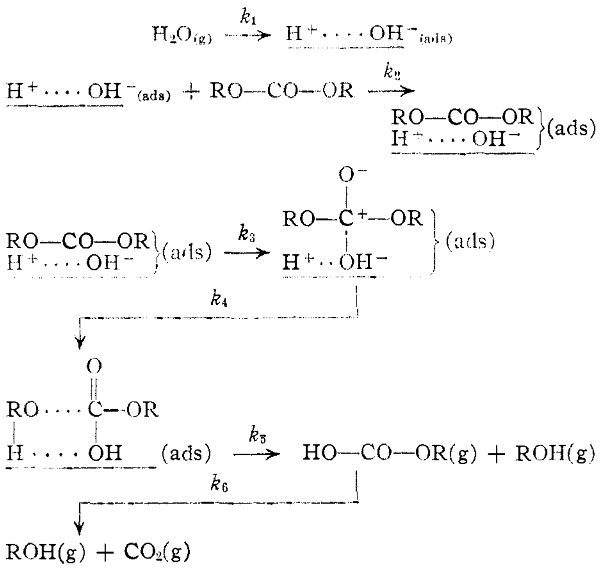

that k_4 is rate-determining. The desorption step k_5 may be rate-determining if the rate of desorption of the half-ester is slow, a point which unfortunately cannot be directly tested because of the instability of this compound but, again, it would be surprising if the energy of activation for this process did not depend on the nature of the surface. Since the reaction rate is not reduced by the addition of ethyl alcohol, the desorption of this compound cannot be the limiting factor. On the whole it seems most probable that k_3 is rate-determining; and this conclusion is in concordance with observations on ester hydrolysis in solution[6] where the overcoming of repulsive forces between water and ester was considered to be the slowest step. This result clarifies the invariance of true activation energies for catalysts chemically quite different, as it implies that the surface with which ethyl carbonate reacts is in fact simply a layer of hydroxyl ions. It is worth noting that the proposed mechanism requires that the critical complex be formed from a layer of previously adsorbed reactant.

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[6] G. Davies and D. P. Evans, *J. Chem. Soc.*, 339 (1940); E. W. Timm and C. N. Hinshelwood, *ibid.*, 864 (1938).

PHILADELPHIA, PENNSYLVANIA

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

Polar and Steric Substituent Constants for Aliphatic and *o*-Benzoate Groups from Rates of Esterification and Hydrolysis of Esters[1]

BY ROBERT W. TAFT, JR.

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Parameters, E_σ, giving nearly *quantitative measures of the polarities of* a large number of aliphatic and *o*-benzoate substituents have been determined from rates of esterification and hydrolysis of esters. Parameters, E_s, giving nearly quantitative measures of the *steric factors associated with* these substituents in rates of such reactions have also been obtained. The equation, (2), used to evaluate E_σ is $(\log k/k_0)_B - (\log k/k_0)_A = E_\sigma(\rho_B - \rho_A)$, where E_σ is a substituent electron displacement (polarity) constant; ρ is a reaction constant measuring the susceptibility of the given reaction series to polar substituents; k/k_0 is the relative rate of hydrolysis or esterification for a substituent of an *o*-substituted benzoate or aliphatic ester reaction series; the subscripts A and B refer to identical acid- and base-catalyzed reaction series, resp. The basic idea involved in Eq. (2) has been previously suggested by Ingold. The equation (3) used to evaluate E_s is $\log k/k_0 = E_s + E_\sigma\rho$. Equation (3) attributes the effect of structure on rates (more properly, free energy of activation) of hydrolysis or esterification of many aliphatic or *o*-substituted benzoate esters to the sum of two distinct terms, one of steric and the other of polar origin. Evidence is given for the fact that steric factors associated with a given substituent are the same in identical acid- and base-catalyzed reaction series (so that Eq. (2) follows directly from Eq. (3)). Further, that, as a first approximation, the relative rates of acid-catalyzed hydrolysis or esterification are determined by steric factors alone, while for base-catalyzed reactions both polar and steric factors are involved. For *o*-substituted benzoates, E_σ values are found to be essentially equal to Hammett σ values for corresponding *p*-substituents. For aliphatic substituents, E_σ values are shown to be in accord with the qualitative English school theory of the polarity of groups. Corresponding E_σ values in the acyl and alkyl components of esters are found to be quantitatively parallel. The order of decreasing E_s values is that of increasing steric requirements. E_s values are not parallel in the acyl and alkyl components. E_s and E_σ values have been applied to other reactions. The logarithms of the relative rates of acid-catalyzed hydrolysis of *o*-substituted benzamides in water at 100° quantitatively parallel E_s values. The logarithms of the relative rates of hydrolysis of a series of formaldehyde acetals and the logarithms of the relative ionzation constants of *o*-substituted benzoic acids in water at 25° quantitatively parallel corresponding E_σ values. For aliphatic carboxylic acids such a parallelism in general is only qualitative.

The English school has developed over a period of years a comprehensive theory of the general polarity of substituents.[2] However, the work of Brown, Hammett and others has emphasized the importance of steric strains, entropy and solvation effects in determining relative reactivity[3] and has indicated that in a number of types of reactions the polar effect plays little, or at least a minor, role. In the aliphatic series, no reaction series has yet been rigorously shown to have relative reactivities which depend only upon the polar effect of substituents so that a quantitative scale of polarities of such groups has been in doubt. The establishment of an acceptable method of evaluating polar effects is of great importance to the problem of determining the relative contributions of polar and steric factors in aliphatic reactions, and to a more complete understanding of the nature of structural factors affecting chemical reactivity.

The present subject is intended to give support

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(1) R. W. Taft, Jr., THIS JOURNAL, **74**, 2729 (1952).

(2) W. A. Waters, "Physical Aspects of Organic Chemistry," D. Van Nostrand Co., Inc., New York, N. Y., 1950, Chapter XI.

(3) (a) H. C. Brown and G. K. Barbaras, THIS JOURNAL, **69**, 1137 (1947); (b) H. C. Brown, R. S. Fletcher, and R. B. Johannesen, *ibid.*, **73**, 217 (1951); (c) I. Dostrovsky, E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 173 (1946); (d) F. P. Price and L. P. Hammett, THIS JOURNAL, **63**, 2387 (1941); (e) T. I. Crowell and L. P. Hammett, *ibid.*, **70**, 3444 (1948); (f) P. M. Dunbar and L. P. Hammett, *ibid.*, **72**, 109 (1950).

to a method proposed in 1930 by Ingold[4] for evaluating the polarity of substituent groups from rates of hydrolysis of esters. Ingold suggested that the ratio of rate constants, k_B/k_A, of base- to acid-catalyzed hydrolysis is a function only of the polarity of substituent groups, even though both k_B and k_A are affected by "steric hindrance." The rate constants k_B and k_A refer to a given ester in a series of esters for which the structure of one component of the ester is held constant and the other varied. Solvent and temperature are the same for both k_B and k_A.

This method was applied to three rather limited reaction series and the results were reported to be in good accord with the general theory of the polarity of groups. Ingold's proposal has been regarded,[5] however, as applicable only to a reaction series GCOOR in which geometrical or steric variations of the groups G or R cannot affect the reaction rate (that is, k_B or k_A).

The reactivity of many *o*-substituted benzoate[6] and aliphatic esters toward hydrolysis and esterification is most certainly affected by steric factors arising from the close proximity of bulky groups to the reaction center.[4,7,8a] This is perhaps best illustrated by noting the respects in which rate data for these esters are in marked contrast to that for *m*- and *p*-substituted benzoates: (1) within a reaction series entropies of activation show pronounced variations with structure[7b,8b]; (2) the Hammett relationship between rate and equilibrium is not followed[9]; (3) rates are in general decreased by substituents with greater steric requirements.[10]

The recent oxygen exchange work of Bender[11] has strongly suggested the existence of a common intermediate in acid- and base-catalyzed ester hydrolysis. One may reason from this that in a large number of cases the steric factors for a given bulky aliphatic or *o*-benzoate substituent should be the same (or nearly so) in acid- as in base-catalyzed hydrolysis. That is, regardless of the importance of steric factors in determining k_B and k_A, the ratio of rates, k_B/k_A, of base- to acid-catalyzed hydrolysis should be essentially independent of steric factors.

On the other hand, base-catalyzed hydrolysis (or esterification) is much more susceptible to polar effects than acid catalyzed. The Hammett reaction constants, ρ, for *m*- and *p*-substituted benzoates summarized in Table III clearly show this. The values of ρ, which give the susceptibilities of the rates of a given reaction series to polar substituents, are large, positive, and very nearly the same for all base-catalyzed reactions. For acid-catalyzed reactions, ρ values are of variable sign, but in all cases quite small, almost negligible by comparison to those for base catalysis.

TABLE III

HAMMETT REACTION CONSTANTS, ρ, FOR ACID- AND BASE-CATALYZED ESTERIFICATION AND HYDROLYSIS OF *m*- AND *p*-SUBSTITUTED BENZOATES

Reaction	ρ	Ref.
A. Acid-catalyzed reactions		
1, Esterification of benzoic acids in methanol at 25°	−0.54	Ref. 1, footnotes 5, 6
2, Esterification of benzoic acids in cyclohexanol at 65°	+ .42	12
3, Hydrolysis of ethyl benzoates in 60% (vol.) aqueous acetone at 100°	+ .03	13
4, Hydrolysis of ethylbenzoates in 60% (vol.) aqueous ethanol at 100°	+ .03	13
B. Base-catalyzed reactions		
1, Hydrolysis of ethyl benzoates in 60% (vol.) aqueous acetone at 25°	+2.40	14, ref. 1, footnote 22
2, Hydrolysis of ethyl benzoates in 85% (vol.) aqueous ethanol at 25°	+2.56	15
3, Hydrolysis of methyl benzoates in 60% (vol.) aqueous acetone at 25°	+2.41	16
4, Hydrolysis of ethyl benzoates in 87.83% (wt.) aqueous ethanol at 30°	+2.50	ref. 1, footnote 11
5, Methanolysis of *l*-menthyl benzoates in methanol at 40°	+2.53	10b

The above information supports the validity of Ingold's original proposal, that is, that the ratio k_B/k_A is a function of the polarity of a substituent. The basic idea involved here can be given expression in the following convenient and useful form[17]

$$(\log k/k_0)_B - (\log k/k_0)_A = E_\sigma(\rho_B - \rho_A) \qquad (2)$$

where E_σ is a *substituent constant*, dependent only upon *electron displacement* (*polar*) *effects*. E_σ is analogous to the Hammett substituent constant, σ, but expressed here by a different symbol to emphasize its different origin.

ρ is a reaction constant; that is, ρ is a constant for all substituents and depends only upon the reaction series. Like the Hammett reaction constant, ρ is a *measure of the susceptibility* of the rates of the given reaction series *to polar substituents.*

k/k_0 is the relative rate of hydrolysis or esterification for any substituent of an *o*-substituted benzoate or aliphatic ester (or acid) reaction series. k_0 is the rate constant for the standard reactant.

B and A (subscripts) refer to identical base- and acid-catalyzed reaction series, respectively, both in the same solvent and at the same temperature.

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(4) C. K. Ingold, *J. Chem. Soc.*, 1032 (1930).

(5) Reference 2, p. 342.

(6) The term *o*-substituted throughout refers to mono-*o*-substituted.

(7) (a) V. Meyer, *Ber.*, **27**, 510 (1894); (b) ref. 1, footnote 15; (c) M. S. Newman, THIS JOURNAL, **72**, 4783 (1950).

(8) (a) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 213; (b) *ibid.*, p. 121.

(9) Reference 8, p. 185.

(10) K. Kindler, ref. 8, p. 191, footnote 3; (b) ref. 1, footnote (8); (c) ref. 8, p. 205.

(11) M. L. Bender, THIS JOURNAL, **73**, 1626 (1951).

(12) R. J. Hartman, H. M. Hoogsteen and J. A. Moede, *ibid.*, **66**, 1714 (1944).

(13) E. W. Timm and C. N. Hinshelwood, *J. Chem. Soc.*, 862 (1938).

(14) E. Tommila and C. N. Hinshelwood, *ibid.*, 1801 (1938).

(15) D. P. Evans, J. J. Gordon and H. B. Watson, *ibid.*, 1430 (1937); C. K. Ingold and W. S. Nathan, *ibid.*, 222 (1936).

(16) E. Tommila, L. Brehmer and H. Elo, *Ann. Acad. Sci. Fennicae*, **Ser A**, Ch. No. 16, 14 (1945); *C. A.*, **41**, 903 (1947).

(17) According to the Hammett equation for *m*- and *p*-substituted benzene derivatives, $\log k/k_0 = \sigma\rho$. For the esterification or hydrolysis of *m*- or *p*-substituted benzoates, it follows that $(\log k/k_0)_B - (\log k/k_0)_A = \sigma(\rho_B - \rho_A)$ (1). The latter equation is analogous to Eq. (2) for *o*-substituted benzoates and aliphatic esters.

TABLE IV

ELECTRON DISPLACEMENT PARAMETERS, E_σ, FOR ORTHO-SUBSTITUTED BENZOATES AND ALIPHATIC SUBSTITUENTS

Benzoate series

Substituent	*o*-Position E_σ	n	r	*p*-Position σ	*m*-Position σ
OCH_3	−0.24	3	0.00	−0.10	+0.11
OC_2H_5	− .15	3	.02	− .08	+ .22
CH_3	.00	5	..	.00	.00
Cl	+ .37	5	.04	+ .40	+ .44
Br	+ .38	5	.07	+ .43	+ .46
I	+ .38	4	.04	+ .45	+ .42
NO_2	+ .95	5	.05	+ .95	+ .77

Aliphatic series[f]

Substituent	Acyl component E_σ	Acyl component n	Acyl component r	Alkyl component E_σ	Substituent	Acyl component E_σ	Acyl component n	Acyl component r	Alkyl component E_σ
Cl_3C	(+6.5)[e]	1	..	.....	$(C_6H_5)(CH_3)CH$	+ .26	3	.07	.....
H_3COCO	(+5.0)	1	..	.....	$(C_6H_5)(C_2H_5)CH$	+0.08	3	0.10	.....
CH_3CO	(+4.1)	1	..	.....	$C_6H_5CH_2CH_2CH_2$	+ .04	4	.06	.....
$ClCH_2$	(+2.6)[e]	1	..	.....	CH_3	.00	13	.10	0.00[a]
CH_3COCH_2	(+1.5)	1	..	.....	Cyclo-$C_6H_{11}CH_2$	− .15	4	.05	.....
C_6H_5	+1.49	6	0.09	+1.04[a]	C_2H_5	− .24	12	.05	− .21[a]
CH_3OCH_2	+1.3[b]	1	..	.....	*n*-C_3H_7	− .28	12	.09	− .26[a]
H	+1.22	8	.15	.....	*i*-C_4H_9	− .31	6	.12	− .34[a,d]
$C_6H_5CH{=}CH$	+1.1	1	..	.....	*n*-C_4H_9	− .32	8	.10	.....
$CH_3CH{=}CH$	+0.9[c]	1	..	.....	*i*-C_3H_7	− .47	11	.10	− .52[a]
$(C_6H_5)_2CH$	+ .67	4	.15	.....	$(C_2H_5)_2CH$	− .72	5	.29	.....
$C_6H_5CH_2$	+ .56	5	.05	.....	*t*-C_4H_9	− .84	10	.12	.....
$C_6H_5CH_2CH_2$	+ .29	5	.09	.....					

[a] $n = 1$. [b] Calcd. from data of M. H. Palomaa, *Suomen Kemistilehti*, **19B**, 53 (1946) and data of ref. 1, footnote 23. [c] Calcd. from data of P. Heinänen, *Ann. Acad. Sci. Fennicae*, Ser. A, II, No. 9, 3 (1943); *C. A.*, **40**, 3672 (1946). [d] Calculated for 62% (wt.) aq. acetone as solvent. [e] Calcd. from data of D. G. Flom's Ph.D. Thesis, The Pennsylvania State College, 1952. [f] Scale of E_σ different than for Benzoate Series—see text.

Equation (1) makes it possible to calculate E_σ values from data for acid- and base-catalyzed reaction series which are not identical.[1] That is, for acid- and base-catalyzed series: (1) for which the structure of the non-variant components of the esters are different; (2) which are carried out in different solvents; (3) for which the attacking reagents are different. For example, E_σ values can be evaluated from relative rate data for the acid-catalyzed esterification of a series of aliphatic acids in pure methanol at 25° and relative rates for corresponding substituents for the base-catalyzed hydrolysis of ethyl esters in 70% (vol.) aqueous acetone at 25°.

The relative free energy of activation[18] in the hydrolysis and esterification of many *o*-substituted benzoate and aliphatic esters can be considered the sum of two terms, one the result of polar factors and the other of steric factors. A measure of the gross steric effect of a substituent, therefore, can be obtained from the equation[19]

$$E_s = \log k/k_0 - E_\sigma \rho \qquad (3)$$

where E_s is a substituent constant which depends upon the gross steric effect of a substituent.

k/k_0, E_σ, and ρ are as previously defined. From the available rate data, Eqs. (1), (2) and (3) have been used to nearly quantitatively separate polar and steric terms (as E_σ and E_s parameters) for a large number of aliphatic and *o*-benzoate substituents.

Substituent Electron Displacement Parameters

Ortho-substituted Benzoates.—In Table IV are given for a number of *o*-substituents the values of E_σ obtained by Eq. (2), n, the number of reactions for which data are available for each substituent, and r, the median deviation of the value of E_σ.

The reaction constants, ρ, used in calculating E_σ are those determined from corresponding reaction series of *m*- and *p*-substituted benzoates (Table III), that is, the corresponding Hammett reaction constants. Data for two identical acid- and base-catalyzed reaction series of *o*-substituted benzoates are not available. However, the reaction constant, f, of Eq. (1) is essentially unity for all reaction series for which data is available[1]; that is, log k/k_0 values show no appreciable dependence upon structure in the alkyl component, solvent, or attacking reagent. It therefore appears justifiable to use directly log k/k_0 values for each of the reaction series listed in Table II in calculating E_σ values. The values of E_σ given in Table IV are averages of the values obtained for each of the possible combinations of the available data. These values are relative to the CH_3 group, since it is not possible by this method to obtain values relative to unsubstituted benzoates.[1]

Aliphatic Esters.—Listed in Table IV are E_σ values for a large number of aliphatic substituents

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(18) Log k/k_0 is proportional to the relative free energy of activation.

(19) Equation (3) cannot be expected to hold for cases involving an attractive interaction between substituent and ester function, such as internal H bonding or the type of interaction proposed by B. Rabinovitch and C. H. Schramm, THIS JOURNAL, **72**, 627 (1950). Equation (3) also does not hold for α,β-unsaturated substituents—see later discussion.

TABLE V

STERIC PARAMETERS, E_S, FOR ORTHO-SUBSTITUTED BENZOATE AND ALIPHATIC SUBSTITUENTS AT 25°

Ortho-substituted benzoates

Substituent	E_s	n	r	Substituent	E_s	n	r
OCH_3	+0.97	3	0.00	CH_3	0.00	5	0.00
OC_2H_5	+ .86	3	.04	I	− .20	4	.07
Cl	+ .18	5	.08	NO_2	− .71	5	.11
Br	+ .01	5	.17	C_6H_5	− .90	1	..

Aliphatic series

Substituent	Acyl component E_s	Alkyl component E_s	Substituent	Acyl component E_s	Alkyl component E_s
H	+1.24	....	Cyclo-C_7H_{13}	−1.10	
CH_3	0.00	0.00	$(CH_3)(C_6H_5)CH$	−1.19	
C_2H_5	− .07	− .09	t-C_4H_9	−1.54	
Cyclo-C_4H_7	− .06		$(C_6H_5)(C_2H_5)CH$	−1.50	
$ClCH_2$	− .19		t-$C_4H_9CH_2$	−1.74^a	
n-C_3H_7	− .36		$(C_6H_5)_2CH$	−1.76	
n-C_4H_9	− .39		(CH_3)(neopentyl)CH	−1.85^a	
n-C_5H_{11}	− .40		$(Br)_2CH$	−1.86	
i-C_5H_{11}	− .35		$(C_2H_5)_2CH$	−1.98	
n-C_8H_{17}	− .33		Cl_3C	−2.06	
t-$C_4H_9CH_2CH_2$	− .34^a		$(n\text{-}C_3H_7)_2CH$	−2.11	
$C_6H_5CH_2$	− .38		$(i\text{-}C_4H_9)_2CH$	−2.47	
$C_6H_5CH_2CH_2$	− .43		$(Br)_3C$	−2.43	
$C_6H_5CH_2CH_2CH_2$	− .45		$(CH_3)_2$(neopentyl)C	−2.57^a	
i-C_3H_7	− .47	− .42	(Neopentyl)$_2$CH	−3.18^a	
Cyclo-C_5H_9	− .51		$(CH_3)_2(t\text{-}C_4H_9)CH$	−3.33^a	
Cyclo-C_6H_{11}	− .79		$(CH_3)_2(t\text{-}C_4H_9)C$	−3.9^a	
i-C_4H_9	− .93	− .23	$(C_2H_5)_3C$	−3.8^a	
C_6H_5	.....	− .30	$(CH_3)(t\text{-}C_4H_9)$(neopentyl)	−4.0^a	
Cyclo-$C_6H_{11}CH_2$	− .98				
$(CH_3)(C_2H_5)CH_2$	−1.13				

[a] Calculated from data for acid-catalyzed esterification of carboxylic acids in methanol. Data kindly sent author by Prof. M. S. Newman, to be published soon by Newman, K. Loening and A. B. Garrett.

obtained by Eq. (2), and also n and r values for each.

Values of ρ for the aliphatic series cannot be obtained in the same manner (or on a comparable scale) as for benzoates. It is, therefore, convenient to define the quantity ($\rho_B - \rho_A$) as unity for certain standard reaction series. For aliphatic acyl-substituents, the reaction series previously chosen as standards (see Table II[1]) conveniently serve this purpose. In as much as these include identical acid- and base-catalyzed reaction series (reaction series 1 of parts 1a and 1b of Table II), E_σ in this case is obtained directly from the substituent constants, A, of Table I of the previous paper by the resulting simplified form of Eq. (2)

$$E_\sigma = A_B - A_A = (\log k/k_0)_B - (\log k/k_0)_A$$

The few values of E_σ given in parentheses were obtained (in the absence of the appropriate data) from $(\log k/k_0)_B - (\log k/k_0)_A$ for the base- and acid-catalyzed hydrolysis of methyl esters in water at 25° (data of footnote 18, ref. 1; see ref. 8, p. 211, 213), and should be regarded as tentative.

For aliphatic alkyl-substituents, the greatest number of comparisons possible at present is for acid- and base-catalyzed hydrolysis of acetate esters in water at 25°. Accordingly ($\rho_B - \rho_A$) is here defined as unity, and E_σ values listed in Table VI were obtained from these data by the relationship $E_\sigma \equiv (\log k/k_0)_B - (\log k/k_0)_A$.

Substituent Steric Parameters

Ortho-substituted Benzoates.—In Table V are given average values of E_s obtained by Eq. (3) using ρ values given in Table III and E_σ values listed in Table IV. Values of n, the number of reactions for which data are available, and r, the median deviation of the value of E_s, are also given. The values of E_s are relative to the o-methyl substituent. For the phenyl group, E_s was obtained from the data of ref. 16 using as the value of E_σ the Hammett σ value for the p-C_6H_5 substituent.

Aliphatic Substituents.—An exact solution of Eq. (3) is not possible in this case. However, it is probably a good approximation to assume that the susceptibility of an acid-catalyzed reaction to polar effects is negligible compared to the susceptibility of a base-catalyzed reaction, *i.e.*, $\rho_A = 0$ and $\rho_B = 1$ for those reaction series previously selected to determine E_σ values ($\rho_B - \rho_A \equiv 1$). In the case of meta- and para-substituted benzoates the approximation $\rho_B - \rho_A \cong \rho_B$ is good (see Table III).

For acyl substituents, the approximate values of E_s listed in V were obtained by the relations $E_s \equiv A_A$, or $E_s \equiv A_B - E_\sigma$ where A_A and A_B values are those listed in Table I[1] and E_σ values are obtained from Table IV.

For alkyl substituents, the approximate values of E_s given in Table V were obtained by the relation E_s = (log $k/k_0)_A$ where log k/k_0 refers to the hydrolysis of acetate esters in 62% (wt.) aqueous acetone at 30° (see references of reaction series 1 of part 2a of Table II[1]).

Discussion

E_σ-Values and Structure.—A comparison of the E_σ-values for *o*-benzoate substituents given in Table IV with the corresponding values of A (Table I—previous paper), or E_s values of Table V shows no direct relationship exists between the electron displacement substituent constants and the free energy or steric substituent constants. Hammett's σ values for corresponding *m*- and *p*-benzoate substituents are listed in Table IV for comparison with the E_σ values for the *o*-benzoate substituents.

It is apparent that electron displacement effects are nearly the same for a given substituent in the ortho and para positions. This result is not entirely unexpected since the resonance effect of a benzoate substituent is equivalent in the ortho- and para-positions; it favors the view that the inductive effect operates in the benzoate series principally through the π-bonds and that this effect is also equivalent in the ortho and para positions.

E_σ values for some aliphatic acyl substituents taken from Table IV are listed below in two series to emphasize the agreement of these electron displacement parameters with the qualitative English school theory of polarity of aliphatic groups. The corresponding free energy substituent constants, A_A and A_B, for acid- and base-catalyzed reactions, are also listed.[1]

Series I

Subst.	$E\sigma$	A_B	$A_A = E_s$
H	+1.22	+2.46	+1.24
CH_3	0.00	0.00	0.00
C_2H_5	− .24	− .31	− .07
n-C_3H_7	− .28	− .64	− .36
n-C_4H_9	− .32	− .71	− .39
i-C_4H_9	− .31	−1.24	− .93
i-C_3H_7	− .47	−0.94	− .47
t-C_4H_9	− .84	−2.38	−1.54

Series II

Subst.	$E\sigma$	A_B	$A_A = E_s$
$(C_6H_5)_2CH$	+0.67	−1.09	−1.76
$C_6H_5CH_2$	+ .56	+0.17	−0.38
$C_6H_5CH_2CH_2$	+ .29	− .14	− .43
$C_6H_5(C_2H_5)CH$	+ .08	−1.42	−1.50
CH_3	.00	0.00	0.00
Cyclo-$C_6H_{11}CH_2$	− .15	−1.13	−0.98
$(C_2H_5)_2CH$	− .72	−2.70	−1.98

In series I electron release, as expected, increases appreciably in each case in the order H < CH_3 < C_2H_5 < *i*-C_3H_7 < *t*-C_4H_9 as shown by the increasingly negative values of E_σ.[20] Successive substitution of an α-methyl group results in a successive decrease in E_σ of about 0.25; the effect appears somewhat greater on the third substitution. As further expected the substituents C_2H_5, *n*-C_3H_7, *n*-C_4H_9 and *i*-C_4H_9, obtained by β-alkyl substitution, all have nearly the same E_σ values. In series II the order of increasing E_σ values is that expected based upon electron withdrawal by a phenyl group. By reference to Table IV it can be seen that the interposition of a CH_2-group between a given substituent and the ester function generally reduces E_σ by a factor of three.[21] This effect appears to be somewhat greater (factor of 4 or 5) for the series H–CH_2, CH_3–CH_2, C_2H_5–CH_2– and *i*-C_3H_7–CH_2–.

It is important to notice that the conclusions reached above do not apply to either of the free energy substituent constants, A_A or A_B, from which the E_σ values are derived.

One might expect to find parallel electron displacement effects in the acyl and alkyl components of an ester. This is confirmed in the limited number of cases where comparison is possible between corresponding E_σ values for the two components (see Table IV). Further, the data available for the acid- and base-catalyzed hydrolysis of a series of glycerate esters in water at 25°[22] fit the relationship log k_B/k_A = 1.45 (E_σ) − 1.52, where E_σ is the electron displacement parameter for the aliphatic acyl-substituent corresponding to that in the alkyl-component of the glycerate ester.

OBSERVED AND CALCULATED VALUES OF LOG k_B/k_A

Glycerate ester, CH_2OH—CHOHCOOR	(log k_B/k_A) exptl.	(log k_B/k_A) calcd.	*d*
CH_3	−1.56	−1.52	0.04
C_2H_5	−1.87	−1.87	.00
n-C_3H_7	−1.93	−1.93	.00
n-C_4H_9	−1.94	−1.98	.04
i-C_4H_9	−1.97	−1.97	.00
i-C_3H_7	−2.24	−2.20	.04

It is interesting to observe that the base-catalyzed hydrolysis of this series of glycerate esters is more susceptible (in the alkyl-component) to polar substituents, (since $\rho_B = \rho_A = +1.45$; $\rho_B \cong +1.45$) than (in the acyl-position) are those reactions taken as standards of reference ($\rho_B - \rho_A \equiv +1.00$; $\rho_B \cong +1.00$). Although the agreement is good for the cases given above, a quantitative parallelism between the electron displacement effects of substituents in the acyl and alkyl components probably should not be expected in every case. For, in the acyl case the substituent is adjacent to carbon and in the alkyl case to oxygen, so that different specific group interactions may result. This may account for the fact that the value of E_σ for the easily polarizable phenyl group, although qualitatively the same, is somewhat lower in the alkyl than in the acyl position (+1.04 compared to +1.49).

The nature of the conclusions reached in this section support the belief that the E_σ values listed in Table IV are a true measure of the polarity of substituent groups.

(20) $E\sigma$ values for these substituents do not parallel corresponding Hammett σ values for these substituents in the para position of a benzene ring. This result suggests that the former are determined largely by inductive and polarization effects whereas the latter have important contributions from resonance of the Baker-Nathan or hyperconjugation type.

(21) For a similar conclusion see C. G. Derick, THIS JOURNAL, **33**, 1152 (1911); (b) also G. E. K. Branch and M. Calvin, "The Theory of Organic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1941, p. 218.

(22) C. M. Groocock, C. K. Ingold and A. Jackson, *J. Chem. Soc.*, 1057 (1930); the ratio k_B/k_A was determined from the *p*H at which the hydrolysis rate is a minimum.

TABLE VI

THE EFFECT OF METHYL, ETHYL AND PHENYL SUBSTITUTION IN THE α-, β- AND γ-POSITIONS OF THE ACYL COMPONENT OF AN ESTER ON THE STERIC SUBSTITUENT PARAMETER, E_s

Substituent	Methyl			Ethyl			Phenyl		
Position	α	β	γ	α	β	γ	α	β	γ
No. substitutions 1	−0.07	−0.36	−0.39	−0.36	−0.39	−0.40	−0.38	−0.43	−0.45
2	− .47	− .93	− .35	−1.98	....	....	−1.76	....	....
3	−1.54	−1.71	− .34[a]	−3.8[a]	....	....	<−1.76[b]	....	....

E_s Values and Structure.—The transition state for base- or acid-catalyzed hydrolysis or esterification of normal esters is probably nearly tetrahedral in structure, whereas sp^2 bonding in an ester or acid requires a linear structure with bond angles of 120°. Consequently in the activation process the coördination number of carbonyl carbon is increased from three to four, and the atoms or groups in the ester bonded to this carbon atom are forced from positions of approximately 120 to 109° apart. In the presence of bulky adjacent groups this may result in[23]: (1) steric strain in the transition state due to increased repulsions between non-bonded atoms[3a,b]; (2) steric hindrance of internal molecular motions resulting from increased interference of adjacent groups or atoms with the internal motions of one another.[3d]

Either or both of these two steric factors would be expected to increase with increasing steric requirements of size and position of substituent groups. The order of the gross steric effect constants, E_s, given in Table V support this conclusion. For ortho-benzoate substituents, E_s values decrease in the order $OCH_3 > OC_2H_5 > Cl > CH_3$, $Br > I > NO_2 > C_6H_5$. If the reasonable assumption is made that as the result of resonance the unsymmetrical OR,[24] NO_2 and C_6H_5 groups have preferred positions in, or as nearly as possible in, the plane of the benzene ring, Fisher–Hirschfelder–Taylor atom models show the above order to be that of increasing approach or overlap of normal positions between substituent and adjacent ester function. Similarly, the order of increasing approach or overlap of ester function with the aliphatic substituents listed in Table V appears on the basis of models to correspond in general to that of decreasing E_s values.

The gross steric effect is very sensitive to both group and position. The effect on E_s of substitution of methyl, ethyl and phenyl groups in the α-, β- and γ-positions of the acyl component of an ester is summarized in Table VI. For methyl groups increasing the number of substitutions decreases reactivity because of steric influence, as can be seen by the decreasing values of E_s, both for α- and β-substitution. In every case methyl substitution is appreciably more effective in the β- than α-position. However, in the γ-position the result of a second or third methyl substitution is essentially equivalent to that for the first in either the β- or γ-position. The larger ethyl and phenyl groups behave similarly to one another. Both are markedly more effective in retarding reactivity when substituted in the α-position than methyl. Yet single substitution of ethyl or phenyl in the β- or γ-positions gives rise to results essentially equivalent to a corresponding methyl substitution, or to α-substitution of one of these groups.

Table V discloses the following additional information. Di- or tri-α-substitution of alkyl groups, particularly highly branched ones, or bulky atoms such as chlorine or bromine, give rise to very large steric effects. The *t*-butyl group is noticeably more effective in this regard than the neopentyl. When two α-alkyl substituents are tied down in a cyclic structure the gross steric effect is greatly reduced. E_s increases from −1.98 to −0.51 in going from $(C_2H_5)_2CH-$ to the cyclopentyl group, and from $(C_2H_5)(CH_3)CH-$ to the cyclobutyl group the steric effect is essentially reduced to that of the standard methyl group (E_s increases from −1.13 to −0.06). Although two β-methyl substitutions produce a large steric effect in the acyl component of an ester ($E_s = -0.93$), in alkyl component the effect is much less ($E_s = -0.23$).

It is interesting to note the qualitative though not quantitative parallel between E_s and E_σ values for the acyl substituents: H, CH_3, C_2H_5, *i*-C_3H_7 and *t*-C_4H_9—see series I listed previously. Although steric factors are very sensitive to position and nature of the substituent and functional group, this result at least suggests an inherent difficulty in making a decision on a *qualitative* basis as to whether reactivity in an aliphatic reaction series is primarily determined by polar or steric factors based upon relative reaction rates for this limited series of aliphatic substituents.

α,β-Unsaturated Substituents.—The E_σ-value (+1.49) of the phenyl group indicates that this group is a strong electron withdrawing substituent, a factor which should increase the relative rate of base-catalyzed esterification or hydrolysis of a benzoate. Yet, for both acid- and base-catalysis, benzoate esters are markedly less reactive than corresponding acetates (see A values of C_6H_5 in Table I[1]). This apparent anomaly is not likely attributable to a steric factor, for in the previous section it was pointed out that the gross steric effect of a phenyl group is comparable to that of an ethyl group for α,- β- and γ-substitution and for a single substitution this is relatively small. The best explanation appears to lie with the resonance which occurs in benzoates between the carbonyl group and the benzene ring. This resonance has been estimated to stabilize benzoates by 4 to 7 kcal. on the basis of resonance energies calculated from heats of combustion.[25] Westheimer and Metcalf[26]

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[23] Relationships between E_σ and E_s values and energies and entropies of activation for these reactions will be the subject of a future publication. Included will be an approximate separation, for a number of aliphatic substituents, of the gross steric effect (E_s) into contributions from these two distinctly different steric factors.

[24] With R oriented away from the ester function.

[25] (a) Reference 21b, p. 285; (b) an average value of 7 kcal. is obtained using appropriate values of resonance energies given by G. W. Wheland, "The Theory of Resonance," John Wiley and Sons, Inc., New York, N. Y., 1944, pp. 69, 70.

[26] F. H. Westheimer and R. P. Metcalf, THIS JOURNAL, **63**, 1339 (1941); see also ref. 25 (b), p. 278.

have pointed out that since the transition state in base-catalyzed hydrolysis of a benzoate ester is saturated, the resonance between the carbonyl group and the benzene ring is not possible in the transition state. Because of the similar reaction mechanism, this state of affairs should also apply to acid catalysis. That is, the relative free energy of activation for the acid- or base-catalyzed esterification or hydrolysis of a benzoate should be greater by the 4 to 7 kcal. of essentially non-polar resonance stabilization in the ester (or acid) which must be overcome in the activation process.[27] Such a resonance contribution is not removed when $(\log k/k_0)_A$ is subtracted from $(\log k/k_0)_B$ to obtain a measure of the polarity of the phenyl group.

Equation (3), therefore, must not be applicable to any case involving a "non-polar" resonance effect. Only for α,β-unsaturated substituents, however, does it seem likely that such an effect can be important. The above explanation also appears to explain the similar apparent anomaly between E_σ values and the reactivity of cinnamates and crotonates (see Tables I and IV).

The idea commonly expressed that a phenyl group may act as both an electron sink or an electron donor now receives clarification. The former effect is according to the present results a polar one whereas the latter is manifest as a non-classical resonance effect. When the phenyl group is present in the alkyl rather than the acyl component, resonance between this substituent and the carbonyl group is not possible, and the phenyl group acts as an electron sink. Accordingly, in contrast to the benzoate case, the base-catalyzed hydrolysis of a phenyl ester proceeds at a markedly greater rate than for a corresponding methyl (or ethyl) ester. For a similar reason a phenylacetate ester is hydrolyzed more readily by base than a corresponding acetate (or *n*-butyrate) ester. Crowe and Lynch[28] have interpreted the facts that benzoic is stronger than acetic acid in water at 25° and that benzamide reacts more readily than acetamide with formaldehyde on the basis of electron attraction by the phenyl group. In both of these cases resonance between carbonyl group and the benzene ring remains essentially undisturbed between initial and final states so that the phenyl group effects reactivity only through its electron attraction.

Application of Results

Reaction Mechanism.—For Eqs. (2) and (3) to be valid it is apparent that the reaction mechanism for any member of the acid- or the base-catalyzed reaction series must not change. Conversely, Eq. (2) should serve as a tool to demonstrate changes in reaction mechanism in certain cases.

Using the methods of the previous section and the data for acid- and base-catalyzed hydrolysis of acetate esters in water at 25°, a value of −2.02 is obtained for E_σ for the t-C_4H_9 substituent in the alkyl-position. The corresponding value for t-C_4H_9 in the acyl-component is −0.84. In accordance with previous discussion, the result for the alkyl-component is unreasonable and must be explained on a basis of a change in reaction mechanism, probably for the acid-catalyzed hydrolysis. Cohen and Schneider[29] have proposed that the acid-catalyzed hydrolysis of *t*-butyl esters proceeds by a carbonium ion type mechanism. The lack of correspondence between E_σ values obtained for the $C_6H_5CH_2$– group in the acyl and alkyl components (+0.56 and +0.06, respectively) suggests the possibility that a similar reaction mechanism may be involved to some extent in the acid-catalyzed hydrolysis of benzyl esters.

To Other Reactions. E_s Values.—The sensitivity of steric factors to structure of substituents in esterification and hydrolysis of esters was pointed out in a previous section. Steric factors are also sensitive to structure of the functional group and the nature of the reaction transition state. The specific nature of the ortho effect in various reactions has been pointed out by Hammett.[30]

An illustration follows of the nature of the sensitivity of steric factors to structure at the reaction center. The rates of acid-catalyzed hydrolysis of *o*-substituted benzamides in water at 100°[31] fit the equation, $\log k/k_0 = E_s\ (+0.80) - 0.06$ (where k_0 = rate constant for *o*-toluamide, and E_s is the steric substituent parameter from Table V corresponding to the *o*-substituted benzamide whose rate constant is k).

OBSERVED AND CALCULATED VALUES OF LOG k/k_0

Substituent	$(\log k/k_0)$obsd.	$(\log k/k_0)$calcd.	d
OCH_3	+0.72	+0.72	0.00
OC_2H_5	+ .63	+ .63	.00
Cl	+ .16	+ .08	.08
CH_3	.00	− .06	.06
Br	− .11	− .05	.06
I	− .32	− .22	.10
NO_2	− .61	− .63	.02

However, a linear relationship does not exist between $\log k/k_0$ values for the acid-catalyzed hydrolysis of a series of thiolacetates at 30°[32] and E_s values from Table V for corresponding alkyl substituents.

Substituent (alkyl component)	$\log k/k_0$	E_s
CH_3	0.00	0.00
C_2H_5	− .16	− .09
i-C_3H_7	− .27	− .42
t-C_4H_9	− .40	-1.5^a
i-C_4H_9	− .34	−0.23

[a] Estimated value (on basis of similar reaction mechanism). Observed value −0.81.

Since the transition states for the hydrolysis of benzamides and thiolacetates are probably similar in nature to those for ester hydrolysis, these results are interpreted as follows. The larger diameter of sulfur than oxygen alters the nature of the re-

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(27) For confirmatory evidence see H. A. Smith, J. B. Conley and W. H. King, THIS JOURNAL, **73**, 4633 (1951).

(28) G. A. Crowe, Jr., and C. C. Lynch, *ibid.*, **72**, 3623 (1950).

(29) S. G. Cohen and A. Schneider, *ibid.*, **63**, 3382 (1941). See also ref. 2, p. 348 and ref. 1, footnote 24.

(30) Reference **8**, p. 204.

(31) E. Reid, *Am. Chem. J.*, **24,** 397 (1900). The susceptibility of this reaction to polar substituents is so small (ρ = +0.16, ref. 8, p. 189) that the effect of polarity is negligible.

(32) (a) R. N. Rylander and D. S. Tarbell, THIS JOURNAL, **72**, 3021 (1950); (b) J. R. Schaefgen, *ibid.*, **70**, 1308 (1948); $\log k/k_0$ values given here are averages of those obtained for 43% (wt.) aq. acetone and 62% (wt.) aq. acetone (maximum deviation from average = 0.05).

action center sufficiently that the steric effects of alkyl substituents are different for thiol than normal esters. On the other hand, because of the similar diameters of nitrogen and oxygen the steric effects of *o*-substituents in benzamides and benzoates are closely related.

Because of the specific nature of steric factors it therefore seems likely that the general quantitative utility of the steric substituent parameters, E_s, for esters (Table V) will be quite limited.

In a strictly qualitative manner there are a number of reactions whose relative rates parallel the ester steric substituent constants. The relative rates for the reaction of thiosulfate ion with alkyl halides,[3e,f] the bromination of monoalkylbenzenes,[33] the reactions of aliphatic alcohols with phenyl isocyanate[34] and *p*-nitrobenzoyl chloride[35] in general parallel E_s values of Table V.

A more nearly quantitative parallelism occurs in the case of the rates of reaction of 2-monoalkylpyridines with methyl iodide in nitrobenzene at 30°.[36] Below are given values of log k/k_0 (k_0 = rate constant for 2-methylpyridine) for this reaction for several alkyl substituents and values of (+2.0) E_s for corresponding aliphatic acyl substituents taken from Table V.

Substituent	log k/k_0	+2.0 E_s
CH_3	0.00	0.00
C_2H_5	− .32	− .14
i-C_3H_7	− .81	− .94
t-C_4H_9	−3.25	−3.08

E_σ Values. To Reaction Series Having Nearly Constant Steric Factors.—In many such a case as this, if E_σ values are true measures of general polarity, one would expect to find a nearly quantitative parallel between E_σ values and corresponding relative free energy changes (rate or equilibrium). The initial condition, however, puts strong limitations (particularly in the aliphatic series) on the type of reaction that may be considered.

All of the ionization constant data for *o*-substituted benzoic acids in water at 25°[37a] available for comparison have been found to fit, approximately, the relationship log K/K_0 = (+1.78) E_σ + 0.43. (where k_0 = ionization constant of benzoic acid, and E_σ is the electron displacement parameter corresponding to the *o*-substituted benzoate whose ionization constant is K).

OBSERVED AND CALCULATED VALUES OF LOG K/K_0

Substituent	log K/K_0 exptl.	log K/K_0 calcd.	*d*
OCH_3	+0.11	+0.01	0.10
CH_3	+ .29	+ .43	.14
C_6H_5	+ .74	+ .75	.01
Cl	+1.26	+1.09	.17
Br	+1.35	+1.11	.24
I	+1.34	+1.11	.23
NO_2	+2.03	+2.12	.09

On the other hand, a plot of log K/K_0 (K_0 = ionization constant of acetic acid) for the ionization constants of aliphatic carboxylic acids in water at 25°[37] *vs.* corresponding E_σ values for aliphatic acyl substituents does not give a good linear relationship (see Fig. 1).

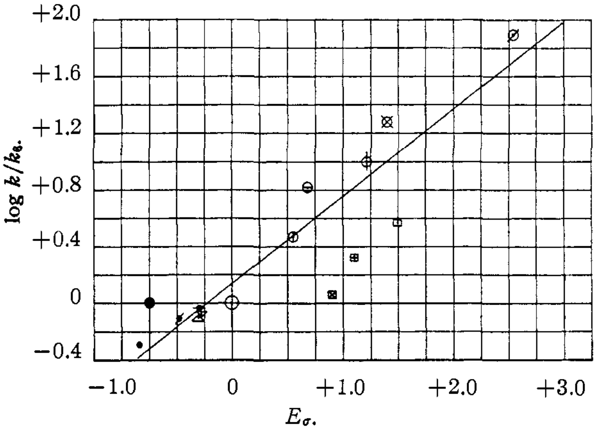

Fig. 1.—Plot of log K/K_0 for the ionization constants of aliphatic carboxylic acids, RCOOH, in water at 25° *vs.* corresponding E_σ values for aliphatic acyl substituents. R is given by the following symbols: ∅, CH_2Cl-; ⊗, CH_3OCH_2-; ⏀, H–; -⊖-, $(C_6H_5)_2CH$–; □, C_6H_5; ⊞, $C_6H_5CH{=}CH$–; ⊠, $CH_3CH{=}CH$–; ⦶, $C_6H_5CH_2$; ○, CH_3–; -●-, *i*-C_4H_9–; ▽, *n*-C_3H_7–; Δ, C_2H_5, *n*-C_4H_9, *n*-C_5H_{11}; ⸝●′, *i*-C_3H_7–; ◎, $(C_6H_5)_2CH$–; ●, *t*-C_4H_9–.

These results are given the following interpretations. The relative ionizations of those *o*-substituted benzoates listed are determined by polar effects of substituents and are not dependent to an appreciable degree upon steric factors.[38] For aliphatic carboxylic acids, relative ionizations are not determined solely by polar effects of substituents but probably by steric factors as well.[39a,b] The substituents which show particular departure from linearity (acid strengthening), $(C_2H_5)_2CH$– and $(C_6H_5)_2CH$–, are those which have large negative steric substituent constants for esterification and hydrolysis. The α,β- unsaturated substituents C_6H_5—, $C_6H_5CH{=}CH$— and $CH_3CH{=}CH$—, also show departures (acid weakening) but this may be the result of a specific resonance effect. However, the fact that Fig. 1 tends to a linear relationship indicates that steric (or other) factors involved in these ionizations are not large, particularly in comparison to those in the esterification or hydrolysis of corresponding esters. The existence of only relatively small steric factors in the ionization of carboxylic acids is reasonable on the basis that there is probably no appreciable change in bond angles about the carbonyl group between initial and final states.

The relative rates of hydrolysis in water at 25° of formaldehyde acetals of the following aliphatic

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(33) E. Berliner and F. Berliner, THIS JOURNAL, **72**, 222 (1950).

(34) T. L. Davis and J. McC. Farnum, *ibid.*, **56**, 883 (1934).

(35) J. F. Norris and A. A. Ashdown, *ibid.*, **47**, 837 (1925).

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

(37) (a) Data of J. F. J. Dippy and co-workers, see ref. 8, p. 186, 205, footnotes 2 and 57; (b) J. F. J. Dippy, *J. Chem. Soc.*, 1222 (1938); (c) W. L. German, G. H. Jeffery and A. I. Vogel, *ibid.*, 1604 (1937); (d) G. F. White and H. C. Jones, *Am. Chem. J.*, **44**, 159 (1910).

(38) The failure of the Hammett relationship between rate and equilibrium (ref. 9) for *o*-substituted benzoates is accordingly the result of steric factors operating only in rates of esterification and hydrolysis.

(39) (a) Reference (8), p. 87; (b) H. C. Brown, M. D. Taylor and S. Sujishi, THIS JOURNAL, **73**, 2465 (1951).

alcohols[40] are found to fit the relationship $\log k/k_0 = -3.45\ (E_\sigma)$, where k_0 is the rate constant for the formaldehyde acetal of methanol, and E_σ is the acyl substituent constant corresponding to the alkyl group in the acetal whose rate constant is k.

OBSERVED AND CALCULATED VALUES OF LOG k/k_0

Alcohol, ROH, of formaldehyde acetal where R is	$(\log k/k_0)$obsd.	$(\log k/k_0)$ calcd.	d
CH_3	0.00	0.00	0.00
C_2H_5	+ .93	+ .87	.05
n-C_3H_7	+ .97	+ .96	.01
i-C_3H_7	+1.67	+1.62	.05
n-C_4H_9	+0.97	+1.10	.13
i-C_4H_9	+1.11	+1.07	.04

This series is admittedly a limited one, but the fit is extremely good. The extension of this series to other alcohols, particularly those producing large polar effects would be desirable. The large negative proportionality constant, −3.45, indicates that this reaction is especially susceptible to polar substituents and is accelerated by electron release. The fact that steric factors are shown by these results to be of essentially no importance in determining relative reactivity indicates that there is probably essentially the same distribution of bond angles in the hydrolysis transition state as in the starting acetal.

To Reaction Series for which Steric Factors are not Constant.—If a method of evaluating the total steric effect of each substituent is available, subtraction of these quantities from relative free energy changes may yield results which parallel the E_σ values of Table IV. For example, values of the quantity $(\log k/k_0)_B - (\log k/k_0)_A$[41] obtained from the data for the base- and acid-catalyzed hydrolysis of thiolacetates in 43% (wt.) aqueous acetone at 30°[42] agree closely with values calculated from the relation $(\log k/k_0)_B - (\log k/k_0)_A = (+0.69)\ E_\sigma + 0.20$, where E_σ is the aliphatic acyl electron displacement parameter (for normal esters) corresponding to the alkyl group in the thiolacetate whose rate constant is k.

Substituent	$(\log k/k_0)_B - (\log k/k_0)_A$ Exptl.	Calcd.	d
CH_3	0.00	+0.20	0.20
C_2H_5	+ .06	+ .04	.02
i-C_3H_7	− .10	− .12	.02
i-C_4H_9	− .02	− .01	.01
t-C_4H_9	− .39	− .38	.01

The probable conclusions to be drawn from these results are that the base-catalyzed hydrolysis of thiolacetates is less susceptible (since $\rho_B - \rho_A = +0.69$; $\rho_B \cong 0.69$) to polar alkyl substituents than the glycerate ester reaction series previously referred to ($\rho_B - \rho_A = +1.45$; $\rho_B \cong +1.45$) and therefore that the inductive effect of alkyl groups is transmitted more effectively by the more polarizing oxygen than sulfur.

Acknowledgment.—The author wishes to express his thanks to Professor L. P. Hammett for numerous discussions relating to the effect of structure on reactivity. The suggestions of Dr. N. C. Deno and one of the Referees in the preparation of this and the previous manuscript are gratefully acknowledged.

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

[41] $(\log k/k_0)_A$ should be an approximate measure of steric factors associated with each thiolacetate.

[42] Data of ref. 32. The rate constant used for the base catalyzed hydrolysis of methyl thiolacetate in 43% (wt.) aqueous acetone at 30° was calculated from the corresponding rate constant at 20° using a value of 12.7 kcal. for the activation energy.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF NEW YORK UNIVERSITY]

Base Catalysis in the Decomposition of Diazomalonic Acid

BY CECIL V. KING AND PAULINE KULKA

RECEIVED NOVEMBER 14, 1951

Data are now available for the decomposition rates when potassium diazomalonate is dissolved in dilute strong acid (perchloric); in buffers of weak acids (trimethylacetic, acetic, glycolic, anilinium perchlorate); and in buffers of intermediate acids (chloroacetic, phosphoric, glycinium perchlorate). In all these solutions the rates may be explained as catalysis, by water and other bases, of the reactions of both the bivalent and univalent (acid) anions of diazomalonic acid.

It was shown in a previous paper[1] that diazomalonic acid decomposes at measurable rates in dilute perchloric acid, and that in acetate and aniline buffers the reaction is catalyzed by water and by the basic components of the buffers. The over-all reaction was assumed to be

$$N_2C(COO)^{=} + H_3O^+ \longrightarrow N_2 + CO_2 + CH_2OHCOO^- \quad (1)$$

The second ionization constant of diazomalonic acid was estimated (wrongly, later experiments show) from the rates.

In strong acid, the bimolecular reaction of hydrogen ion with the bivalent diazo ion was previously assumed to be rate controlling. Water catalysis and possible reaction of the acid diazo anion were not considered. However, if in weak acid buffers the entire reaction is one of water and anion catalysis, there seems no reason why water catalysis should not be present in solutions of strong acid. Further, in phosphate buffers, it was found that as increasing amounts of phosphoric acid were added to a fixed concentration of sodium primary phosphate, the rate increased too much to be explained by the increases in hydrogen ion and phosphate ion unless there were simultaneous reactions of the acid diazo ion. If this ion reacts in buffers, it is necessary to assume that it also reacts in perchloric acid solutions. The entire reaction in strong acid is then a water catalysis, and the effect of hydrogen ion, in addition to completing the reaction, is to shift the second ionization equilibrium of the diazomalonic acid.

In all solutions the rate-controlling steps are then

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[1] C. V. King, P. Kulka and A. Mebane, THIS JOURNAL, **72**, 1906 (1950).