10 ml. of water, 200 ml. of ethanol and 200 ml. of dioxane. Titration with acid and Karl Fischer reagent showed it to be 0.73 *M* in potassium hydroxide and 1.90 *M* in water. The procedures employing these two reagents were identical.

To 1.4 g. (0.004 mole) of triphenylbenzylsilane in a 50-ml. glass-stoppered volumetric flask was added 20 ml. of reagent D. The flask was placed, with occasional shaking, in a constant temperature bath at 60 ± 0.5° for 1 hour. The reaction mixture was then poured into excess cold dilute hydrochloric acid (1:50), and the solid filtered off. It was washed with 35 ml. of 90% aqueous methanol to leave 1.06 g. (76%) of starting material, m.p. 96–97°. No hexaphenyldisiloxane was formed in the cleavages employing reagent D, and it was found that triphenylsilanol is soluble to the extent of 2.5 g. per 100 ml. of 90% aqueous methanol, whereas the silanes themselves were practically insoluble in this solvent. This procedure was therefore used to determine the amount of starting material uncleaved by reagents C and D, and hence the extent of the cleavage.

Cleavage of (Trichloromethyl)-triphenylsilane.[21] **A. With *n*-Butyllithium.**—To a suspension of 10 g. (0.0264 mole) of (trichloromethyl)-triphenylsilane in 100 ml. of ether at 25° was added 0.08 mole of *n*-butyllithium in 90 ml. of ether. A vigorous reaction ensued, during which the reaction mixture became reddish-brown. The mixture was refluxed overnight under nitrogen at which time Color Test I[22] was still positive. The reaction mixture was hydrolyzed with dilute sulfuric acid, the ether layer removed and dried, and the ether distilled. The residue was a viscous oil which was distilled to give 13.5 g. of straw-colored distillate boiling in the range 195–200° (0.25 mm.) and 1.3 g. of amber liquid boiling at 235–240° (0.2 mm.). The former fraction partially solidified to yield crystals melting over the range 68–76°, which after recrystallization from petroleum ether (b.p. 60–70°) gave 1.3 g. (15.5%) of solid melting at 86°. A mixed melting point of this solid with an authentic sample of *n*-butyltriphenylsilane[23] showed no depression.

B. With Phenyllithium.—A solution of 0.05 mole of phenyllithium in 80 ml. of ether was added slowly, with stirring, at 0°, to a suspension of 6.2 g. (0.0164 mole) of (trichloromethyl)-triphenylsilane in 100 ml. of ether. After standing overnight under nitrogen, the resulting solution gave a negative color Test I. The solution was hydrolyzed with water, and the ether layer separated and distilled on a water-bath. The residue was heated at 100° and 20 mm. pressure, and was then extracted with petroleum ether (b.p. 79–122°). The 0.3 g. (5.4%) of residue from this extraction melted at 232–234°, and its mixed melting point with tetraphenylsilane showed no depression. The petroleum ether extract was a brown viscous material from which no definite product was isolated.

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[21] H. Gilman and L. S. Miller, This Journal, **73**, 968 (1951).

[22] H. Gilman and F. Schulze, *ibid.*, **47**, 2002 (1925).

[23] H. Gilman and H. W. Melvin, *ibid.*, **71**, 4050 (1949).

AMES, IOWA

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

The Separation of Relative Free Energies of Activation to Three Basic Contributing Factors and the Relationship of These to Structure

BY ROBERT W. TAFT, JR.

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Relative rates for many reactions may be attributed to three basic factors: (1) electrical effects; (2) steric strain effects; and (3) entropy or "steric hindrances to motions" effects. Experimental data are utilized to make this separation for relative rates of hydrolysis (or esterification) of aliphatic esters, RCOOR′, in which structure is varied in the acyl component, R. The effect of structure on factors (2) and (3) is discussed. A working hypothesis called the Strain–Entropy principle is proposed. The steric strains for the formation of the ester transition states are found to be one-fourth that of the strain energies for the formation of the corresponding homomorphic amine–trimethylboron addition compounds. This important linear strain energy relationship has been realized only because of the indicated separation of relative free energies of activation.

The effect of structure on reactivity is properly discussed in terms of the relative free energies, heats and entropies of activation which are thermodynamic functions of the hypothetical equilibrium.[1]

$$\mathrm{A} + \mathrm{A}_0^{\ddagger} \rightleftarrows \mathrm{A}^{\ddagger} + \mathrm{A}_0$$

A is a general reactant of a reaction series and A_0 is the reactant selected as the standard of comparison. The starred terms refer to corresponding reaction transition states. According to basic relations of statistical thermodynamics, the following equations apply[2]

$$\Delta\Delta F^{\ddagger} = -RT\ln k/k_0 = \Delta\Delta E_{\mathrm{p}}^{\ddagger} - RT\ln \Pi Q \quad (1)$$

where $\Delta\Delta F^{\ddagger}$ = relative free energy of activation; the free energy change accompanying the above reaction; k/k_0 = relative rate constant; $\Delta\Delta E_{\mathrm{p}}^{\ddagger}$ = relative potential energy of activation, the energy change that would accompany the above reaction if both reactant and transition states were completely deprived of all their energies of motion. $\Pi Q = q_{\mathrm{A}^{\ddagger}}q_{\mathrm{A}_0}/q_{\mathrm{A}_0^{\ddagger}}q_{\mathrm{A}}$, where q's are partition functions involving kinetic energies of motion. These include motions of solvent molecules involved in solvation as well as all motions at absolute zero.

$$\Delta\Delta H^{\ddagger} = \Delta\Delta E_{\mathrm{p}}^{\ddagger} + RT^2\,(\mathrm{d}\,(\ln \Pi Q)/\mathrm{d}T) \quad (2)$$

where $\Delta\Delta H^{\ddagger}$ = relative heat of activation, the enthalpy change accompanying the above reaction.

$$\Delta\Delta S^{\ddagger} = R\ln \Pi Q + RT(\mathrm{d}\ln \Pi Q)/\mathrm{d}T \quad (3)$$

where $\Delta\Delta S^{\ddagger}$ = relative entropy of activation, the entropy change accompanying the above reaction.

It has been previously suggested that in many reactions the relative potential energy of activation, $\Delta\Delta E_{\mathrm{p}}^{\ddagger}$, is a composite of two terms, namely[3]

$$\Delta\Delta E_{\mathrm{p}}^{\ddagger} = \Delta\Delta E_{\mathrm{e}}^{\ddagger} + \Delta\Delta E_{\mathrm{R}}^{\ddagger} \quad (4)$$

where $\Delta\Delta E_{\mathrm{e}}^{\ddagger}$ = relative potential energy of activation resulting from electronic energy differences, *i.e.*, a term due to inductive, polarization and resonance effects. Solvent effects which arise from these effects are included. $\Delta\Delta E_{\mathrm{R}}^{\ddagger}$ = relative potential energy of activation resulting from

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[1] F. P. Price, Jr., and L. P. Hammett, This Journal, **63**, 2387 (1941).

[2] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 193.

[3] This is a modified expression of the type given by G. E. K. Branch and M. Calvin, "The Theory of Organic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1941, p. 193.

changes in repulsions between non-bonded atoms (including solvent), *i.e.*, a steric strain term. By combining eq. 1 and 4 we obtain

$$\Delta\Delta F^{\ddagger} = \Delta\Delta E_{e}^{\ddagger} + \Delta\Delta E_{R}^{\ddagger} - RT \ln \Pi Q \qquad (5)$$

In effect, eq. 5 attributes the effect of structure on reactivity (relative rates) to three basic factors: (1) electrical effects; (2) steric strain effects; and (3) effects which we may properly call "steric hindrances to motions."

The present subject is concerned with demonstrating that the separation of reactivity to these three basic factors as proposed in eq. 5, at least in the following most favorable cases, can be realized from experimental quantities. It is also shown that this is a highly profitable separation from the standpoint of its contribution to a more complete understanding of the nature of structural factors affecting chemical reactivity.

The rates to be considered are for the hydrolysis of aliphatic esters, RCOOR′, or the esterification of corresponding carboxylic acids, in which structure is varied in the acyl component, R. By appropriate comparisons of rates of corresponding basic and acid-catalyzed reactions, it was shown in an earlier paper that the separation of terms according to the following equation may be made for these reactions[4a]

$$\Delta\Delta F^{\ddagger} = \Delta\Delta E_{e}^{\ddagger} + \Delta\Delta E_{S}^{\ddagger} \qquad (6)$$

where $\Delta\Delta E_{S}^{\ddagger}$ is the term which may be called the relative total steric energy of activation. By eq. 5 $\Delta\Delta E_{s}^{\ddagger}$ equals $\Delta\Delta E_{R}^{\ddagger} - RT \ln \Pi Q$, and is therefore the sum of the potential energy and the kinetic energy steric effects. The separation of $\Delta\Delta F^{\ddagger}$ according to eq. 6 which has been achieved for these reactions is an essential feature of the further separation according to eq. 5. If the present treatment is to be extended to other reaction series for which both $\Delta\Delta E_{e}^{\ddagger}$ and $\Delta\Delta E_{s}^{\ddagger}$ terms are generally appreciable, the separation according to eq. 6 must first be accomplished.

Values of $\Delta\Delta E_{e}^{\ddagger}$ and $\Delta\Delta E_{s}^{\ddagger}$ for various aliphatic groups, R, in the ester reactions may be calculated from the polar and steric substituent constants, σ^* and E_S, respectively, previously reported by the defining equations[4a,b]

$$\Delta\Delta E_{e}^{\ddagger} = -2.303\ RT(\sigma^*\rho^*)$$

and

$$\Delta\Delta E_{s}^{\ddagger} = -2.303\ RT(E_{s})$$

In acid-catalyzed reactions, the reaction constant, ρ^*, is very small so that $\Delta\Delta E_{e}^{\ddagger}$ is nearly negligible in these reactions.[4a] In the alkaline reactions, however, the term may be quite appreciable.[4a]

The problem of separating the relative free energies of activation of the ester reactions into the three components of eq. 5 is simplified by two important factors. First, relative rates (and therefore $\Delta\Delta F^{\ddagger}$) are very nearly independent of wide variations in the nature of the solvent.[5] Thus the contribution of solvent to the $-RT \ln \Pi Q$ terms must be essentially negligible. The $-RT \ln \Pi Q$ and $\Delta\Delta E_{R}^{\ddagger}$ terms arise because of increased interference with the internal motions of the R group and the adjacent functional center, and increased repulsions between the non-bonded atoms of the two, respectively.[4a] That these terms should be very appreciable is reasonable because of the increase in the coördination number of the carbonyl carbon from three to four, and the decrease in bond angles about this carbon from approximately 120 to 109° in the activation process.[4a]

The second simplifying factor results from the fact that plots of log *k* *vs.* $1/T$ are linear within experimental uncertainty over appreciable temperature intervals (30–40°).[6] Thus to a good first approximation the terms $d \ln \Pi Q/dT$ are negligible and eq. 2 and 3 reduce to

$$\Delta\Delta H^{\ddagger} = \Delta\Delta E_{P}^{\ddagger} = \Delta\Delta E_{e}^{\ddagger} + \Delta\Delta E_{R}^{\ddagger} \qquad (2')$$

$$\Delta\Delta S^{\ddagger} = R \ln \Pi Q \qquad (3')$$

The determination of heats and entropies of activation therefore permits a separation of $\Delta\Delta F^{\ddagger}$ to $\Delta\Delta E_{P}^{\ddagger}$ and $RT \ln \Pi Q$ terms. This is not the same separation as made by eq. 6. The difference in the separation of terms contributing to $\Delta\Delta F^{\ddagger}$ by the two methods is by no means unfortunate, for the combined methods lead to a determination of each of the three basic effects which determine relative rates (eq. 5). The evaluation of the steric strain term, $\Delta\Delta E_{R}^{\ddagger}$, may be made by the relationship

$$\Delta\Delta E_{R}^{\ddagger} = \Delta\Delta H^{\ddagger} - \Delta\Delta E_{e}^{\ddagger} = \Delta\Delta H^{\ddagger} + 2.303\ RT\ (\sigma^*\rho^*) \qquad (7)$$

Making use of the reliable temperature coefficient of rate data from the literature, the steric strains, $\Delta\Delta E_{R}^{\ddagger}$, associated with various aliphatic derivative groups, R, have been calculated and are listed in Table I. The corresponding total steric energies of activation, $\Delta\Delta E_{s}^{\ddagger}$, and steric hindrances of internal motions, $-RT \ln \Pi Q$, at 30° are also listed. The values of $\Delta\Delta E_{R}^{\ddagger}$ and $-RT \ln \Pi Q$ given in Table I are, wherever possible, averages obtained from $\Delta\Delta H^{\ddagger}$ and $\Delta\Delta S^{\ddagger}$ values for both acid- and base-catalyzed reactions. Deviations from the average in no case exceed 0.3 kcal. $\Delta\Delta E_{R}^{\ddagger}$ was taken as zero if a value between ±0.2 was obtained. The total steric energies of activation, $\Delta\Delta E_{s}^{\ddagger}$, were obtained by the relationship $\Delta\Delta E_{s}^{\ddagger} = -2.303\ RT \log E_{S}$, from the steric substituent constants, E_S, reported earlier.[4a] Because of the methods employed, the sums of the $\Delta\Delta E_{R}^{\ddagger}$ and $-RT \ln \Pi Q$ terms do not in every case total exactly to $\Delta\Delta E_{s}^{\ddagger}$. The sources of data used are the following: (1) the acid-catalyzed esterification of carboxylic acids with methanol[6-8]; (2) the acid-catalyzed hydrolysis of ethyl esters in 70% (vol.) aq. acetone[9]; (3) the base-catalyzed hydrolysis of ethyl esters in 85%

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[4] (a) R. W. Taft, Jr., THIS JOURNAL, **74**, 3120 (1952); (b) **75**, 4231 (1953).

[5] R. W. Taft, Jr., *ibid.*, **74**, 2729 (1952).

[6] See for example, H. A. Smith, *ibid.*, **61**, 254 (1939). Also refs. 7–11.

[7] H. A. Smith and J. Burn, THIS JOURNAL, **66**, 1494 (1944).

[8] K. Loening, A. B. Garrett and M. S. Newman, *ibid.*, **74**, 3929, (1952).

[9] H. A. Smith and R. R. Myers, *ibid.*, **64**, 2362 (1942).

(vol.) aq. ethanol[10]; and (4) the base-catalyzed hydrolysis of benzyl esters in 60% (vol.) aq. acetone.[11]

TABLE I

CONTRIBUTIONS OF STERIC STRAIN AND STERIC HINDRANCE OF MOTIONS TO THE TOTAL STERIC EFFECT OF ALIPHATIC GROUPS, R, IN RATES OF ESTERIFICATION AND ESTER HYDROLYSIS (RCOOR′) AT 30°

Subst. R	Total steric energy of activation $\Delta\Delta E_s^{\ddagger}$ at 30°, kcal./mole	Steric strain $\Delta\Delta E_R^{\ddagger}$, kcal./mole	Steric hindrance of motions $-RT \ln \Pi Q$ at 30°, kcal./mole
H–	(0.0)	(0.0)	(0.0)
CH_3–	+1.7	.0	+1.6
C_2H_5	+1.8	.0	+1.8
n-C_3H_7, n-C_4H_9, n-C_5H_{11}–	+2.2	.0	+2.1
$C_6H_5CH_2$–	+2.2	.0	+2.2
$C_6H_5CH_2CH_2$–	+2.3	.0	+2.2
i-C_3H_7–	+2.4	.0	+2.5
i-C_4H_9–	+3.0	.0	+2.8
Cyclo-$C_6H_{11}CH_2$–	+3.0	+ .7	+2.4
s-C_4H_9–	+3.1	+ .5	+2.6
s-$C_4H_9CH_2$–	+3.1	+ .4	+2.7
t-C_4H_9–	+3.8	+1.4	+2.2
Neo-C_5H_{11}–	+4.1	+1.8	+2.3
$(C_6H_5)(C_2H_5)CH$–	+3.8	+1.2	+2.6
$(C_6H_5)_2CH$–	+4.2	+1.8	+2.3
$(C_2H_5)_2CH$–	+4.4	+2.0	+2.4
$(i$-$C_4H_9)_2CH$–	+5.1	+2.6	+2.4
(Neo-C_5H_{11})$(CH_3)_2C$–	+5.3	+2.7	+2.5
(Neo-$C_5H_{11})_2CH$–	+6.0	+3.5	+2.4
$(t$-$C_4H_9)(CH_3)CH$–	+6.2	+3.6	+2.5
$(C_2H_5)_3C$–	+6.8	$+4.3^a$	$+2.5^a$
$(t$-$C_4H_9)(CH_3)_2C$–	+6.9	$+4.4^a$	$+2.5^a$
$(t$-$C_4H_9)$(neo-C_5H_{11})$(CH_3)C$–	+7.1	$+4.6^a$	$+2.5^a$

[a] Steric strains have been estimated from the total steric energy of activation, $\Delta\Delta E_s^{\ddagger}$ using the apparent limiting value of $-RT \ln \Pi Q$ of approximately 2.5 kcal./mole.

There are insufficient data available at the present time to permit the same type of analysis to be carried out for structure variation in R′ of RCOOR′.

There are a number of important conclusions to be drawn from the results given in Table I. First, introduction of a straight chain alkyl group in place of the standard hydrogen substituent results in an increase in activation energy due to steric hindrance of motions. With the lower members of the homologous series, this hindrance increases with the number of carbon atoms introduced. This is a result in accord with the principle of Price and Hammett.[1] The more entropy that is introduced into the system *via* the substituent group, R, the more is frozen out in the transition state. It is to be noted, however, that the entropy which is frozen out is that introduced close to the reaction center. The introduction of alkyl groups beyond the γ-position leads to no further increase in the $-RT \ln \Pi Q$ term.

Secondly, the introduction of any aliphatic derivative in place of hydrogen leads to steric hindrance of motions, but not necessarily to steric strain. The former factor is the only steric factor involved in a number of cases and is accordingly more sensitive to such a structural change than the latter. It is further important to notice that for the highly branched groups the steric hindrance of motions term appears to reach a limiting value of about 2.5 kcal. Thus the introduction of alkyl groups into a sufficiently branched aliphatic derivative leads to no further freezing out of entropy in the transition state. This result implies that such groups have considerably restricted motions in the reactant state.

Thirdly, steric strain becomes increasingly greater with branched chain substituents the larger the number and the greater the steric requirements of the branched groups. In a number of cases the steric strain term makes the much larger contribution to the total steric effect. There is, however, no substituent which leads to steric strain for which the steric hindrance of motions is negligible. This important result may be given by the more general statement: "If a group such as H or CH_3 be replaced by a group with many more internal degrees of freedom and, if the activation process is such that these groups are compressed into positions resulting in greater repulsions between the function center and latter substituent than the former, then the activation process will also be accompanied by a greater loss of internal motions." This statement will be referred to as the Strain–Entropy (SE) principle and it is proposed as a working hypothesis to account for the parallel retarding effects frequently observed in relative heats and entropies of activation resulting from structure variation. This principle obviously is not intended to apply to those reactions in which bulky groups lead to a freezing out of solvent, but rather to those like the present where solvent is not involved in determining $\Delta\Delta E_R^{\ddagger}$ and $-RT \ln \Pi Q$ terms.

In view of the large number and variety of groups for which the SE principle holds without exception, there is the strong implication that the absence of a steric hindrance of motions term for the type of substitution specified in the SE principle requires the absence of a steric strain term, $\Delta\Delta E_R^{\ddagger}$. That is, the existence of the appropriate steric hindrance of internal motions is a necessary but not a sufficient condition for the existence of a steric strain, and thus the former may serve as a device for testing for the absence of the latter.

Applications of the Strain–Entropy Principle.—Consider the case of a benzoate compared to the standard formate (R is C_6H_5 and H, respectively). The $-RT \ln \Pi Q$ term for the phenyl group is +0.3, which within experimental uncertainty is zero. By the SE principle this requires that $\Delta\Delta E_R^{\ddagger}$ for the phenyl group also be near zero. Yet the $(\Delta\Delta H^{\ddagger} + 2.303\ RT\sigma^*\rho^*)$ term for phenyl is +4.6 kcal./mole.[12] However, the resonance between the benzene ring and the carbonyl group which stabilizes the benzoate but not its transition state

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(10) H. S. Levenson and H. A. Smith, *ibid.*, **62**, 2324 (1940).

(11) E. Tommila, *Ann. Acad. Sci. Fennicae*, Ser. A 59, No. 4, 3 (1942); *C. A.*, **42**, 4031 (1948).

(12) Obtained from σ^*-value of ref. 4b and av. $\Delta\Delta H^{\ddagger}$ value of ref. 11 and H. A. Smith and R. B. Hurley, THIS JOURNAL, **72**, 112 (1950).

must be considered.[4a,13] If the strain entropy principle has lead to a proper conclusion, the 4.6 kcal./mole term must be a measure of this resonance energy. This value is indeed in excellent agreement with other estimates.[14]

A second interesting application of the SE principle is for nucleophilic displacements by 2-monoalkyl pyridines on methyl iodide in nitrobenzene at 30°.[15] The appropriate data are summarized below:

R	log k/k_0	$\Delta\Delta H^{\ddagger}$, kcal.	$\Delta\Delta S^{\ddagger}$, e.u.
H	0.00	0.0	0.0
CH_3	− .33	+ .1	−1.2
C_2H_5	− .65	+ .3	−1.9
i-C_3H_7	−1.14	+ .9	−2.1
t-C_4H_9	−3.58	+3.6	−4.6

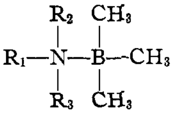
The decrease of $\Delta\Delta S^{\ddagger}$ in the series Me, Et, *i*-Pr, *t*-Bu is consistent with the possibility that reactivity is determined to an appreciable degree by steric strains. The close correlation of log k/k_0 values with E_s, the ester steric substituent constants,[16] supports the conclusion of Brown and Cahn that steric factors, not polarity, are the important ones determining rate for this reaction series.[15]

Comparison of Steric Strains in the Formation of Ester Transition States and Homomorphic Amine–Borontrimethyl Addition Compounds.—The vertical deviations in a plot of heats of dissociation of amine–trimethylboron addition compounds *vs.* corresponding polar substituent constants, σ^*, have been used to evaluate the increase in steric strains in the addition compounds.[4b] A comparison of these steric strains with those reported in Table I is given in Table II. A most important result is apparent. To a good precision the strains for the formation of the ester transition states are one-fourth that for the corresponding homomorphic amine addition compounds. The strains for the latter are listed in the first column of Table II as $\Delta\Delta E_R$, and the $\Delta\Delta E_R^{\ddagger}$-values for the former are listed in the second column. The third column of Table II lists values of $\Delta\Delta E_R/4.0$. The differences between corresponding values of the second and third columns of Table II in no case exceed the combined uncertainties of the data upon which these values are based, not to mention the approximations made by present methods.

TABLE II

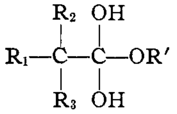
COMPARISON OF STERIC STRAINS IN THE FORMATION OF ESTER TRANSITION STATES WITH CORRESPONDING QUANTITIES FOR HOMOMORPHIC AMINE–BORONTRIMETHYL ADDITION COMPOUNDS

Amine, $R_1R_2R_3N$	Addn. cpd. steric strain, $\Delta\Delta E_R$, kcal./mole	Aliphatic groups $R_1R_2R_3C$	Transition state steric strain, kcal./mole $\Delta\Delta E_R^{\ddagger}$ (obsd.)	$\Delta\Delta E_R^{\ddagger}$ (calcd.)	*d*
NH_3	0.0	CH_3	0.0	0.0	0.0
CH_3NH_2	.0	CH_3CH_2	.0	.0	.0
$C_2H_5NH_2$	.0	$C_2H_5CH_2$	.0	.0	.0
n-$C_3H_7NH_2$	.0	*n*-$C_3H_7CH_2$	.0	.0	.0
n-$C_4H_9NH_2$	.0	*n*-$C_4H_9CH_2$	.0	.0	.0
i-$C_3H_7NH_2$	1.5	*i*-$C_3H_7CH_2$	.0	.4	.4
s-$C_4H_9NH_2$	1.6	*s*-$C_4H_9CH_2$	.4	.4	.0
t-$C_4H_9NH_2$	6.7	*t*-$C_4H_9CH_2$	1.8	1.7	.1
$(CH_3)_2NH$	1.7	$(CH_3)_2CH$	0.0	0.4	.4
$(CH_3)_3N$	6.9	$(CH_3)_3C-$	1.4	1.7	.3
n-$C_4H_9(CH_3)_2N$	10.2	Neo-$C_5H_{11}(CH_3)_2C-$	2.7	2.5	.2
$(C_2H_5)_2NH$	6.1	$(C_2H_5)_2CH$	2.0	1.5	.5
$(C_2H_5)_3N$	(17)	$(C_2H_5)_3C$	4.3	(4.2)	.1
				Av.	0.2



$$\begin{array}{ccccc} & R_2 & & CH_3 & \\ & | & & | & \\ R_1- & N & - & B & -CH_3 \\ & | & & | & \\ & R_3 & & CH_3 & \end{array}$$

Addition compound



$$\begin{array}{ccccc} & R_2 & & OH & \\ & | & & | & \\ R_1- & C & - & C & -OR' \\ & | & & | & \\ & R_3 & & OH & \end{array}$$

Ester transition state (minus or plus proton)

R′ is CH_3, C_2H_5 or $CH_2C_6H_5$

The direct proportionality between the two series of steric strains indicates that strain energies are not necessarily highly specific to the kind of atoms present, but are directly related when the geometries of two systems are closely the same. The structural formulas listed at the bottom of Table II illustrate how the transition state geometry is probably related to that of the addition compound. Although the substituents for which the correlation has been obtained are all aliphatic, they are of sufficient number and variety to firmly establish the validity of the correlation.

The value of separating reactivity according to eq. 5 is well demonstrated by the steric strain correlation. A fundamental relationship has been established which does not exist between corresponding free energy or total steric energy differences. It should also be remembered that the strain energy correlation establishes that structure affects analogous rate and equilibrium quantities in a parallel manner. Such correlations are well known for quantities determined by polar effects[17] but only recently have been indicated for strain energies.[18] It is worthy of note that the presence of solvent in the one reaction series has not prevented the determination of basic molecular parameters which are simply related to corresponding quantities determined for a second reaction series in the absence of solvent.

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(13) In the benzoate case $\Delta\Delta E_e^{\ddagger}$ is determined by both polar and resonance effects, *i.e.*, $\Delta\Delta E^{\ddagger} = \Delta\Delta E_{\sigma}^{\ddagger} + \Delta\Delta E_{\psi}^{\ddagger}$ where the former term is the polar and the latter is the resonance term. Strictly, therefore, it is not $\Delta\Delta E_e^{\ddagger}$ but $\Delta\Delta E_{\sigma}^{\ddagger}$ that equals $-2.303RT\ \sigma^*\rho^*$. However, in the case of the aliphatic derivatives, $\Delta\Delta E_{\psi}^{\ddagger}$ is negligible and $\Delta\Delta E_{\sigma}^{\ddagger}$ and $\Delta\Delta E_e^{\ddagger}$ become equal.

(14) (a) Reference 3, p. 285; (b) D. M. Coulson and W. R. Crowell, THIS JOURNAL, **74**, 1294 (1952).

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

(16) R. W. Taft, Jr., THIS JOURNAL, **75**, 4538 (1953).

(17) (a) L. P. Hammett, ref. 2, p. 186; (b) ref. 4b.

(18) H. C. Brown and R. M. Horowitz, abstract of papers presented at Boston, Mass., Division of Organic Chemistry, American Chemical Society Meeting, April 2, 1951.