was 3 N and the ferric chloride solution was 5% ferric chloride in 0.1 N hydrochloric acid. The aqueous stock hydroxylamine solution was prepared by neutralizing a 28% hydroxylamine solution (w./v.) with an equal volume of 14% sodium hydroxide solution (w./v.). This solution was buffered with an equal volume of a solution made by mixing 4 parts of 0.1 M sodium acetate solution and 1 part of 0.1 M acetic acid. The resulting stock hydroxylamine solution was usable for over a week if kept under refrigeration.

Kinetic Measurements.—All experiments were carried out in aqueous solutions adjusted to a calculated ionic strength of 1.0 M with KCl. The hydroxylamine and imidazole served as their own buffers in the pH range employed. The buffering capacity of all solutions was great enough to assure against pH drift during the studies. The concentration of hydroxylamine was sufficiently large, as compared to lactone, so that pseudo-first-order kinetics were always obtained. The pH of each kinetic run was routinely determined at 0 and ∞ time.

Imidazole Catalyzed Lactone Hydrolysis at 78°.—The hydrolysis of approximately 0.02 M solutions of lactone were followed at two pH's (6.45 and 6.83) and at two imidazole concentrations (0.5 M and 1.0 M) at each pH. The kinetic procedure employed was a modification of that of Lippmann and Tuttle.[15] One-ml. aliquots of the aqueous lactone-imidazole solution were pipetted into 15 × 135 mm. screw-cap (neoprene lined) Pyrex vials. The tightly capped vials were thermostated at 78°. To determine lactone concentration at the desired time intervals, tubes were periodically removed from the 78° bath and quenched in an ice-bath. Two ml. of the buffered hydroxylamine stock-solution was introduced and the tube heated at 100° for 1 hour (to prevent evaporation of the water solvent the tubes were capped with marbles). The hydroxamic acid ferric ion complex was then developed by introducing to the cooled solution 1 ml. each of the stock hydrochloric acid and ferric chloride solutions. The absorbance was measured at 540 mμ. The reactions were followed to 50% of completion with a minimum of ten points (tubes). The pseudo-first-order constants (k_{obs}) were obtained from the slope of the plot of log [O.D.$_i$/O D.$_t$] against time. The catalytic constants for imidazole were obtained by plotting $k_{obs}-k_w$ (where k_w is the solvolytic constant in the absence of imidazole) against IM_T ($K_a/(K_a + a_H)$).

Hydroxylaminolysis of Lactones.—One-ml. aliquots of the aqueous lactone (0.01-0.02 M) hydroxylamine solution were pipetted into screw-cap vials (*vide supra*) which were thermostated at 30° (± 0.01°). For the general base catalysis studies the imidazole (0.20-1.20 M) was included in the hydroxylamine (0.40-0.80 M) solution. Tubes were withdrawn from the water bath at appropriate time inter-

vals and quenched by the addition of 2 ml. of 3 N HCl. The hydroxamate ferric ion complex color developed instantly on addition of 2 ml. of the stock ferric chloride solution and the absorbance was determined spectrophotometrically as before. The hydroxylaminolysis reactions were followed to 75% completion employing 12-13 readings (tubes) plus final readings in duplicate. The pseudo-first-order rate constants (k_{obs}) were obtained by plotting log [O.D.$_\infty$/O.D.$_\infty$ − O.D.$_t$] vs. time. Precise first-order plots were invariably obtained.

D_2O *Solvent Kinetic Isotope Effect.*—The rates of hydroxylaminolysis of δ-valerolactone were determined in D_2O by the same procedure followed above, taking care that all solutions remained anhydrous. In the determination of a_D the glass electrode correction formula of Fife and Bruice[16] was employed. The ion product of deuterium oxide at 30° was calculated to be 0.224×10^{-14} from the values K_{D_2O} = 0.154×10^{-14} (25°),[17] K_w = 1.47×10^{-14} (30°)[5] and K_w = 1.008×10^{-14} (25°)[18] by assuming that the change in K_{D_2O} from 25 to 30° is proportional to the change in K_w from 25 to 30°.

pK *Determinations.*—The pK's of hydroxylamine and imidazole were determined by the method of half-neutralization and serial dilution maintaining a calculated ionic strength of 1.0 M (KCl) at 30°. The apparent pK_a' values did not change on dilution. Using the determined values of pK_a' it was possible to calculate accurately (±0.02 pH unit) the desired composition of all reaction solutions. Thus, final adjustment of reaction solutions to the desired pH was not necessary. The pK_a' of hydroxylamine in D_2O agreed with the value predicted from the equation of Li[19] within 0.05 pK unit; see Table I for the determined dissociation constants.

While the pK_2' values for H_2NOH in H_2O and D_2O are too large to be determined with any accuracy by the half-neutralization technique,[20] they were shown to be far beyond the range of pH employed in this study. Thus, the species $H_2NO^\ominus$ could only be present in trace amounts.

(16) T. H. Fife and T. C. Bruice, *J. Phys. Chem.*, **65**, 1079 (1961).

(17) R. W. Kingerley and V. K. LaMer, *J. Am. Chem. Soc.*, **63**, 3256 (1941).

(18) H. S. Harned and R. A. Robinson, *Trans. Faraday Soc.*, **36**, 973 (1940).

(19) N. C. Li, Abstract of paper presented to the A. C. S. Meeting in St. Louis, Mo., March 21-30, 1961, Division of Phys. Chem., Paper 14.

(20) P. Ballinger and F. A. Long, *J. Am. Chem. Soc.*, **81**, 1050 (1959).

(15) F. Lippmann and L. C. Tuttle, *J. Biol. Chem.*, **159**, 21 (1945).

The Interrelation of Reaction and Substituent Constants and the Role of Electronegativity in Linear Free Energy or Enthalpy Relationships

BY W. F. SAGER AND CALVIN D. RITCHIE

An equation is derived relating the reaction constant ρ with the substituent constants of the groups involved in reactions which are not complicated by variable resonance or steric interactions. The relationship between electronegativity and substituent constants is discussed. Application of the equation is made to the linear free energy relationships of Grunwald and Winstein and of Swain and Scott, as well as to reactions involving ambient groups.

In recent years, increasing progress has been made toward solving the troublesome problem of separating the interlocking factors which govern reaction rates and equilibria. The Hammett equation, which allows the separation of steric and other factors within aromatic series, has had a major influence on the development of structure-reactivity correlations.[1] Extended insight has been gained from the

work of Taft, who, by separation of polar and steric factors, was able to show the existence of linear free energy relationships in the aliphatic series.[2]

(1) L. P. Hammett, *Chem. Revs.*, **17**, 125 (1935); H. H. Jaffé, *ibid.*, **53**, 191 (1953).

(2) For a recent review of the development and applicability of the Taft equation, see R. W. Taft, Jr., in M. S. Newman, "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1959, p. 556 ff.

These linear free energy relationships, although characteristic of reaction series with constant steric and entropy factors, are not limited to those of constant entropy. This point has been discussed in detail by Leffler.[3]

Hine has recently used symmetry arguments to show that ρ in the Hammett equation is a function of the σ-values of the reaction site groups.[4] He has calculated empirically a "transmission constant" from data of several ionic reactions which establishes the slope of the linear relation between ρ- and σ-values. A justification of these relationships in terms of the Kirkwood–Westheimer dipole-dipole theory was presented.

In all of these correlations, polar, resonance, steric and medium effects are involved. The Hammett and Taft relations separate the steric factor by employment of series for which this factor is constant. Taft has described a method for separation of polar and resonance effects in the Hammett series.[5] Also, Hammett has proposed an approximate expression for estimating the medium effect[6]

$$\Delta F^0 = \Delta E_n + A/\epsilon \tag{1}$$

It can be seen, then, that by means of these methods, a complete separation of parameters can be made in carefully selected series. Our purpose is to outline a way in which existing data may be utilized for the prediction of one of these parameters, namely the change in enthalpy due to alteration of the inductive effects which result from change in structure. It should be emphasized that the method may be expected to lead to accurate values for reaction rates and equilibria only in series where the resonance and steric factors are constant and where the effect of the medium can be evaluated. General application should be found, however, in the prediction of that part of the change in rate or equilibrium which is due to change in the inductive influence on a reacting group. The method will be applied to the calculation of ρ-values, to the Grunwald–Winstein[7] and Swain–Scott[8] equations, and to the ratio of products formed from ambident groups.

Development of Equations

Free energy relationships of the sort proposed by Hammett and Taft may be viewed as correlations of equilibrium constants for exchange reactions of the type

$$G_{s1}G_{r1} + G_{s2}G_{r2} \rightleftharpoons G_{s1}G_{r2} + G_{s2}G_{r1} \tag{2}$$
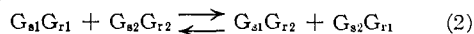
For example, the equilibrium constant for ionization of substituted benzoic acids relative to benzoic acid is given by the equation

$$\log K/K_0 = \rho\sigma = \log K' \tag{3}$$

where K is the ionization constant for the substituted acid, K^0 that of benzoic acid, and K' is the equilibrium constant for an exchange reaction of the above type, in which G_{s1} stands for the substituted

(3) J. E. Leffler, *J. Org. Chem.*, **20**, 1202 (1955).

(4) J. Hine, *J. Am. Chem. Soc.*, **81**, 1126 (1959).

(5) R. W. Taft, Jr., and I. C. Lewis, *J. Am. Chem. Soc.*, **81**, 5343 (1959).

(6) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1950, p. 83.

(7) E. Grunwald and S. Winstein, *J. Am. Chem. Soc.*, **70**, 846 (1948).

(8) C. G. Swain and C. B. Scott, *ibid.*, **75**, 141 (1953).

phenyl group, G_{s2} for the reference phenyl group, and G_{r1} and G_{r2} are the groups exchanged in the course of the reaction, namely the carboxyl and carboxylate ion groups, respectively. Needless to say, the choice of G_{r1} and G_{r2} is arbitrary. For example, the groups G_{s1} and G_{s2} in the case cited could equally well be considered as the phenyl carbonyl group (X-C_6H_4CO-), in which instance the groups G_{r1} and G_{r2} would correspond to the hydroxyl and oxy anion groups. When rates rather than equilibria are dealt with, the groups G_{r1} and G_{r2} stand for the reaction site group in the transition state.

The enthalpy change for such exchange reactions should be a function of the electronegativities of the atoms involved, provided steric and medium factors remain constant, and if resonance effects do not interfere. For application to the problem at hand, the basic concept of electronegativity must be modified, since a fixed value for each atom would permit no change in enthalpy. To circumvent this difficulty, one may employ "intrinsic electronegativities"[2] defined directly from bond energies by the following equation, which was used by Pauling

$$D_{AB} = (D_{AA} + D_{BB})/2 + 23(x_A - x_B)^{2} \tag{4}$$

The terms x_A and x_B in this instance refer to intrinsic electronegativities chosen to fit the actual bond energies. A direct evaluation by means of the above equation is not at all practical. The following section deals with indirect means for evaluating this difference.

Consider any bond in a complex molecule of the sort indicated in the equation for the exchange reaction given earlier. Let x_i and x_i' represent the intrinsic electronegativities of the bonded atoms. The indices i and i' are used to label individually each end of each of the bonds in all the product and reactant molecules. The enthalpy change for an exchange reaction of the type given in eq. 2 is

$$\Delta H = 23.06 \sum_{i,i'} (x_i - x_i')^2{}_{\text{prod}} - \sum_{i,i'} (x_i - x_i')^2{}_{\text{react}} \tag{5}$$

The assignment of i and i' is made to give the proper sign to each term in eq. 7.

Assume that

$$x_i = x_{oi} + \sum_j k_{ij} x_{oj} \tag{6}$$

where the index j refers to each of the atoms in the molecule, the constants k_{ij} relate the influence of the atom j on the electronegativity of one atom of bond i, and x_{oi} represents a constant in some way characteristic of the atom i. The conditions for constancy of x_{oi} will be discussed in connection with eq. 10. With reference to an exchange reaction as illustrated in eq. 2, the enthalpy change due to modification of a substituent will be

$$\frac{\partial \Delta H}{\partial x_{os}} = 46.1 \sum_i \left(x_{oi} \sum_j k_{ij} x_{oj} \right) - \sum_{i'} x_{oi'} + \sum_j k_{i'j} x_{oj} \right) \frac{\partial x_i}{\partial x_{os}} \tag{7}$$

On the assumption that the k's are functions of the bond location and not of x_{oj}, one may write the

(9) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1939, p. 60.

equations

$$\partial \Delta H / \partial x_{os} = 46.1(x_{or2} - x_{or1})\left(\sum_i k_{ir} + \sum_{i'} k_{i'r}\right)\left(\sum_i k_{is} + \sum_{i'} k_{i's}\right) \quad (8)$$

and

$$\partial \Delta H / \partial x_{or} = 46.1(x_{os2} - x_{os1})\left(\sum_i k_{ir} + \sum_{i'} k_{i'r}\right)\left(\sum_i k_{is} + \sum_{i'} k_{i's}\right) \quad (9)$$

where the subscripts of the k's, ir and is, stand for the constants relating the influence of the group a_1 the site of r or s on the bond i, and r_2, r_1, s_2 and s_1 refer to the subscripts in eq. 2.

For exchange reactions of the sort exemplified by eq. 2 and for which the free energy change is governed by the enthalpy change, it is possible to correlate the Taft or Hammett equations with eq. 8 and 9. This may be done when the entropy change is zero or constant within a given reaction series. For other reaction series which follow linear free energy relationships but which do not show constant entropy changes a modified treatment is necessary as will be discussed subsequently.

Comparison of the Taft or Hammett equations with 8 and 9 subject to these restrictions gives

$$\rho(\sigma_{s2} - \sigma_{s1}) \text{ or } \rho^*(\sigma^*_{s2} - \sigma^*_{s1}) = (46.1/2.3 \, RT)(\Sigma \, k_{ir} + \Sigma \, k_{i'r})(\Sigma \, k_{is} + \Sigma \, k_{i's})(x_{or2} - x_{or1})(x_{os2} - x_{os1}) \quad (10)$$

On this basis, the values of ρ and σ should be linearly related to electronegativities, in the absence of resonance influences. That this is not generally the case indicates that the assumptions made are subject to limitations. The correspondence between electronegativities and σ^*-values has been discussed by Taft.[10] He has pointed out that σ^*-values are at least qualitatively related to Mulliken's orbital electronegativities, as calculated by Moffitt. He also showed that Pauling's scale of electronegativities does not even qualitatively parallel σ^*-values. The explanation of this fact is apparently that the bonding orbitals used by groups for attachment to carbon differ from those used in other attachments. This point is strikingly illustrated by the fact that dipole moments of the hydrogen halides parallel Pauling's electronegativities of the halides, while the dipole moments of the methyl halides do not even approximately parallel these values, but rather parallel the σ^*-values of the halides. Because of this we cannot use a straightforward application of Pauling's electronegativities to organic systems.

Nevertheless, the very existence of linear relationships requires that the above equations must hold provided the substituents are sufficiently removed from the reaction site. Under these circumstances, the change in x_0-values due to interaction of the groups will be negligible. Within this limitation it follows that x_i is linearly related to σ_s and hence

$$\rho(\sigma_{s2} - \sigma_{s1}) = \alpha^2(\sigma_{s2} - \sigma_{s1})(\sigma_{r1} - \sigma_{r2})/T$$

or

$$\rho = \alpha^2(\sigma_{r1} - \sigma_{r2})/T \quad (11)$$

The constant relating intrinsic electronegativities

(10) R. W. Taft, Jr., *J. Chem. Phys.*, **26**, 93 (1957).

of all the bonds in a group to its σ-value will depend on the particular reaction series (*e.g.*, Taft series or Hammett series). For reactions following the Taft equation, the following symbols will be used

$$\rho^* = a^2(\sigma_{r1}^* - \sigma_{r2}^*)/T \quad (12)$$

$$\Delta x_0 = \beta \Delta \sigma^* \quad (13)$$

$$a^2 = (46.1/2.3R)\beta^2 \quad (14)$$

The groups s_2, s_1, r_2, r_1 are chosen by cleaving the molecule into two parts, one containing the substituent and the other the reaction site.

By proper choice of reaction series, it is possible to relate the different ρ- and σ-values as the following example will indicate. If a reaction series R–Ph–A follows the Hammett equation where σ-values for the group R are used, it is evident that it must also follow the Taft equation where the σ^*-value for the entire group R–Ph would be used. Since Taft has defined σ^*-values so that $\rho_R^* = \rho_{RPh}$ for the saponification rates of esters, it follows that $\rho_I \cong \rho^*$.

It must be recalled that ρ^* in eq. 12 is evaluated only on the basis of polar effects. In those reactions where steric and/or resonance effects contribute to the net change in the free energy, there will be additional, additive terms. Taft[5] has discussed the separation of these effects and has presented an experimental method for the determination of a ρ-value, designated ρ_I, which is dependent only on these polar effects in the Hammett series. In all of the following discussions where Hammett ρ-values are used, we shall where possible use these ρ_I-values, thus eliminating the need for treating resonance effects.

Equation 12 has also neglected effects due to the medium. For those reactions involving charged groups, medium effects must be considered. From eq. 1 and 12

$$\Delta F = 2.3Ra^2 \, (\sigma_{s2}^* - \sigma_{s1}^*)(\sigma_{r2}^* - \sigma_{r1}^*) + A/\epsilon$$

It appears that many ionic reactions follow the Taft and Hammett equations quite well.[1,2] In these cases, then, the observed ρ-value must be the sum of the reaction constants due to inductive effects and that due to medium effects. That is

$$\rho_{obsd} = \rho_{calcd} + \rho_{el}/\epsilon T = a^2 (\sigma_{r1}^* - \sigma_{r2}^*)/T + \rho_{el}/\epsilon T \quad (15)$$

In this instance ρ_{calcd} is the ρ-value one might expect in absence of strong solvent interaction with the reactant groups and substituents and is the parameter obtained by use of eq. 12. It will be shown later in this paper that ρ_{el} can be approximately evaluated from data independent of the value for ρ. The evaluation of a in eq. 12 and 17 is also accomplished in a later section.

The Grunwald–Winstein Equation.—The Grunwald–Winstein equation relates the rates of reactions in which the solvent is one of the reactants to structure through the use of two constants, one of which is characteristic of the solvent and the other characteristic of the other reactant. This problem of relative rates of solvolysis can be formulated in terms of an exchange reaction of the type discussed, where we shall let P–A be the transition state of the solvolysis of P in the solvent A, Q–B that for the solvolysis of Q in solvent B, etc. Application of the

Grunwald–Winstein equation and of eq. 10 to this situation gives

$$(m_P - m_Q) = b_1(x_{oP} - x_{oQ}) \qquad (16)$$

and

$$(Y_A - Y_B) = b_2(x_{oA} - x_{oB}) \qquad (17)$$

where $b_1 b_2 = 46.1/2.3RT = 33$. The evaluation of b_1 and b_2 from reported data on the values of m and Y, and from Hammett and Taft correlations of various solvolyses is discussed in a later section of this paper and provides evidence for the validity of this treatment.

The observed limitation of the Grunwald–Winstein equation to the correlation of reactions which occur by the S_N1 mechanism is simply explained by this treatment. The normalization used for the evaluation of the constants in the equation involves the use of the same component as one of the reactants and one of the products in every reaction treated. From the previous discussion of the variability of electronegativities, it is seen that this is equivalent to defining the bonding states which must be used for the equation to apply. Since the normalization component, t-butyl chloride in 80% ethanol, is characteristic of the S_N1 reaction, the other components considered must also be S_N1 transition states. It should be noted that although the Grunwald–Winstein equation does not apply to S_N2 reactions, the treatment given here indicates that an analogous equation, using different normalization components, should be applicable. Hine[11] has in fact suggested such an equation and noted that the results obtained by its use would appear to be only slightly poorer than those generally obtained by the linear free energy equations.

The Swain–Scott Equation.—If eq. 10 is applied to the problem of relative rates of solvolysis in reactions where both electrophilic and nucleophilic attachments of the solvent occurs, we find

$$\log k_B{}^P/k_A{}^P - \log k_B{}^Q/k_A{}^Q = zb(x_P{}' - x_Q{}')(x_A{}' - x_B{}') + yb(x_P - x_Q)(x_A - x_B) \qquad (18)$$

if the number of solvent molecules involved in the electrophilic and nucleophilic attachments are the same for every reaction treated, and are equal to z and x, respectively. This equation is identical in form to that which is obtained by application of the Swain–Scott equation. The failure of the requirement regarding the number of solvent molecules is quite probably the main factor in the failure of the Swain–Scott equation to give values of the constants which are reasonable on theoretical grounds.[12]

Numeral Correlations

The constant a in eq. 12 could in principle be evaluated directly from a knowledge of intrinsic electronegativity values. These are, however, not known for atoms bonded to carbon. It thus becomes necessary to evaluate a experimentally. In order to avoid the approximation of solvent effects in ionic reactions, it is desirable to have data on several non-ionic reactions for this evalua-

(11) J. Hine, "Physical Organic Chemistry," McGraw–Hill Book Co., Inc., New York, N. Y., 1956, p. 158.

(12) E. S. Gould, "Mechanism and Structure in Organic Chemistry," Henry Holt and Co., Inc., New York, N. Y., 1959, p. 36 ff.

tion. Two such reactions, the formylation of anilines and the hydrogenation of acetophenones, have been studied.[1]

In the formylation of anilines, the following assignments are made relative to the exchange reaction 2: G_{s1} is the substituted phenyl group, G_{s2} is the phenyl group, G_{r1} is the amino group and G_{r2} is the formamido group. The σ^*-value for the amino group can be estimated from the σ_I-value reported $(0.10)^5$ and from the relationship $\sigma_G{}^* = 2.8\, \sigma_{IG}/0.45$.[13] The value thus obtained is $\sigma^* = 0.62$. The σ^*-value for the formamido group may be estimated as equal to that of the acetamido group. From the tabulated value $(0.28),^5$ a value of $\sigma^* = 1.74$ may be obtained by the above method. The ρ^*-value for the reaction is (-1.47). Thus, from eq. 12

$$a = \sqrt{\frac{\rho^* T}{\sigma_{r1}{}^* - \sigma_{r2}{}^*}} = 22.1 \qquad (19)$$

In the hydrogenation of acetophenones, let G_{r1} be the acetyl group and G_{r2} the $-CHOHCH_3$ group. The σ^*-value for the acetyl group has been tabulated as 1.65.[2] The value for the hydroxyethyl group is estimated from the σ^*-values for the ethyl group, the methyl group, and the hydroxymethyl group

$$\sigma_{CHOHCH_3}{}^* - \sigma_{CH_2OH}{}^* = \sigma_{CH_2CH_3}{}^* - \sigma_{CH_3}{}^*$$

We find $\sigma^* = 0.45$. For this reaction $\rho_I = +2.30$. Therefore, $a = 23.9$.

Several approximate methods have been examined for correction of the above equations for the effect of solvent. One approach has been suggested by Hammett, who indicated that for reactions of this type $\Delta S = -0.005\, A/\epsilon$ for aqueous solutions at $25°$. One set of data for the evaluation of A/ϵ is given in Table I and indicates the sort of precision that may be obtained with this method. This approach is discussed by Bell in considerable detail.[14] ρ_{el} may also be obtained

TABLE I

THE EVALUATION OF $\rho_{el}{}^a$

Series	ΔS	Subst.	$\Delta \sigma$	A/ϵ, kcal.	$\epsilon_{el} \times 10^{-3}$
Benzoic	0.0	p-Br	0.20	0	0
acids[b,c]	0.3	m-Br	.34	0.6	3.0
	1.3	m-CN	.48	2.6	9.3
	1.8	p-CN	.57	3.6	11.0
	2.3	p-NO₂	.67	4.6	11.9
	−1.2	p-OH	−.32	−2.4	13.0
	0.5	p-Cl	.20	1.0	8.6
	−0.2	m-Cl	.32	−0.4	−2.2

^{a} Evaluated by $\rho_{el} = -\dfrac{A}{2.3R(\Delta\sigma)}$. ^{b} Ref. 7, p. 50. ^{c} Values of ΔS and $\Delta\sigma$ are relative to the unsubstituted derivative.

by differentiation of eq. 15 with respect to $1/\epsilon$. For this purpose the data in Table II may be used. Since ρ can be more precisely determined than any single value of ΔS, the values shown in Table II are more reliable than those of Table I.

(13) N. C. Deno, R. W. Taft, Jr., and P. S. Skell, in "Annual Reviews of Physical Chemistry," Vol. 9, Annual Reviews Inc., Palo Alto, Calif., 1958, p. 287 ff.

(14) R. P. Bell, "The Proton in Chemistry," Cornell University Press, Ithaca, N. Y., 1959, p. 46 ff.

TABLE II

THE EVALUATION OF ρ_{el}

Solv.	ρ_I	$1/\epsilon \times 10^2$	$\rho_{el} \times 10^{-2b}$

(1) Ionization of benzoic acids[a]

H_2O	1.00	1.27	8.6
MeOH	1.55	3.18	7.0
EtOH	1.67	4.14	

(2) Ionization of anilinium ions[b]

H_2O	2.90	1.27	17.2
MeOH	4.00	3.18	19.2
EtOH	4.75	4.14	

[a] R. W. Taft and I. C. Lewis, *J. Am. Chem. Soc.*, 81, 5343 (1959). [b] From: $\rho_{el} = \dfrac{\partial \rho}{\partial(1/\epsilon)} T$.

Pauling has presented a method whereby the difference in the electronegativity of nitrogen in the ammonia molecule and of that in the ammonium ion can be evaluated as -0.33.[15] The difference in the σ^*-values for the NH_2 and the NH_3^+ group is -4.7. Application of eq. 13 gives $\beta = 0.07$. If we estimate σ^*-values of the OH and O^- groups by the relationships proposed by Taft,[13] we find $\beta = 0.06$. The much lower value of β obtained in the case of ionic groups implies that the solvent participates in the transmission of the polar influences between substituents and reactants. If the magnitude of this influence is taken to be proportional to the electronegativity difference between the ionized and unionized groups as suggested by eq. 15, it becomes possible to estimate ρ-values for ionization reactions. Pauling's method indicates that the electronegativity difference should have a constant value, at least for the atoms in which we are most interested, O, N, S and C. By the use of a ρ_{el} value of 20 and eq. 15 in connection with the data of Table II it is possible to obtain a series of values for σ^*. It is assumed that the σ^*-values for groups with charged atoms attached to the aromatic ring are greater by a factor of 2.8^n than those separated from the ring by n atoms (strictly, n methylene groups). With this correction the σ^*-values vary from 1.02 to 1.11 with an average of 1.06. This compares with a value of 1.5 which is obtained by Pauling's method of calculating the electronegativity difference that attends ionization and the use of eq. 13. With the aid of this empirical value of 1.06 for electronegativity differences of ionization and the ρ_{el} value of 20, eq. 15 may be written

$$\rho = (1.78 + 67/\epsilon)(1.06/2.8^n) \text{ at } 25° \quad (15a)$$

where n stands for the number of atoms separating the charged atom from the aromatic ring. A number of comparisons of calculated and observed values of ρ are given in Table III.

As discussed earlier, the use of ρ_I-values has eliminated the need to treat resonance interactions between reaction site and substituent. One type of resonance which has not been taken into consideration and which could lead to considerable improvement of the results shown in Table III is resonance within the reaction site group. One example of this effect is the anomalous value of ρ for the ionization of phenylboric acids. Taft has

(15) L. Pauling, ref. 9, p. 65.

TABLE III

COMPARISON OF OBSERVED AND CALCULATED VALUES OF ρ_I AT 25°

Series	Solvent	ρ_I obsd[a]	ρ_I calcd
RPhCOOH $\rightleftharpoons$	H_2O	1.0	1.0
RPhCOO$^-$	MeOH	1.55	1.5
	EtOH	1.67	1.7
	n-BuOH	1.56	2.1
	Ethylene glycol	1.32	1.3
RPhCH$_2$COOH $\rightleftharpoons$	H_2O	0.46	0.35
RPhCH$_2$COO$^-$			
RPhCH$_2$CH$_2$COOH $\rightleftharpoons$	H_2O	0.24	0.13
RPhCH$_2$CH$_2$COO$^-$			
RPhNH$_3^+$ $\rightleftharpoons$	H_2O	2.90	2.8
RPhNH$_2$	MeOH	4.00	4.1
RPhOH $\rightleftharpoons$	H_2O	2.36	2.8
RPhO$^-$			
RPhSH $\rightleftharpoons$	95% EtOH	2.9[c]	4.5
RPhS$^-$	48% EtOH	2.7	3.3
RCOOH $\rightleftharpoons$	H_2O	1.5[c]	1.0
RCOO$^-$			
RCH$_2$OH $\rightleftharpoons$	i-PrOH	1.2	1.8
RCH$_2$O$^-$			
RNH$_3^+$ $\rightleftharpoons$	H_2O	2.8[b]	2.9
RNH$_2$			
RPhPO$_3$H$_2$ $\rightleftharpoons$	H_2O	0.76	0.99
RPhPO$_3$H$^-$			
RPhPO$_3$H$^-$ $\rightleftharpoons$	H_2O	1.2	0.99
RPhPO$_3$$^=$			
RPhBO$_2$H $\rightleftharpoons$	25% EtOH	2.2	1.1[d]
RPhBO$_2$$^-$			

[a] ρ_I values are used where available; R. W. Taft, Jr., and I. C. Lewis, *J. Am. Chem. Soc.*, 81, 5343 (1959). [b] H. K. Hall, *ibid.*, 79, 5441, 5444 (1957). [c] R. W. Taft, ref. 2. [d] See following discussion.

TABLE IV

CALCULATION OF $\sigma^*_{reactant} - \sigma^*_{transition}$

Solvolysis reaction	ρ	$\Delta\sigma^*_{r-t}$	Y_s	Ref.
ArC(CH$_3$)$_2$Cl	-4.35	-1.07	-1.549	[a]
in 90% aq. acetone				
ArCH$_2$OTs	-2.30	-0.64	-0.25	[a]
76% aq. acetone				
Ar(C$_6$H$_5$)CHCl	-4.00	$-.95$	-1.974	[a]
ethanol				
ArCH$_2$Cl	-1.43	$-.46$	$+0.25$	[a]
50% aq. acetone				
R$_3$CCl	-2.86	$-.82$	0.00	[b]
80% aq. ethanol				

[a] R. W. Taft, Jr., and I. C. Lewis, *J. Am. Chem. Soc.*, 81, 5343 (1959). [b] A. Streitwieser, Jr., *Chem. Revs.*, 56, 697 (1956).

explained this value by assuming that resonance within the boric acid group places a major part of the charge on the boron. This leads to a ρ-value which is close to that of acids such as phenols in which the proton is lost from an atom attached to the phenyl group.[16]

Evaluation of the Constants in the Grunwald–Winstein Equation.—From eq. 16 and 17 and values for m, Y and σ^* (related to electronegativities by the factor calculated in the previous section) we can evaluate the constants b_1 and b_2. A number of SN_1 displacement reactions have been correlated by the Taft or Hammett equations. The ρ-values

(16) R. W. Taft, Jr., and I. C. Lewis, *J. Am. Chem. Soc.*, 80, 2436 (1958).

reported are used in eq. 15-a to calculate the difference in σ^*-values for the transition state reaction sites. The calculated values are reported in Table IV.

The plot of these values of $\Delta\sigma^*$ vs. Y for the solvent is shown in Fig. 1. The line shown is defined by the equation $Y = 4.9 \Delta\sigma^* + 3.2$, $^1\Delta Y/\beta\Delta\sigma^* = b_2$, and therefore $b_2 = 21$. Data on the evaluation of m for a number of R groups involving the same halide are scarce. If those values which are available[17] are plotted vs. σ^* for the alkyl groups, two widely separated lines of nearly the same slope are obtained, as shown in Fig. 2. From the average of these two slopes, we obtain $\Delta\sigma^*/\Delta m = -2.5 = 1/b_1\beta$. Thus, $b_1 = 1.8$.

From this rather crude evaluation, then, we find $b_1b_2 = 38$, which is in better agreement with the predicted value of 33 than can be expected from the scatter of the points in Fig. 1.
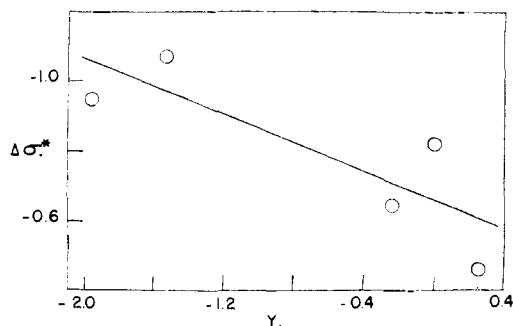

Fig. 1.—The relationship between Grunwald's Y-values for solvents and σ^*-values.

Relative Amounts of Product Formed from Ambient Groups.

—As mentioned in the introduction, the relative amounts of products formed from ambient groups, such as NO_2, CN, CNS, acetoacetic ester, etc., can be expressed in terms of an equilibrium constant for a general reaction of the type

$$(P - AB) + (Q - BA) \rightleftharpoons$$
$$(P - BA) + (Q - AB) \quad (22)$$
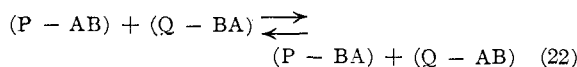
$$\log (k_{AB}{}^Q/k_{BA}{}^Q) = (\sigma_Q{}^* - \sigma_P{}^*)(\rho_{AB} - \rho_{BA}) + \log (k_{AB}{}^P/k_{BA}{}^P) \quad (23)$$

In those cases where the transition states for the formation of the two products differ only in the point of attachment with the ambient group, the difference in ρ-values in eq. 23 will be equal to the negative difference in the σ^* values for the two points. Thus

$$\log (k_{AB}{}^Q/k_{BA}{}^Q) = (\sigma_Q{}^* - \sigma_P{}^*)(\sigma_{BA}{}^* - \sigma_{AB}{}^*)1.7 + \log (k_{AB}{}^P/k_{BA}{}^P) \quad (24)$$

Then, the amount of product formed by attachment to the point of highest σ^*-value will decrease as σ_Q increases. Since groups with a high $\sigma_Q{}^*$-value would generally tend to react via an $S_{N}2$ mechanism, it is seen that the prediction here is in accord with the observations of Kornblum[18] that the $S_{N}2$

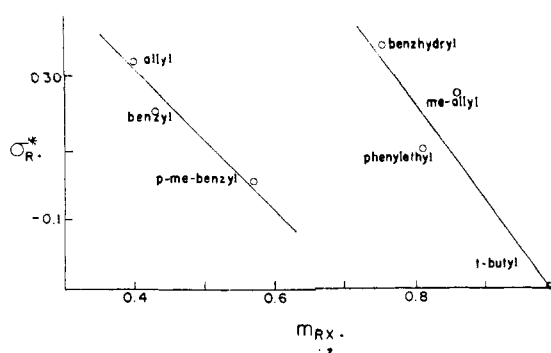(17) Ref. 7, and A. Streitwieser, Jr., *Chem. Revs.*, **56**, 636 (1956).

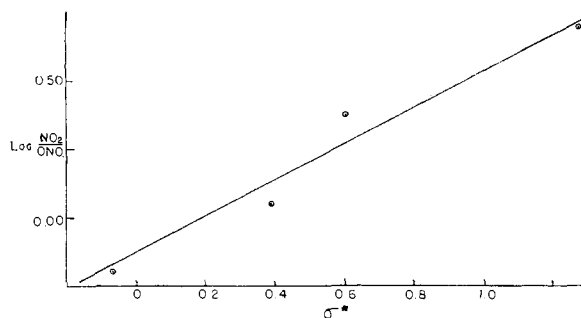Fig. 2.—The relationship between Grunwald's m-values and σ^*-values.

Fig. 3.—The effect of the polar nature of alkyl groups on the ratio of products formed from ambient groups.

mechanism tends to produce more attachment to the less electronegative atom.

The data given by Kornblum for the reaction of benzyl bromides with silver nitrite is shown in Table V. A plot of $\sigma_Q{}^*$ vs. the log of the ratio of products is shown in Fig. 3, and is seen to be nearly linear as predicted by eq. 23.

Equation 23 would also be expected to be applicable to aromatic substitution m-/p- ratios. From the data given by Brown,[19] however, the assumption regarding the similarity of transition states does not seem to be valid for these cases. For example, the ρ-value for deuterium exchange in DBr is larger than the ρ-value for nitration, opposite to that which would be expected from eq. 15 if the assumption of similar transition states is made. Other anomalous ρ-values are apparent in the data given by Brown.

TABLE V
AgNO$_2$ + Benzyl Bromide[a]

Subst.	$\sigma_R{}^+$	$\sigma_{R-\phi}{}^*$	NO$_2$/ONO	log (NO$_2$/ONO)
p-NO$_2$	0.778	1.27	5.25	0.72
H	0	0.600	2.33	.37
p-CH$_3$	−0.24	.39	1.08	.04
p-OCH$_3$	−0.778	− .07	0.64	− .19

[a] N. Kornblum, R. A. Smiley, R. K. Blackwood and D. C. Iffland, *J. Am. Chem. Soc.*, **77**, 6269 (1955).

(18) N. Kornblum, R. A. Smiley, R. K. Blackwood and D. C. Iffland, *J. Am. Chem. Soc.*, **77**, 6269 (1955).

(19) H. C. Brown and T. M. Stock, *ibid.*, **81**, 3323 (1959).