[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS, THE PENNSYLVANIA STATE COLLEGE]

Linear Steric Energy Relationships

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Rates for a limited number of reaction series in which the polar effects of substituents are quite small have been found to follow with fair precision eq. 1 $\log k/k_0 = \delta E_s$, where E_s is a steric substituent constant obtained from rates of ester hydrolysis and esterification, and δ is a reaction constant giving the susceptibility of a reaction series to steric effects. Relative heats of reaction or activation for two reaction series fit relationship (2), $\Delta H - \Delta H_0$ (or $\Delta\Delta H^{\ddagger}$) $= \delta E_s$. The importance of determining the limits of structure variation permitted by eq. 1 is emphasized.

In an earlier paper, steric substituent constants, E_s, were reported.[1] These parameters measure the total relative steric effects of various substituents, R, in the rate of hydrolysis (or esterification) of aliphatic esters (RCOOR′), or of ortho substituents, X, in benzoates for rates of similar reactions. The logarithms of the relative rates (k/k_0) of the acid-catalyzed hydrolysis of ortho substituted benzamides in water at 100° were shown to quantitatively parallel corresponding E_s values. Since this reaction series is one for which polar effects of substituents are quite small in even the most favorable case,[2] $\log k/k_0$ measures nearly quantitatively the total steric effect of a given substituent relative to the standard of comparison (the CH_3 group).

The relationship followed by the rates of hydrolysis of ortho substituted benzamides may be called a linear steric energy relationship, and can be represented by the equation

$$\log k/k_0 = \delta E_s \qquad (1)$$

where δ is a proportionality constant, dependent only upon the nature of the reaction series and independent of the substituent groups. The value of δ gives a measure of the relative susceptibility of the reaction series to steric effects of substituents. E_s and k/k_0 are as defined above.

In effect it was established in the earlier report that eq. 1 is not completely general. It fails, for example, for the acid-catalyzed hydrolysis of a series of thiolacetates, CH_3COSR, in aqueous acetone at 30°.[1] The conclusion was reached from these hydrolysis data that reaction rates would be expected to follow eq. 1 only when the geometries of the reactant and transition states are closely similar to those for ester hydrolysis or esterification.[1]

In the present paper, rate data from the literature which have been found to fit eq. 1 with reasonable precision are summarized. In each case the polar effects of substituent groups are negligible or nearly so. This decision is based upon the fact that the Hammett ρ-values for corresponding reactions of the *m*- and *p*-substituted analogs are very small (< 0.4). Listed in Table I are descriptions of the reactions following eq. 1, the corresponding steric susceptibility constant, δ, and its probable error (obtained by methods of least squares), the probable error of the fit of a single observation, *r*, and a list of the substituents which fit the correlation. The median probable error of Table I is 0.10 in the logarithm, or 13% in the value of the relative rate constant. The correlations cover maximum variation in rates of two thousand. The fit of data to eq. 1 apparently is not as precise as for correlations determined by polarity of substituents in aliphatic reactions.[3] However, the existence of only approximate linear steric energy relationships may prove of value not only in developing a further understanding of structural factors determining reactivity, but in useful applications to mechanism work.

A relationship which is truly a linear steric energy relationship might be expected to be satisfied not only by relative free energies but by other parameters such as relative heats or entropies, which also are functions only of the steric effect of substituent groups. Heats of reaction or activation for two reaction series have been found to fit approximately the relationship.

$$\Delta\Delta H \text{ (or } \Delta\Delta H^{\ddagger}) = \delta E_s \qquad (2)$$

The reactions following eq. 2 are listed in Table II with notations similar to those used in Table I. The median probable error of Table II is 0.3 kcal./mole for correlations covering a maximum variation in relative heats of 8.5 kcal./mole.

Discussion

The first four reaction series of Table I very likely proceed by analogous mechanisms involving reactant and transition states in which all of the atoms adjoining the carbonyl carbon are of closely the same diameters. By the previous generalization, the correlation of these rates by eq. 1 is not unexpected. There is, however, no theoretical basis for eq. 1, and it is not readily apparent that steric effects of substituents even within the range of structure variations in these four reactions should be so simply related.

Reaction series 5 of Table I is one for which there is little apparent resemblance to esterifications, ester or amide hydrolysis. Yet the precision of the fit of the data to eq. 1 is close to the median probable error of Table I. This reaction series as well as all those of Table II provide examples of permissible structure variation much beyond that suggested previously. The close relationship of these latter reactions to one another has been pointed out.[7]

The most important conclusion to be drawn from the present results is that it is now of the utmost importance to establish the limits of structure variation permitted by eq. 1 and 2. The objective is to provide a basis for predicting the types of reactions and substituents which may be expected

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[1] R. W. Taft, Jr., THIS JOURNAL, **74**, 3126 (1952).

[2] Reference 1, footnote 31.

[3] R. W. Taft, Jr., *ibid.*, **75**, 4231 (1953).

TABLE I

STERIC REACTION CONSTANTS, δ, FROM EQ. 1

	Reaction	δ	r	Subst.
1.	Acid-catalyzed hydrolysis of *o*-substituted benzamides in water at 100°[4]	+0.812 ± 0.032[a]	0.05	OCH_3, OC_2H_5, Cl, CH_3, Br, I, NO_2
2.	Acid-catalyzed methanolysis of β-naphthyl esters, $RCOO\beta{-}C_{10}H_7$, in methanol at 25°[5]	+1.376 ± .057[b]	.07	Me, Et, *n*-Pr, *i*-Pr, *n*-Bu, *t*-Bu
3.	Acid-catalyzed *n*-propanolysis of β-naphthyl esters, $RCOO\beta{-}C_{10}H_7$, in *n*-propylalcohol at 25°[5]	+1.704 ± .093[b]	.11	Me, *n*-Pr, *i*-Pr, *n*-Bu, *t*-Bu
4.	Acid-catalyzed *i*-propanolysis of β-naphthyl esters, $RCOO\beta{-}C_{10}H_7$, in *i*-propyl alcohol at 25°[5]	+1.882 ± .106[b]	.13	Me, Et, *n*-Pr, *i*-Pr, *n*-Bu, *t*-Bu
5.	Reaction of methyl iodide with 2-monoalkyl pyridines in nitrobenzene at 30°[6]	+2.065 ± .096[b]	.12	Me, Et, *i*-Pr, *t*-Bu

TABLE II

STERIC REACTION CONSTANTS, δ, FROM EQ. 2

	Reaction	δ	r	Subst.
1.	Activation energy for reaction of methyl iodide with 2-monoalkylpyridines in nitrobenzene[6]	+2.235 ± 0.089[b]	0.11	Me, Et, *i*-Br, *t*-Bu
2.	Heat of reaction of 2-monoalkyl pyridines with boron trifluoride in nitrobenzene[7]	+5.49 ± .36[b]	.45	Me, Et, *i*-Pr, *t*-Bu

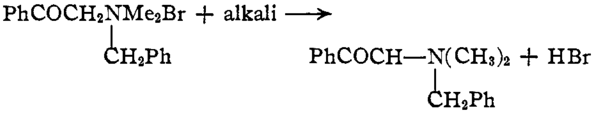
[a] E_s values used are those for *o*-substituted benzoates (ref. 1). [b] E_s values used are for the substituent R in the acyl component of the ester, RCOOR′ (ref. 1).

to follow these relationships. Although the possibility of predicting many new reaction rates or heats from δ-values of Tables I and II and the E_s-values given previously for various groups is implied, there can be no guarantee of their validity until this objective has been accomplished.

Both eq. 1 and 2 may be expected to fail for any reaction series in which the polar effects of substituents are appreciable because polar and steric factors are completely different functions of structure.[3]

The E_s-values are composite terms, consisting of contributions from both potential energy steric effects (steric strains) and kinetic energy steric effects (steric hindrances to motions).[8] It seems likely, therefore, that eq. 1 and 2 may be less fundamental than, for example, linear relationships between strain energies alone. Such relations have been previously reported.[7,8] Equation 1 will, of course, be followed by a reaction series for which the above two steric effects parallel one-another, if one alone has values paralleling E_s-values. Such a condition implies also a parallel of these two effects in determining E_s-values. Although just this relationship is apparently required by both $\log k/k_0$ and $\Delta\Delta H^{\ne}$ paralleling E_s for reaction series 5 of Table I and 1 of Table II, the results obtained in the previous paper indicate there are few substituents involved in ester hydrolysis or esterification that satisfy this condition.[8] The possibility of a number of only apparent correlations by eq. 1 is therefore evident.

All of the δ-values of both Tables I and II are positive, indicating that in each case the steric requirements of substituents are greater in the transition or final than the initial state. *A priori* there is no reason why this situation might not be reversed, giving rise to a negative value of δ. At least qualitatively, rates of the Stevens rearrangement represent such a case.[9] The reaction is



$$\underset{\displaystyle CH_2Ph}{PhCOCH_2\overset{}{N}Me_2Br} + \text{alkali} \longrightarrow PhCOCH{-}\underset{\displaystyle CH_2Ph}{N}(CH_3)_2 + HBr$$

Relative rates for *o*-substituents in the benzyl radical increase markedly in the order $OCH_3 < CH_3$, Cl, Br < I < NO_2, the last member of the series being about 500 times faster than the first. In the *m*- and *p*-positions these substituents lead to only small changes in rate (up to 4×).[10] The above order of substituents corresponds definitely to that of increasing steric requirements (see E_s-values of ref. 1) and not that of increasing electron withdrawal (for which the order is $OCH_3 < CH_3 <$ Cl, Br, I < NO_2).[1,3] This reaction, therefore, is one in which substituents of increasing size cause rates to be facilitated as a result of the greater steric requirements of the substituents in the reactant than the transition state.[11]

Equation 1 very definitely shows that the proportionality of corresponding $\log k/k_0$ values between two reaction series is not a sufficient condition for demonstrating the existence of solely polar effects of substituent groups.

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(4) E. E. Reid, *Am. Chem. J.*, **24**, 397 (1900).

(5) M. Harfenist and R. Baltzly, THIS JOURNAL, **69**, 362 (1947).

(6) H. C. Brown and A. Cahn, abstract of papers presented at Boston, Mass., Division of Organic Chemistry, American Chemical Society Meeting, April 2, 1951.

(7) H. C. Brown and R. M. Horowitz, abstract of papers, A.C.S. Meeting, Boston, Mass., April, 1951.

(8) R. W. Taft, Jr., THIS JOURNAL, **75**, 4534 (1953).

(9) T. Thomson and T. S. Stevens, *J. Chem. Soc.*, 55 (1932); the author is indebted to Professor D. Y. Curtin for this reference.

(10) The *p*-nitro substituent is an exception, there being an increase in rate by a factor of 70. The data for substituents *m*-NO_2 and *m*- and *p*-OMe, CH_3, Cl, Br, and I all fit a rough Hammett plot with $\rho \sim +0.8$. The *p*-NO_2 data do not fit this relationship. Whether this is the result of a side reaction or an error in reporting the value of the rate constant cannot be judged from the published data.

(11) This conclusion is shown to be reasonable on the basis of atom models using the mechanism pictured for this reaction (see J. H. Brewster and M. W. Kline, THIS JOURNAL, **74**, 5179 (1952), and C. R. Hauser and S. W. Kantor, *ibid.*, **73**, 1437 (1951)).