allowed for any stabilizing hyperconjugation. A similar calculation by the D–S–P method yields 62 kcal./mole as the strain. Presumably these represent maximum values since alteration of bond length and angles would tend to reduce the strain but a large error would not be expected. Hence it appears that the three possible isomers are all of comparable stability if, of course, cyclobutadiene has a stable ground state.

The heat of formation at 0°K. of hypothetical tricycloöctane may be calculated to be 160 kcal./mole from Pitzer's bond energies and the strain energy of 130 kcal./mole. The heat of formation of cycloöctatetraene as obtained from heat of combustion data by Person, Pimentel and Pitzer[51] is 76.3 kcal./mole. The approximate nature of the calculated value for tricycloöctane can hardly account for this large a difference and it appears that the cubic structure is thermodynamically highly unstable with respect to cycloöctatetraene.

It does not appear that the rate of transition of tricyclobutane to the more stable isomers considered here would be rapid at room temperature. These isomerizations involve the breaking of carbon–carbon bonds and the difference in strain energy between the isomers does not appear large enough to lower the activation energy sufficiently for a rapid reaction to occur. Tricycloöctane is a more dubious case and may or may not be capable of synthesis.

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[51] W. B. Person, G. C. Pimentel and K. S. Pitzer, THIS JOURNAL, **74**, 3437 (1952).

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

The General Nature of the Proportionality of Polar Effects of Substituent Groups in Organic Chemistry

BY ROBERT W. TAFT, JR.

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Rates or equilibria for a number of reactions involving bulky groups adjacent to the reaction center have been found to fit an equation, (2) $\log k/k_0$ (or K/K_0) $= \sigma^*\rho^*$. The polar substituent constants, σ^*, are those determined previously from rates of acidic and basic esterification and hydrolysis of esters.[2b] The σ^*-values for aliphatic groups are shown to be additive. The correlations of eq. (2) serve to demonstrate the general nature of the proportionality of polar effects of substituents. If steric factors are variable in a reaction series, eq. (2) is not followed, but the polar contributions to the logarithms of rates or equilibria, P_σ, follow a similar equation, (3) $P_\sigma = \sigma^*\rho^*$. Physical properties, such as dipole moments, have been found in a number of cases to follow eq. (3). Applications of the basic principle of proportionality of polar effects in reaction rates and equilibria of this type are discussed and examples given.

Rates and equilibria for a great number of reactions of meta and para substituted benzene derivatives have been found to fit with reasonable precision the Hammett eq.[1a]

$$\log k/k_0 \text{ (or } K/K_0) = \sigma\rho \qquad (1)$$

where k refers to the rate of a reaction of a *m*- or *p*-substituted benzene derivative. K refers to the equilibrium constant for such a reaction.

The subscript zero refers to the corresponding unsubstituted derivative. σ is a substituent constant, measuring the polarity of a given substituent relative to hydrogen. The definition of σ is $\sigma \equiv \log K/K_0$ for the ionization of substituted benzoic acids in water at 25°. ρ is a proportionality constant. It is a measure of the susceptibility of a given reaction series to polar substituents.

Equation (1) demonstrates that the corresponding polar effects of substituents on free energy differences are proportional from one reaction series to another—a relationship which is independent of reaction mechanism, attacking reagent, solvent, temperature or nature of the functional groups involved in the initial or final states of the process. That is, although these variables determine the value of the reaction constant, ρ, the fit of the data to the eq. (1) is independent of these.

The same may not be said for reactions of ortho substituted benzene derivatives or the multitude of various reactions in the aliphatic series. Rates and equilibria do not generally follow eq. (1).[1] A typical illustration is given in Fig. 1. The relatively few cases where proportionality exists between the corresponding effects of substituents on free energies are definitely determined by the nature of the above-mentioned variables.[2a]

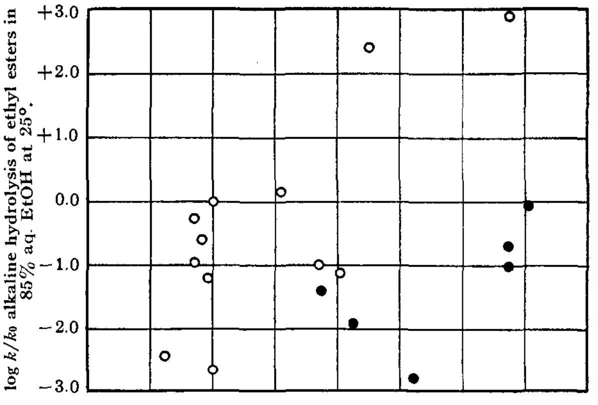


Fig. 1.—Failure of Eq. (1): ○, aliphatic carboxylic acid, RCOOH; ●, ortho substituted benzoic acids.

The failure of eq. (1) to apply to this important class of reactions must depend on one or both of the

[1] (a) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc, New York, N. Y., 1940, pp. 186–193; (b) p. 222.

[2] (a) R. W. Taft, Jr., THIS JOURNAL, **74**, 2729 (1952); (b) **74**, 3126 (1952).

following factors: (1) the polar effects of corresponding substituents are simply not proportional between one reaction series and another; (2) the effect of structure on free energy differences is determined by additional steric, resonance, or other effects which are completely different functions of structure than is polarity and whose function depends upon the nature of the reaction series (the variables given above). If the latter alone be the cause then the possibility of proportionality of polar effects in reactions of this type is by no means excluded. For the condition stipulated is that log k/k_0 (or K/K_0) is not generally a measure of substituent polarity and thus would not follow a relationship like eq. (1) even if the proportionality between the polar contributions to these parameters exists.

The Proportionality of Polar Effects for Reactions Having Bulky Groups Adjacent to the Reaction Center.—In an earlier paper a quantitative separation of the polar and steric contributions of substituents, R, to rates of esterification and hydrolysis of esters, RCOOR′, was made.[2b] The former was given as a polar substituent constant, E_σ, and the latter as a steric substituent constant, E_s.[3] The speculation was made that reaction series having essentially constant steric and resonance factors would quite generally have free energy charges (rate or equilibria) proportional to corresponding polar substituent constants. Confirmation of this hypothesis for reaction series involving bulky groups adjacent to the reaction center would clearly limit the failure of eq. (1) to apply to this type of reaction to the second cause given above.

Literature values of rates and equilibria for reactants R-Y in a wide variety of types of reactions have been found to fit with relatively good precision

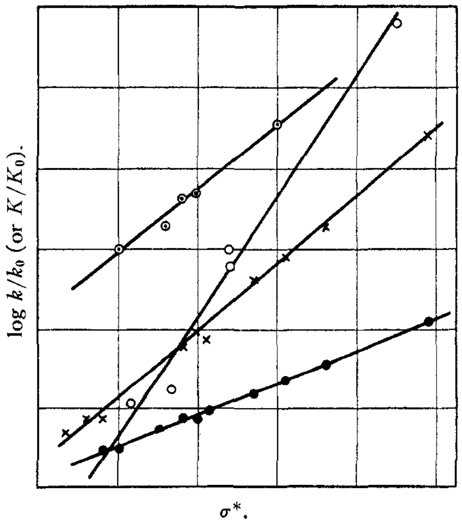


Fig. 2.—Typical examples of reactions following eq. (2): ●, 2, catalysis of the dehydration of acetaldehyde hydrate by general acids, RCOOH; ×, 5, ionization of acids, RCOOH; ⊙, 4, base-catalyzed bromination of ketones, $C_6H_5COCHR_1R_2$; ○, 3, ionization of ortho substituted anilinium ions. Numbers refer to these reactions as listed in Table I. The positions of both ordinate and abscissa are arbitrary. Unit scale of former is one log unit, and of latter is 0.5 polarity unit.

an equation perfectly analogous, in respect to the proportionality of polar effects, to that of Hammett, namely

$$\log k/k_0 \text{ (or } K/K_0) = \sigma^*\rho^* \qquad (2)$$

where σ^* is a polar substituent constant for the group R relative to the standard CH_3 group. The polar constants are obtained from the ester rate data in a manner previously discussed.[2b,3] ρ^* is a constant giving the susceptibility of a given reaction series to polar substituents. Its value depends upon the nature of the reaction center Y, the attacking reagent, etc.

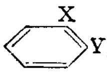
Certain reactions of ortho substituted benzene derivatives,  also follow eq. (2). For ortho substituents, X, σ^* values (which are not the same as for corresponding R's of R-Y) are relative to the unsubstituted (X = H) derivative.

Table I summarizes the reactions following eq. (2). Figure 2 illustrates several typical examples. Given in Table I are descriptions of the reactions, a notation as to whether data are for rates or equilibria (R or E, resp.), the reaction constant, ρ^*, and its probable error (obtained by methods of least squares), the probable error of the fit of a single observation, r, and a listing of the substituents, which fit the correlation. The latter is given by numbers which refer to those assigned the substituents in Table V. The median probable error of Table I is 0.06 in the logarithm or eleven per cent. in the value of the relative constant. The correlations cover maximum variation in the constants, k or K, of ten thousand and of three hundred thousand in the constants determining σ^* values.

Reaction series 5 and the Brönsted catalysis law[1b] require reaction series 2, 8, 9 and 10 to follow eq. (2). No attempt has been made to include in Table I all reactions following the Brönsted relation. Two reaction series of each the acid and the base type which involve the greatest number of substituents are the only ones included. The precision with which the data fit eq. (2) is appreciably better than for the Brönsted relation. Reaction series 12 and 13 are included to show that the effect of alkyl groups in the meta position of a benzene derivative produce effects on reactivity paralleling that of alkyl groups directly attached to the functional group. In these as in the case of reaction series 2 and 3 for ortho-substituted benzene derivatives, eq. (2) is not followed by the unsubstituted derivative.

It is desirable to direct attention to Fig. 1. The ordinate—log k/k_0 values for ester hydrolysis—is given by parameters which are simultaneous functions of both polar and steric effects.[2b] The abscissa—log K/K_0 values for the ionization of carboxylic acids—is given by parameters which are determined essentially by polarity alone.[2b] The result is typical of that to be expected of plots with coordinates so determined. *This is because polar*

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[3] Polar substituent constants obtained in reference 2b were given by the symbol $E\sigma$. This has regrettably proved to be an awkward symbol and the change to σ^* seems appropriate. In Table V, polar substituent constants, σ^*, are given on a different scale than the $E\sigma$ values originally reported (see later section). It is hoped that changing both symbol and scale of the polar constants will lead to a minimum of confusion.

TABLE I

REACTION CONSTANTS FROM EQ. (2)

	Reaction	ρ^*	r	Subst.
1	R. Sulfation of alcohols, ROH, equimolar sulfuric acid, initial H_2O/H_2SO_4 = 1.290, 25°[4]	$+4.600 \pm 0.149$	0.03	23;25;27;28;30
2	R. Catalysis of dehydration of acetaldehyde hydrate by general acids, RCOOH, acetone, 25°[5]	$+0.801 \pm .015$	.02	3; 5; 6; 7; 11; 14; 15; 16; 18;20;23;25[a]
3	R. Hydrolysis of formaldehyde acetals, $H_2C(OR)_2$, water 25°[6]	$-8.345 \pm .30$	.05	23;25;26;27;28;30;31
4	R. Bromination of ketones, $C_6H_5COCHR_1R_2$, base catalyzed, water, 25°[7]	$+1.590 \pm .079$	.06	23, 23; 14, 30; 14, 25; 14, 23; 14, 14
5	E. Ionization of acids, RCOOH, water, 25°[8]	$+1.721 \pm .025$	.06	6;8;12;14;17;18;20;23; 25;26;27;28;30;34[b]
6	E. Acidities of alcohols, R–CH_2OH, isopropyl alcohol, 27°[9]	$+1.364 \pm .027$	.09	8; 11; 13; 14; 23; 25; 26; 30[c]
7	Rates of alkaline hydrolysis of acetatopentammine cobalt(III) ions $[Co[NH_3)_5X]^{+3}$, where X = $RCCOO^-$, water, 25°[10]	$+0.786 \pm .037$	.11	1;3;6;12;23;25;30;34
8	R. Catalysis of iodination of acetone by general acids, RCOOH, water, 25°[11]	$+1.143 \pm .022$	.02	6; 12; 17; 23; 25
9	R. Catalysis of decomposition of nitramide by general bases, $RCOO^-$, water, 25°[12]	$-1.426 \pm .035$	.07	3;6;14;18;23;25;34[d]
10	R. Catalysis of depolymerization of dimeric dihydroxyacetone by general bases, $RCOO^-$, water, 25°[13]	$-1.362 \pm .069$	.07	6;14;18;23;34
11	R. Vapor phase reaction of alkyl chlorides, RCl, with sodium[14]	$-2.480 \pm .174$	.05	23;25;26;30;34[e]
12	R. 3-Monoalkylpyridines with methyl iodide, nitrobenzene, 30°[15]	$-0.357 \pm .037$	.01	23;25;30;34
13	R. Decomposition of metamonoalkyl phenyldiazonium chlorides, water, 30°.[16]	$-1.672 \pm .191$	.05	23;25;34
	Ortho Substituted Benzene Derivatives			
1	R. Catalysis of dehydration of acetaldehyde hydrate by general acids, acetone, 25°[5]	$+0.771 \pm .019$	.02	1;3;4;5;8
2	E. Ionization of benzoic acids, water, 25°[8]	$+1.787 \pm .13$	.12	1;3;5;6;7;8[f]
3	E. Ionization of anilinium ions, water, 25°[17]	$+2.898 \pm .15$	.19	1;3;5;6;8;[f,g]

[a] Correlation fails for subst. 34. [b] Correlation fails for substs. 11, 15, 32. It was reported earlier[2b] that the fit for this reaction series was only qualitative. However, omitting the designated substituents leads to a satisfactory quantitative fit. [c] Dihydroxy alcohols do not fit correlation. [d] Correlation fails for subst. 11. [e] Correlation fails for substs. 27 & 28. [f] Correlation fails for unsubst. deriv., 4. [g] σ'-Value used for NO_2 group is Hammett σ value for *p*-NO_2 in phenol and aniline derivatives. NOTE ADDED IN PROOF:—The rates of alkaline hydrolysis of ethyl 4-X-bicyclo[2,2,2]octane-1-carboxylates, X-$C_6H_{12}CO_2Et$, in 87.83% (wt.) aq. ethanol, 30° (J. D. Roberts and W. T. Moreland, Jr., THIS JOURNAL, **75**, 2167 (1953)) follow eq. (2) using σ^* values for R = XCH_2- ($\rho^* = 0.975 \pm .045$; r = 0.04; Subst. = 5,7,12,23). This is an important correlation for it shows that the electrical effects of XCH_2– groups quantitatively parallel those of X operating across the rigid bicyclo ring system (see also Fig. 1 of the above authors).

and steric effects are completely different functions of structure. The condition of variable steric factors in a reaction series is a sufficient one to cause the type of scatter observed in Fig. 1. Corresponding values of σ^* and E_s for several typical substituents are given in Table II.[2b] The difference in the nature of these functions is so complete as to make it probable that the conclusion reached above applies not only to rates of esterification and ester hydrolysis but to all reactions in general. Bearing this in mind, the simple proportionality between log k/k_0 (or K/K_0) values and corresponding polar substituent constants, σ^*, (*i.e.*, contrast Figs. 2 and 1) requires that steric factors remain essentially constant in each of the reaction series following eq. (2).

TABLE II

POLAR AND STERIC SUBSTITUENT CONSTANTS FROM ESTER RATE DATA[2b]

Substituents, *R*, in *R*COOR′	σ^*	E_s	Substituents, X, in *o*-substituted benzoates	σ^*	E_s
Cl_3C	+2.65	−2.06	OC_2H_5	−0.15	+0.86
H	+0.490	+1.24	CH_3	0.00	0.00
$(C_6H_5)_2CH$	+ .405	−1.76	C_6H_5	+ .01	− .90
$(C_6H_5)(CH_3)CH$	+ .105	−1.19	Cl	+ .37	+ .18
CH_3	.00	0.00	Br	+ .38	+ .01
t-Bu	− .320	−1.54	I	+ .38	− .20
$(C_2H_5)_3C$	− .34(est.)	−3.8	NO_2	+ .95	− .71

It must be re-emphasized that eq. (2) is general only for those reactions in which polarity alone determines relative rates or equilibria. Since the number of reaction series involving bulky groups

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(4) N. C. Deno and M. S. Newman, THIS JOURNAL, **72**, 3852 (1950).

(5) R. P. Bell and W. C. E. Higginson, *Proc. Roy. Soc.* (*London*), **197A**, 141 (1949).

(6) A. Skrabal and H. H. Eger, *Z. physik. Chem.*, **122**, 349 (1926).

(7) D. P. Evans and J. J. Gordon, *J. Chem. Soc.*, 1434 (1938).

(8) See ref. 1, p. 210; ref. 2, p. 3127, footnote 37; ref. 5.

(9) J. Hine and M. Hine, THIS JOURNAL, **74**, 5266 (1952).

(10) F. Basolo, J. G. Bergmann and R. G. Pearson, *J. Phys. Chem.* **56**, 22 (1952).

(11) H. M. Dawson, G. V. Hall and A. Key, *J. Chem. Soc.*, 2849 (1928).

(12) See A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 222.

(13) R. P. Bell and E. C. Baughan, *J. Chem. Soc.*, 1947 (1937).

(14) H. V. Hartel, N. Meer and M. Polanyi, *Z. physik. Chem.*, **B19**, 139 (1932).

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

(16) E. S. Lewis and E. B. Miller, THIS JOURNAL, **75**, 429 (1953).

(17) (a) C. M. Judson and M. Kilpatrick, *ibid.*, **71**, 3110 (1949); (b) N. F. Hall and M. R. Sprinkle, *ibid.*, **54**, 3469 (1932).

TABLE III

REACTION CONSTANTS FOR PARAMETERS FOLLOWING EQ. 3

	Reaction and Parameter	ρ^*	r	Subst.
1	R. log k_B/k_A, ratio base to acid-catalyzed hydrolysis of glycerate esters, $CH_2OHCHOHCOOR$, water, 25°[2b,21]	+3.328 ± 0.112	0.02	23; 25; 26; 27; 28; 30
2	R. log k_B/k_A, ratio base to acid-catalyzed hydrolysis of thiolacetates, CH_3COSR, 43% (wt.) aq. acetone, 30°[22,2b]	+1.490 ± .188	.04	23; 25; 27; 30; 34
3	R. Driving force parameters, *m*, for front-side participation in the solvolysis of alkyl bromides, RBr[23]	−2.123 ± .263	.06	23; 25; 30; 34
4	$E_{1/2}$. Polarographic reduction of α-bromoacetic acids, $R_1R_2C(Br)COOH$, 9.5% (vol.) aq. ethanol, *p*H 1.1, 0°[24]	−0.397 ± .012	.012	14, 14; 23, 14; 25, 24; 23, 23; 23, 25; 25, 25
5	E. Structural parameters for ammonium ions, $R_1R_2R_3NH^+$, from dependence of ionization constants upon solvent, ethanol–water system, 25°[25]	−0.997 ± .082	.111	14, 14, 14; 11, 14, 14; 23, 14, 14; 25, 14, 14; 23, 23, 14; 23, 23, 23
6	E. Heats of dissociation of trimethylboron addition compounds with straight chain primary amines, RNH_2, kcal./mole[40]	−7.26 ± .21[a]	.1 kcal.	14, 23, 25, 26, 28

[a] See equation in last section.

adjacent to the reaction center for which steric and resonance factors remain constant is surely but a very small fraction of the total, it will frequently fail. However, the reaction series which follow eq. (2) involve such a wide variety of functional groups, reaction mechanisms, attacking reagents, etc., that it leaves no doubt that the proportionality of corresponding polar effects on free energy differences is quite as general as in eq. (1). *Equation (2) provides especially powerful proof of this since the polar substituent constants, σ*, are obtained from reactions for which rates are simultaneous functions of steric (and resonance in a few cases) as well as polar effects.*[2b] *The correlations obtained by eq. (2) therefore show that corresponding polar effects are proportional not only between reaction series in which steric and resonance effects are constant, but as well between those in which there are marked variations in the latter effects.*

Thus an equation of very great generality—one encompassing all reactions, those involving bulky substituents adjacent to the reaction center as well as those following the Hammett equation—must exist, namely

$$P_\sigma = \sigma^*\rho^* \text{ (or } \sigma\rho) \qquad (3)$$

where σ^*, ρ^*, σ, and ρ are as previously defined.

P_σ = any parameter (having dimensions of energy) dependent upon the polar effect of a substituent group relative to a standard of comparison.

Equation (3) is simply an expression of the great generality of the near quantitative proportionality of polar effects.[18] In fact it may be taken as the definition of a polar effect. In the case of reaction series following eq. (1) or (2), which are special cases of eq. (3), the polar parameter P_σ, is obtained from a rate or equilibrium measurement, *i.e.*, $P_\sigma \equiv \log k/k_0$ (or K/K_0). In the case of all other reactions P_σ cannot be obtained from a rate of equilibrium measurement, *i.e.*, $P_\sigma \neq \log k/k_0$ (or K/K_0). Instead, P_σ, the polar contribution to $\log k/k_0$ (or K/K_0), must be quantitatively separated by some suitable means from the other factors which determine these rates or equilibria. In general such a separation is by no means an easy one.

Parameters, other than the $\log k/k_0$ (or K/K_0) values, which have been found to fit eq. (3) are listed in Table III. The description of each series gives some indication of the manner in which the polar contributions have been separated from the free energy parameters. The original reference should be consulted for greater details. The precision of the fit of the parameters of Table III is closely the same as that in Table I.

Polarity and Physical Constants.—Both rates and equilibria are determined by free energy differences between initial and final (transition in the former, product in the latter) states. In the polar effects of substituents on rates and equilibria we are dealing therefore with free energy differences rather than the free energy's of single states. However, the completely general nature of the proportionality of free energy differences between all varieties of initial and final states implies that the proportionality may frequently exist as well between corresponding energies of single states. The correlation of Hammett sigma values with physical properties such as F^{19} nuclear magnetic shielding in substituted fluorobenzenes[19] and nuclear quadrupole coupling frequencies of substituted chlorobenzenes[20] support this conclusion.

Physical parameters measuring the polar effect of aliphatic derivatives on single states have also been found to fit eq. (3). These are summarized in Table IV. Calculated and observed values for the dipole moments of hydrogen and alkyl iodides in carbon tetrachloride at 20° and of aliphatic amines in benzene at 25° are given below to illustrate the nature of these correlations. Deviations of calcu-

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(18) The condition of proportionality between the effects of substituents on the logarithm of rates or equilibria is a necessary but not a sufficient criterion of polar effects. Linear free energy relationships determined by steric effects of substituents exist (ref. 2b, p. 3126). Such relationships are, however, very limited. It is the completely general nature of the proportionality which serves as the criterion distinguishing linear free energy relationships determined by polarity from those determined by steric factors.

(19) H. S. Gutowsky, D. W. McCall, B. R. McGarney and L. H. Meyer, THIS JOURNAL, **74**, 4809 (1952).

(20) H. C. Meal, *ibid.*, **74**, 6121 (1952).

(21) C. M. Groocock, C. K. Ingold and A. Jackson, *J. Chem. Soc.*, 1057 (1930).

(22) R. N. Rylander and D. S. Tarbell, THIS JOURNAL, **72**, 3021 (1950); J. R. Schaefgen, *ibid.*, **70**, 1308 (1948).

(23) S. Winstein, E. Grunwald and H. W. Jones, *ibid.*, **73**, 2700 (1951).

(24) J. M. Markowitz, M.S. Thesis, The Pennsylvania State College, June, 1952; unpublished data of P. J. Elving and J. M. Markowitz.

(25) B. Gutbezahl and E. Grunwald, THIS JOURNAL, **75**, 559 (1953).

TABLE IV

PHYSICAL PARAMETERS FOLLOWING EQ. (3)

	Description	Equation	*r*	Subst.
1	Dipole moments (Debyes) of RCl, vapor state, 290 to 400°K.[21]	$= (-1.416 \pm 0.069)\,\sigma^* + 1.823$	0.05 Debye	14; 23; 25; 26; 27; 28; 30; 31; 34
2	Dipole moments (Debyes) of RI, carbon tetrachloride, 20°[21]	$= (-2.200 \pm .067)\,\sigma^* + 1.611$	.05 Debye	14; 23; 25; 26; 27; 30; 31; 32; 34
3	Dipole moments (Debyes) of amines $R_1R_2R_3N$, in benzene at 25°[21]	$= (+0.530 \pm .019)\,\sigma^* + 0.920$	.02 Debye	23, 14, 14; 25, 14, 14; 28, 14, 14; 31, 14, 14; 34, 14, 14; 23, 23, 14; 25, 25, 14; 23, 23, 23; 25, 25, 25
4	Dipole moments (Debyes) of alkyl cyanides, RCN, in benzene, 25°[21]	$= (-0.444 \pm .024)\,\sigma^* + 3.51$	.01 Debye	23; 25; 26; 28; 30; 34
5	Carbon–oxygen stretching spectra for alcohols, ROH, (8–10μ) in wave no.[27a,b]	$= (-229 \pm 35)\,\sigma^* + 1049$	22 cm.$^{-1}$	18; 23; 25; 26; 27; 28; 29; 30, 31; 32; 33; 34[27b]
6	Bond energy (kcal./mole) of alkyl-hydrogen bonds, D_{R-H}, (from pyrolysis of RI)[28a,b]	$= (+54.1 \pm 4.7)\,\sigma^* + 102.0$	1.1 kcal.	23; 25; 28; 30; 34

lated and experimental values are not on the average outside of uncertainties in the latter. The last two correlations listed in Table IV (series 4 and 5) are better described as qualitative than quantitative.

RI	μ calcd., Debye	μ expl.[26] Debye	*d*	Amine	μ calcd., Debye	μ expl., Debye	*d*
H	0.53	0.50	0.03	CH_3NH_2	1.47	1.46	0.01
CH_3	1.61	1.56	.05	$C_2H_5NH_2$	1.39	1.37	.02
C_2H_5	1.82	1.89	.07	*n*-$C_4H_9NH_2$	1.37	1.40	.03
i-C_3H_7	2.05	2.08	.03	*s*-$C_4H_9NH_2$	1.33	1.28	.05
n-C_3H_7	1.86	1.92	.06	*t*-$C_4H_9NH_2$	1.27	1.29	.02
i-C_4H_9	1.88	1.92	.04	$(CH_3)_2NH$	1.18	1.17	.01
s-C_4H_9	2.07	2.10	.03	$(C_2H_5)_2NH$	1.08	1.13	.05
$(C_2H_5)_2CH-$	2.11	2.09	.02	$(CH_3)_3N$	0.86	0.92	.06
t-C_4H_9	2.32	2.20	.12	$(C_2H_5)_3N$	0.77	0.79	.02
		Av.	.05			Av.	.03

A Further Criterion of Polar Effects.—In addition to the proportionality of polar effects, there is a second important feature of the Hammett relationship. The polar substituent constants, σ, are very nearly additive.[1,19] That is, for example, the polarity constant of a 3,4-dimethylbenzene derivative is the sum of that for single meta and para methyl substituents.[1] If more than one equivalent benzene ring is present as in $(C_6H_5)_3P$, the combined polarity constant to be used is the sum of that for each substituent present in each ring.[29] Steric substituent constants for rates of ester hydrolysis are definitely not additive.[2b]

The polar substituent constants, σ^*, for aliphatic derivative groups adjacent to the reaction center meet the same criterion of additivity as do the Hammett sigma values. Table V lists σ^*-values from which it is seen that the replacement of hydrogen by CH_3, C_6H_5 or Cl on the same C atom gives approximately (within uncertainties of σ^*-values) the same change for each successive substitution. The appropriate comparisons are for substituents numbered: (1) 23, 25, 30, and 34 (or 25, 26, 27, 29); (2) 16 and 18, and 9, 12, and 18 (also 18, 19 and 25); and (3) 1, 3 and 6. For the latter series additivity does not appear as good as for the others but this may be largely because the σ^*-value for the CCl_3 group is tentative. Tentative values are listed in Table V as previously[2b] in parentheses. The fact that there is a very nearly regular increase in the Cl^{35} quadrupole spectra of solid chloroacetic acids[30] involving (1), (3) and (6) as well as a regular increase in the half-wave potential for the polarographic reduction of ethyl chloroacetates[31] support the additivity principle for this series. Reaction series 4 of Table I, 4 and 5 of Table III and 3 of Table IV are further illustrations of the additivity principle. The σ^*-values used in these correlations are the sum of σ^*-values for the R groups involved at the reaction center (see description of reactions).

Comparison of the σ^*-values for the following pairs of substituents indicates that the polar effect of the carbonyl group, the Cl atom, and the phenyl group are decreased by a factor of 2.7 by the interposition of a CH_2 group: 4, 10; 6, 17; 11, 18; 18, 20. This is in contrast to the factor of about 5.4 for hydrogen and alkyl groups.[2b]

The electrical effects of substituents operating on the functional center through a methylene group are in general appreciably greater than when the substituent operates from the meta position across the benzene ring. This is illustrated by the ratios given below of σ^*-values for XCH_2 groups to corresponding Hammett sigma values for X in the meta position. Although the σ^*/σ ratios are by no means constant, in each case they are positive and generally appreciably greater than unity. This result, together with the relatively large reaction constants, ρ^*, for certain reactions of Tables I and III,

(26) Taken from L. G. Wesson, "Tables of Electric Dipole Moments," The Technology Press, M.I.T., 1948.

(27) (a) H. H. Zeiss and M. Tsutsui, *ibid.*, **75**, 897 (1953); (b) in obtaining this correlation, the substituents Me(*i*-Pr)CH, $(i\text{-Pr})_2CH$, $(t\text{-Bu})_2CH$, and Me(Et)(*i*-Bu) were also included. The σ^*-values were estimated for these groups on the basis of the additivity principle. The precision of the fit for this correlation is not as good as others. The correlation is generally good qualitatively but leaves much to be desired quantitatively. There appear to be trends in certain cases opposite to that predicted. For example, for the class of substituents $C_6H_5(R)CH$, where R is 23, 25, 30 and 34, cm.$^{-1}$ fits with reasonably good precision a correlation of opposite sign to that given above.

(28) (a) Taken from M. Szwarc, *Chem. Rev.*, **47**, 75–173 (1950); (b) although bond energies for $H-CH_3$ and $H-C_2H_5$ have been determined by methods considered to be more accurate than those obtained from the pyrolysis data, it seemed desirable for present purposes to use bond energies for the entire series obtained by a single method and investigation (M. Polanyi, *et al.*, see above ref.)

(29) P. D. Bartlett, unpublished results.

(30) H. C. Allen, Jr., THIS JOURNAL, **74**, 6074 (1952).

(31) P. J. Elving and C. S. Tang, *ibid.*, **72**, 3244 (1950).

TABLE V

POLAR SUBSTITUENT CONSTANTS

	Subst., R	σ^*	n	r	Source		Subst., R	σ^*	n	r	Source
	I. For R-Y, where R is substituent, Y is functional group										
1	Cl_3C	(+2.65)	2		Ref. 2b	18	$C_6H_5CH_2$	+0.225	6	0.052	Ref. 2b
2	CH_3OOC	(+2.00)	1		Ref. 2b	19	$(C_6H_5)(CH_3)CH$	+ .105	1		Ref. 2b
3	Cl_2CH	+1.940	4	0.017	5	20	$C_6H_5(CH_2)_2$	+ .080	3	.048	Ref. 2b
4	CH_3CO	(+1.65)	1		Ref. 2b	21	$(C_6H_5)(C_2H_5)CH$	+ .040	1		Ref. 2b
5	$CNCH_2$	+1.300	2	.014	5	22	$C_6H_5(CH_2)_3$	+ .020	1		Ref. 2b
6	$ClCH_2$	+1.050	7	.020	5	23	CH_3	.000	24	.025	Ref. 2b
7	$BrCH_2$	+1.030	2	.018	5	24	Cyclo-$C_6H_{11}CH_2$	− .06	1		Ref. 2b
8	$C_6H_5OCH_2$	+0.850	2	.034	Av. 2 & 5	25	C_2H_5	− .100	23	.023	Ref. 2b
9	$(C_6H_5)(OH)CH$	+ .765	1		5	26	*n*-C_3H_7	− .115	11	.019	Ref. 2b
10	CH_3COCH_2	(+ .60)	1		Ref. 2b	27	*i*-C_4H_9	− .125	9	.021	Ref. 2b
11	C_6H_5	+ .600	4	.062	Ref. 2b	28	*n*-C_4H_9	− .130	11	.020	Ref. 2b
12	$HOCH_2$	+ .555	4	.063	2	29	(*t*-C_4H_9)CH_2	− .140	2		1
13	CH_3OCH_2	+ .52	2	.19	Ref. 2b	30	*i*-C_3H_7	− .200	16	.027	Ref. 2b
14	H	+ .490	13	.032	Ref. 2b	31	*s*-C_4H_9	− .210	6	.005	1
15	$C_6H_5CH{=}CH$	+ .410	2	.030	Av. ref. 2b & 2	32	$(C_2H_5)_2CH$	− .225	4	.037	1
16	$(C_6H_5)_2CH$	+ .405	3	.042	5	33	(*t*-C_4H_9)$(CH_3)CH$	− .285	2		1
17	$ClCH_2CH_2$	+ .385	3	.010	7	34	*t*-C_4H_9	− .320	14	.050	Ref. 2b
	II. For Ortho-Substituted, X, Benzene Derivatives										
1	OCH_3	−0.41	4	0.01	Ref. 2b, 1	5	Cl	+0.20	4	0.03	Ref. 2b, 1
2	OC_2H_5	− .32	1		Ref. 2b, 1	6	Br	+ .21	3	.07	Ref. 2b, 1
3	CH_3	− .17	4	.09	Ref. 2b, 1	7	I	+ .21	2	.07	Ref. 2b, 1
4	H	.00	1		1	8	NO_2^a	+ .78	3	.05	Ref. 2b, 1
						9	NO_2^b	+1.22	1		3

[a] To be used for benzene derivatives other than anilines. [b] To be used for derivatives of aniline.

indicates that polar effects in aliphatic reactions may be extremely large.

Substituent, X	σ^* for XCH_2-	σ for meta-X-	σ^*/σ
CN	+1.30	+0.68	1.9
Cl	+1.05	+ .37	2.8
Br	+1.03	+ .39	2.6
CH_3O	+0.52	+ .12	4.3
H	.00	.00	...
C_6H_5	+ .23	+ .22	1.0
CH_3CO	+ .60	+ .31	1.9
CH_3	− .10	− .07	1.4

In originally reporting polar substituent constants, those for ortho substituted benzoates were given on a different scale than for aliphatic substituents adjacent to the carboxy function.[2b] A suitable means now appears available for converting all of the polar substituent constants to the same scale.[3] Using E_σ-values given previously, the ratio of ρ^*-values for ortho substituted benzoic acids to ρ^*-values for aliphatic carboxylic acids in the general acid-catalyzed dehydration of acetaldehyde hydrate is 2.39 and in the ionization constants of the acids is 2.57. The average ratio for these two reaction series is therefore 2.48. This value is the factor converting (at least approximately) all of the σ^*-values to the same scale.[32] The value of 2.48 is indeed a reasonable one if the susceptibility of rates of esterification and ester hydrolysis to polar substituents is the same for groups attached directly to the carboxy group as for *m*- and *p*-substituted benzoates. This is so because the E_σ-values given formerly for ortho benzoate substituents were on the same scale as the Hammett sigma values for *m*- and *p*-substituents while the E_σ values for aliphatic derivatives were based upon the definition $\rho^*_B - \rho^*_A \equiv 1$ for base and acid-catalyzed rates of esterification and hydrolysis. The average value of ρ_B- ρ_A obtained from rates of esterification and hydrolysis of *m*- and *p*-substituted benzoates is 2.49.[2b]

The correlations obtained in eq. (2) and (3) have made it possible to assign several new σ^*-values. Table V lists σ^*-values, including new ones, all converted to the same scale, *i.e.*, with values for aliphatic groups 1/2.48 of the E_σ-values given previously. Included are notations to the reaction series in Table I used as a source of the σ^*-value, the number of correlations, n, for which data for each substituent are available, and the median deviation, r, of the value of σ^*.

Reaction series 1 of Table I has made it possible to give σ^*-values for ortho substituted benzene derivatives relative to the unsubstituted derivative. The phenyl as well as ortho substituted phenyl groups follow eq. (2) for this reaction series. The polar substituent constants for ortho substituted benzoates were previously given relative to the CH_3 group.

Discussion

Equations (2) and (3) constitute the most rigorous tests now known of σ^* as true polarity measures. These correlations confirm the original assumption that steric effects in rates of ester hydrolysis are the same for corresponding acidic and basic reactions.

The reaction series listed in Table I are of such nature that in the reactant states there are important steric interactions between substituents and

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(32) It should be noted, however, that using this factor does not give ρ^*-values for the ionization constants for aliphatic carboxylic acids or ortho substituted benzoic acids the same as ρ (+1.000) for *m*- and *p*-substituted benzoic acids. The requirement of two reaction constants, one for ortho substituents, and the second for *m*- and *p*-substituents for a given reaction appears to be not uncommon.

functional groups. Yet, eq. (2) requires that for a given reaction series steric factors are constant. These two conditions are consistent only because of the fact that relative rates and equilibria are not determined by free energy differences between reactant states, but rather by the differences in free energy differences between initial and transition or product states. Steric (or other) factors in reactivity are therefore dependent to just as great an extent upon the nature of the transition or product as the initial state. Thus, even though suitable comparisons (perhaps of heats or free energies of formation) may show important steric compressions exist in a given molecule, this same molecule may fit in a reaction series for which rates or equilibria are determined only by the polarity of substituent groups *if* the difference in steric interactions between initial and transition or final states is the same as for other members of the reaction series. The present results emphasize the conclusion that the presence of compressed groups is a necessary but not a sufficient condition for the existence of important substituent steric effects in reactivity.

Reaction series in which there is a constant difference in substituent steric interactions between initial and transition or product states may be expected when there is essentially no change in bond angles about the reaction center between the two states and an atom at the reaction center has gained or lost a small coördinating group (a proton, for example). An inspection of the types of reactions given in Table I indicates that many of these are probably of this nature.

The correlations of eq. (2) and (3) make it very likely that σ^*-values for alkyl groups are determined only by inductive and polarizability effects. The functional centers adjacent to substituents in reaction series 1, 3, 6 and 11 of Table I and 1, 2, 3, and 5 of Table III are saturated in the reactant and probably also in the transition or final states. On the other hand reaction series 2, 4 and 5 of Table I, as well as those on which σ^*-values are based,[2b] involve substituents adjacent to an unsaturated function. The correlation of all of these cases by eq. (3) at least excludes the possibility of important contributions to σ^*-values for alkyl groups from CH (but not necessarily CC) type "no bond" hyperconjugation.

A number of the reaction series listed in Tables I and III involve a rather limited group of substituents. These reaction series therefore do not provide a critical test of eq. (2) or (3) over a wide range of substituent electrical properties. In most cases the correlations cover a sufficient variety of groups to make very unlikely coincidental fits. This possibility remains however as long as the range of electrical properties tested is relatively narrow. Work is presently under way in our laboratory to determine rates for a number of these reactions over wider ranges of polarity.

Applications.—The underlying basic principle of proportionality of polar effects expressed by eq. (3) can be a very valuable tool if properly used. For example, the sign and magnitude of the reaction constant, ρ^*, can be used, as the Hammett rho values have, to obtain important evidence for the nature of a reaction mechanism. In addition, it is possible to determine for reaction series involving bulky groups adjacent to the reaction center whether steric, resonance, or effects other than polarity are constant. This too may provide valuable information on the mechanism. The criterion is that rates or equilibria must follow eq. (2). If certain types of substituents follow eq. (2) but others do not, it is possible to quantitatively evaluate the factors causing the latter to deviate. These factors may include steric or resonance effects, or changes in reaction mechanisms. Examples, which illustrate the utility of eq. (2) in evaluating each of these effects in certain reactions, are given below.

Reaction Mechanism.—Departure of the polar parameter, $P_\sigma = \log k_B/k_A$, for the *t*-butyl group from eq. (3)[2b] for the hydrolysis of acetate esters in water, 25°, supports the evidence for a change in mechanism of the acid-catalyzed hydrolysis of *t*-butyl esters.[33] Similarly the correlation of the *t*-butyl group in reaction series 2 of Table III is in accord with the evidence that the normal mechanism is involved in the hydrolysis of *t*-butyl thiolacetate.[23]

Resonance Effects.—As a result of cross-conjugation[34] groups such as phenyl or cinnamyl have less extensive resonance with the adjacent carbonyl group in the anion than in the free carboxylic acid. The fact that the phenyl and cinnamyl groups do not follow eq. (2) in the ionization of carboxylic acids (reaction series 5, Table I)—the acids are weaker than the correlation with σ^*-values predicts—is in accord with this hypothesis. On the basis of this deviation, the decrease in conjugation in the anion for both of these groups (and accompanying solvent effect) amounts to about 700 cal./mole.

Of equal importance is the correlation of phenyl and cinnamyl groups in reaction series 2 of Table I. This result supports the original assumption made in obtaining the σ^*-values for these groups that *both* their resonance and steric factors (relative to the standard CH_3 group) are the same in corresponding acidic and basic rates of ester hydrolysis,[2b] and thus that $\sigma^* = 1/2.48\,[(\log k/k_0)_B - (\log k/k_0)_A]$. It further indicates that in the acid catalysis there is essentially no loss in the $\mathrm{\overset{\curvearrowright}{R{-}C}\overset{\curvearrowright}{{=}O}}$ resonance of these groups between the free acid and the reaction transition state and therefore there are no specific resonance effects of these groups in this reaction series.

Steric Effects.—The condition of variable steric effects in an aliphatic reaction series is probably the most frequent cause of non-parallelism between free energies (or heats) and corresponding polar substituent constants. Thus plots of the logarithms of relative rates *vs.* corresponding polar substituent constants, σ^*, show much the same high degree of scatter as in Fig. 1 for the following reactions: aliphatic alcohols with phenyl isocyanate in benzene at 26°,[35] and with *p*-nitrobenzoyl chlo-

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[33] S. G. Cohen and A. Schneider, THIS JOURNAL, **63**, 3382 (1941).

[34] G. E. K. Branch and M. Calvin, "The Theory of Organic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1941, p. 235.

[35] T. L. Davis and J. McC. Farnum, THIS JOURNAL, **56**, 883 (1934); ref. 1, p. 210.

ride in ether at 25°[36]; aliphatic acid chlorides with β-chloroethanol in dioxane at 25°[37]; the ammonolysis of methyl esters and acetate esters in anhydrous ethylene glycol at 30°.[38] Such results indicate that reaction rates in these cases are dependent upon important steric effects of the substituents.

The correlations obtained for reaction series 5 of Table III and 3 of Table IV suggest that the heats of dissociation, ΔH_d, of the addition compounds of aliphatic amines with trimethylboron should follow eq. (3) in cases where steric strains are constant.[39] Such a correlation does indeed exist for the simple straight chain primary amines: NH_3, CH_3NH_2, $C_2H_5NH_2$, n-$C_3H_7NH_2$ and n-$C_4H_9NH_2$. The equation is ΔH_d (kcal./mole) $= (-7.26 \pm 0.21)(\sigma^*) + 24.54$, where σ^* is the sum of σ^*-values for the R's of $R_1R_2R_3N$. The median deviation of the predicted and experimental values of ΔH_d is 0.1 kcal./mole, for an experimental range of ΔH_d's covering 4.7 kcal./mole.[40] However, the heats of dissociation predicted from this correlation are appreciably greater than measured values for branched primary, secondary, or tertiary amines. The deviations are a measure of the greater and variable steric compressions or strains in the addition compounds.[42,44] Table VI lists the steric strains evaluated in this manner.

TABLE VI

STRAIN ENERGIES OF AMINE—TRIMETHYLBORON ADDITION COMPOUNDS

Amine	σ^*	$\Delta H_{d(\text{cald.})}$ kcal./mole	$\Delta H_{d(\text{obs.})}$ kcal./mole	Steric strain kcal./mole	Estd. strain of homomorphic hydrocarbons kcal./mole
NH_3	+1.470	13.9	13.8[41]	0	0.0[45]
CH_3NH_2	+0.980	17.4	17.6[41]	0	0.2[45]
$C_2H_5NH_2$	+ .880	18.1	18.0[41]	0	0.2[46]
n-$C_3H_7NH_2$	+ .865	18.2	18.1[41]	0	0.7[46]
n-$C_4H_9NH_2$	+ .850	18.4	18.4[41]	0	..
i-$C_3H_7NH_2$	+ .780	18.9	17.4[42]	1.5	2.5[46]
s-$C_4H_9NH_2$	+ .770	18.9	17.3[42]	1.6	..
t-$C_4H_9NH_2$	+ .660	19.7	13.0[42]	6.7	5.2[43]
$(CH_3)_2NH$	+ .490	21.0	19.3[47a]	1.7	2.2[45]
$(C_2H_5)_2NH$	+ .290	22.4	16.3[47a]	6.1	..
$(CH_3)_3N$	.000	24.5	17.6[47a]	6.9	5.0[45]
$(n$-$C_4H_9)(CH_3)_2N$	− .130	25.5	15.3[44]	10.2	..
$(C_2H_5)_3N$	− .300	26.4	(10)[40b]	(17)	..

The results are within the limits estimated by Spitzer and Pitzer[44] in cases where comparison can be made, and in general are in reasonable accord with the steric strains estimated for the corresponding homomorphic hydrocarbons.[43,45] The results indicate that steric strains are not additive, but frequently tend to telescope with an increasing number of substitutions on a given C atom.

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[36] J. F. Norris and A. A. Ashdown, THIS JOURNAL, **47**, 837 (1925); ref. 1, p. 210.

[37] R. Leimu, *Ber.*, **70B**, 1040 (1937); ref. 1, p. 214.

[38] M. Gordon, J. G. Miller and A. A. Day, THIS JOURNAL, **71**, 1245 (1949).

[39] Heats of dissociation rather than free energies are chosen since there are small but appreciable entropy effects in the dissociations.[40,44]

[40] Further support for this method comes from a consideration of the heats of dissociation of the boron trimethyl addition compounds of cyclic imines ((a) H. C. Brown and M. Gerstein, THIS JOURNAL, **72**, 2926 (1950), and (b) H. C. Brown and S. Sujishi, *ibid.*, **70**, 2878 (1948)). If one considers trimethylenimine to have a σ^*-value the sum of that for H, Me, and Et (the latter two are here tied together) groups the above equation leads to a predicted ΔH_d value of 21.7 kcal./mole; the experimental value is 22.5 kcal./mole. The agreement is satisfactory considering the approximation made for σ^*, and it indicates that the methyl and ethyl groups tied down in this cyclic imine exert no compression upon the CH_3 groups attached to boron in the addition compound. Using a similar procedure, steric strains in the following cyclic imime addition compounds have been estimated; pyrrolidine, 2 kcal./mole; piperidine, 3 kcal./mole; quinuclidine, 7 kcal./mole. These results therefore support the conclusion of Brown and Gerstein that there is less F-strain in the addition compounds of pyrrolidine than piperidine and in both there is less strain than in corresponding open chain amines.

[41] H. C. Brown, M. D. Taylor and S. Sujishi, THIS JOURNAL, **73**, 2464 (1951).

[42] H. C. Brown and G. K. Barbaras, *ibid.*, **75**, 6 (1953).

[43] H. C. Brown, *et al.*, *ibid.*, **75**, 1 (1953), and previous references.

[44] H. C. Brown and R. B. Johannesen, *ibid.*, **75**, 16 (1953).

[45] R. Spitzer and K. S. Pitzer, *ibid.*, **70**, 1261 (1948).

[46] Obtained by method of Spitzer and Pitzer[44] from data of "Selected Values of Hydrocarbons," U. S. Government Printing Office, Washington, D. C., 1947, p. 159.

[47] (a) H. C. Brown, H. Bartholomay, Jr., and M. D. Taylor, THIS JOURNAL, **66**, 435 (1944); (b) H. C. Brown and M. D. Taylor, *ibid.*, **69**, 1332 (1947).