = A_{0j} + \sum_k \alpha_{jk}\beta_{ik}, \qquad (22.1)$$

where $A_{ij} = \log k_{ij}$ or some physical parameter of the given compound, A_{0j} is a similar function for the standard compound in a given series, β_{ik} are parameters characteristic of the i-th compound (constants of the substituents), j represents the reaction series, and k the factor influencing the reactivity (inductive effect, etc.).

An equation of type (22.1) can always be converted to the form

$$\sum_k A_{ijk} = \sum_k (A_{0jk} + \alpha_{jk}\beta_{ik}). \qquad (22.2)$$

Instead of (22.2) we can write a series of independent equations

$$A_{ijk} = A_{0jk} + \alpha_{jk}\beta_{ik}. \qquad (22.3)$$

Study of the properties of Eqn. (22.1) can therefore be reduced to that of the properties of (22.3). The latter is similar in form to the Taft equation (5.1) or the Hammett equation (9.1). Below, therefore, we shall consider only an equation of the Hammett type

$$\log k_{ij}/k_{0j} = \rho_j\sigma_i. \qquad (22.4)$$

In this section the properties of an equation of the type (22.4) will be examined to assess the practical possibility of including a sufficiently large number of organic reactions with the correlation equations discussed in the preceding sections.

The chief problem which arises here is the practically unlimited number of possible organic reactions. Consequently, the number of velocity and equilibrium constants which must be known for a quantitative characterisation of these reactions is also unlimited.

In this connection the most relevant property of an equation of the type (22.4) is that the experimental determination of a certain number N_0 of parameters for certain compounds of a given series (velocity constants, etc.) makes it possible to calculate an even larger number N of analogous parameters for other compounds in this series, providing that the appropriate σ values are known. The greater the ratio N/N_0 the greater the practical usefulness of the correlation. The quantity $N/N_0 = \varphi$ can be termed the efficiency of the correlation. Clearly, if N is a very large number, φ too must be quite large, so that the task of the experimental determination of N_0 parameters should not go beyond the bounds of practical possibility.

The position will be different in this respect if reaction series of a different type are considered. In this case the reaction series is characterised by the number m of independent substituents X_i whose structure can be varied without leaving the given reaction series. In this sense the simplest case is provided by reaction series for which $m = 1$, of the type

$$X_i - Y_i + a \rightarrow \text{reaction products.}$$

To this belong all unimolecular reactions (a absent) and those bimolecular processes in which the structure of one of the reactants remains unchanged, *e.g.* $a = Cl^-$, etc. In this case the number of quantities to be correlated ($\log k_{ij}$) is equal to the number n of substituents having known σ_i constants, which are universal parameters, and for the present will not be included in the assessment of φ. Hence $N = n$, $N_0 = 2$ (ρ and $\log k_{0j}$), and $\varphi = \frac{1}{2}n$. For correlation it is necessary to know two specific parameters for each reaction series and n universal parameters; n should be sufficiently large to cover all substituents which are in practice met relatively often.

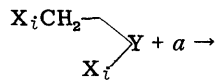
The problem of cross correlations investigated by Miller[210] is more complicated. He uses graphical analysis to solve the general problem of the superposition of

§ The widely held view that the applicability of the Hammett equation is explained by constancy of the entropy factor is erroneous.

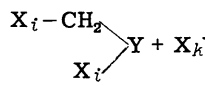
several correlation equations. The essentials of the final formulae which he obtained will be given below, but solutions will be obtained analytically, which will make it easier to understand the physical meaning of the parameters in these formulae.

With such reaction series, $m > 1$, for example

$X_i - Y_1 + X_j - Y_2 \rightarrow$ reaction products; $m = 2$



$m = 2$



$m = 3$

etc.

If $m = 2$, we have

$$\log k_{ij}/k_{0j} = \rho_{(-j)}\sigma_i, \qquad (22.5)$$

$$\log k_{ij}/k_{j0} = \rho_{(i-)}\sigma_i. \qquad (22.6)$$

Eqns. (22.5) and (22.6) cover every possible k_{ij} if all k_{0j} and $\rho_{(-j)}$ ($j = 0, 1, \ldots, n$) or all k_{i0} and $\rho_{(i-)}$ ($i = 0, 1, \ldots, n$) are known. In other words, a complicated reaction series can be divided into n simple reaction series. It would appear at first sight that $2n$ specific and n universal parameters would have to be known for correlation, φ retaining the same value as in the case of a simple reaction series in which $m = 1$. Actually, however, the value of φ is considerably larger owing to the overlapping of the two equations (22.5) and (22.6). On combining these in a different sequence we obtain

$$\log k_{ij}/k_{00} = \rho_{(-j)}\sigma_i + \rho_{(0-)}\sigma_j = \rho_{(-0)}\sigma_i + \rho_{(i-)}\sigma_j. \qquad (22.7)$$

This equation has two solutions, the first of which is

$$\rho_{(-j)} = \rho_{(-0)} \text{ and } \rho_{(i-)} = \rho_{(0-)}.$$

Hence

$$\log k_{ij}/k_{00} = \rho_{(-0)}\sigma_i + \rho_{(0-)}\sigma_j, \qquad (22.8)$$

where $\rho_{(-0)}$ and $\rho_{(0-)}$ are "sensitivity" constants for the following simple reaction series

$X_i - Y_i + X_0 - Y_2 \rightarrow$ reaction products;

$X_0 - Y_1 + X_j - Y_2 \rightarrow$ reaction products.

The second possible solution can be written in the form

$$\frac{\rho_{(i-)} - \rho_{(0-)}}{\sigma_i} = \frac{\rho_{(-j)} - \rho_{(-0)}}{\sigma_j}, \qquad (22.9)$$

whence we obtain

$$\rho_{(i-)} = (\rho_{(-k)} - \rho_{(-0)})\sigma_i/\sigma_k + \rho_{(0-)} \qquad (22.10)$$

and

$$\rho_{(-j)} = (\rho_{(k-)} - \rho_{(0-)})\sigma_j/\sigma_k + \rho_{(-0)}, \qquad (22.11)$$

where k refers to some arbitrarily chosen substituent. Keeping k constant, we can calculate all the $\rho_{(i-)}$ or $\rho_{(-i)}$ values. On substituting (22.10) and (22.11) respectively in (22.7) we obtain

$$\log k_{ij}/k_{00} = \rho_{(-0)}\sigma_i + \rho_{(0-)}\sigma_j + \frac{\rho_{(-k)} - \rho_{(-0)}}{\sigma_k}\sigma_i\sigma_j \qquad (22.12)$$

and

$$\log k_{ij}/k_{00} = \rho_{(-0)}\sigma_i + \rho_{(0-)}\sigma_j + \frac{\rho_{(k-)} - \rho_{(0-)}}{\sigma_k}\sigma_i\sigma_j.$$

If the first solution is adopted, a reaction series having $m = 2$ is correlated by three specific parameters ($\rho_{(-0)}$, $\rho_{(0-)}$, and $\log k_0$) and $\varphi = n^2 : 3$. With the second solution a further specific parameter $\rho_{(k-)}$ (or $\rho_{(-k)}$) is added, and $\varphi = n^2 : 4$.

The physical meaning of the two solutions is as follows. If for some value of k, $\rho_{(-k)} \neq \rho_{(-0)}$ or $\rho_{(k-)} \neq \rho_{(0-)}$, this inequality must necessarily extend to all the remaining values of k, and Eqn. (22.12) must be used. If in the case of some one value of k, $\rho_{(-k)} = \rho_{(-0)}$ or $\rho_{(k-)} = \rho_{(0-)}$, such equality holds for all other values of k as well. In such a case (22.12) reduces to (22.8), and the first solution can be used.

When X_i and X_j are arranged symmetrically relative to the reactive centre, solution (22.8) reduces to the additivity rules considered in sections IV and IX. Jaffe[221] used (22.8) also in the case of two substituents in two benzene nuclei linked unsymmetrically to the reactive centre, and obtained a satisfactory result. The first solution proved to be applicable also in the case of the reaction series involving interaction of *meta*- and *para*-substituted diphenyldiazomethanes with *meta*- and *para*-substituted benzoic acids[212].

The problem of the choice between the first and the second solutions has been discussed by Exner[83]. He gives an actual example in which it is necessary to use a formula of the type (20.12) (see section XVII). He shows that the first solution cannot be applied universally.

The case in which $m = 3$ can be considered in an analogous manner to the above[210].

XXIII. CONCLUSION

Consideration of the information given above indicates that the LFE rule and the principle of the independence and the additivity of the individual terms of $\Delta\Delta F$ can be used for a quantitative investigation of the dependence of the reactivity of organic compounds on their structure, and also on the nature of the solvent, for a great variety of types of compounds and reactions. In several cases the Hammett and Taft equations (involving the polar and the steric components) can be used only when preparative data are available (percentage yield)[213].

Consequently we are dealing with quite general, although possibly approximate, laws of Nature, which can be regarded as the basis for a very general quantitative theory of the reactivity of organic compounds. An important point is that this theory utilises several well-known qualitative ideas about the structure and the reactivity of these compounds, so that in most cases the various constants in the correlation equations can be given a concrete physical meaning. Therefore the LFE rule and the additivity principle provide not only a means for practical calculations but also an extremely useful tool for investigating problems of the detailed structure of organic compounds and of the mechanisms of reactions.

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