where h is a scalar. Now assume that $f(V_{n+1} + xD_n)$ is approximately a quadratic in x (in practice the validity of this assumption depends mainly on the choice of h). Then

$$f(V_{n+1} + xD_n) = f_0 + u\Delta f + \frac{u(u-1)}{2}\Delta^2 f$$

where

$$u = \frac{x}{h}, \Delta f = f_1 - f_0, \Delta^2 f = f_2 - 2f_1 + f_0$$

This expression for f may now be minimized with respect to x by setting the derivative equal to zero. One finds that $f(V_{n+1} + sD_n)$ is minimum for

$$s = h\left(\frac{1}{2} - \frac{\Delta f}{\Delta^2 f}\right)$$

and the vector $V = V_{n+1} + sD_n$ may be used to start a new series of iterations. In the course of the problem values of s of 10–20 were usual, although much larger numbers were encountered in certain circumstances. The size of s is, of course, dependent to some extent on the number of iterations between extrapolations. This number was varied somewhat in the course of running the problem, though it was usually found that three to five iterations gave good results. Running time for this problem, starting either with given approximations or with all starting values equal to unity, was about one hour.

CAMBRIDGE 39, MASSACHUSETTS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Correlation of Rates of Solvolysis with a Special Two-parameter Equation[1]

BY C. GARDNER SWAIN, DONALD C. DITTMER[2] AND LAURA E. KAISER

RECEIVED AUGUST 30, 1954

A special two-parameter equation, $\log (k/k^0)_A - \log (k/k^0)_{A^0} = ab$, is tested, where k is the first-order rate constant for solvolysis of any organic chloride or bromide (A) or of the standard compound, methyl bromide (A^0), in any solvent, k^0 is the corresponding rate constant in a standard solvent (80% ethanol) at the same temperature, a is a constant depending on only the chloride or bromide and b is a constant depending on only the solvent. Values of a are reported for 15 compounds ranging from picryl chloride to t-butyl chloride, and values of b for 19 solvents ranging from triethylamine to formic acid. These values were determined from the above equation and a total of 124 $\log (k/k^0)$ data by the method of least squares. The minimum, mean and maximum ranges in observed rates for compounds are factors of 10, 2×10^3 and 3×10^6, respectively. The mean and maximum errors in the calculated rates are factors of 1.5 and 7.6. A measure of goodness of fit which is applicable to any correlation of rate or equilibrium constants is proposed and is evaluated for typical applications of the Brönsted catalysis law, the Hammett equation, and various two- and four-parameter correlations of rates of solvolysis.

This paper describes a test of a special two-parameter equation

$$\log (k/k^0)_A - \log (k/k^0)_{A^0} = ab \quad (1)$$

where k is the first-order rate constant for solvolysis of any organic chloride or bromide (A) or of the standard compound, methyl bromide (A^0), in any solvent, k^0 is the corresponding rate constant in a standard solvent (80% ethanol–20% water) at the same temperature, a is a constant depending on only the chloride or bromide and b is a constant depending on only the solvent.

As the standard solvent we chose 80% ethanol–20% water by volume because more data were available for it than for any other solvent. Table I lists $\log k_0$ in 80% ethanol for all of the 15 compounds not previously given in Table I of the previous paper.[3]

TABLE I

ADDITIONAL RATES IN 80% ETHANOL

Compound[a]	$\log_{10} k^0$, sec.$^{-1}$	Temp., °C.	Ref.
PicCl	−5.30	50	5
$PhCOCH_2Br$	−5.80	50	5
i-BuBr	−7.61	50	6
t-BuBr	−3.44	25	7

[a] Pic = picryl (2,4,6-trinitrophenyl); Ph = C_6H_5 or p-substituted C_6H_4; Me, Et, Pr, Bu = CH_3, C_2H_5, C_3H_7, C_4H_9.

Table II lists 42 of the 124 $\log (k/k^0)$ values which were used. The other 82 $\log (k/k^0)$ values are for the compounds listed in Table III and the solvents listed in Table IV, and may be found in Table II of the previous paper.[3,4] One half (62) of the 124 values were measured in this Laboratory.

The compounds correlated are all chlorides or bromides, but include p-nitrobenzoyl, methyl, benzhydryl and t-butyl. The solvents are especially varied, including n-butylamine, triethylamine, alcohols, water and anhydrous formic acid.

We used the method of least squares in a simple iterative procedure to obtain the best values of a and b (see method of calculation below). To make the solution unique three conditions were imposed arbitrarily as follows: b = 0.00 for 80% EtOH; a = 0.00 for MeBr; a = 1.00 for t-BuCl. A renormalization for any other choice of scale factor (γ) may be made easily using the equations

$$a^* = \gamma a$$
$$b^* = b/\gamma$$

for new values (denoted by superscript stars). When data for a secondary standard $A^{0'}$ are used

(1) Further details and discussion may be found in D. C. Dittmer, Ph.D. thesis, M.I.T., September, 1953. *Cf.* also C. G. Swain and D. C. Dittmer, THIS JOURNAL, **75**, 4627 (1953); *Science*, **118**, 576 (1953). The work carried out by Miss Kaiser (kinetics of picryl chloride and phenacyl bromide) was supported by the Office of Naval Research.

(2) National Science Foundation Fellow, 1952–1953.

(3) C. G. Swain, R. B. Mosely and D. E. Bown, THIS JOURNAL, **77**, 3731 (1955).

(4) The log (k/k^0) values for α-phenylethyl chloride used in this treatment were the correctly calculated ones (*cf.* footnote j in Table II of the previous paper[3]). The omissions were log (k/k^0) values for 40% ethanol, 83.3% formic acid and 97.5% acetic anhydride and the value for p-nitrobenzoyl chloride in acetic acid.

TABLE II

RELATIVE RATES OF SOLVOLYSIS

Compound[a]	Solvent[b]	log (k/k^0)	Temp., °C.	Ref.
PicCl	MeOH, 96.7	−0.22	50	5
PicCl	MeOH, 69.5	− .02	50	5
PicCl	EtOH	− .50	50	5
PicCl	EtOH, 50	− .09	50	5
PicCl	Me_2CO, 90	−1.01	50	5
PicCl	Me_2CO, 70	−0.44	50	5
PicCl	Me_2CO, 50	− .36	50	5
$PhCOCH_2Br$	MeOH, 96.7	− .29	50	5
$PhCOCH_2Br$	MeOH, 69.5	+ .26	50	5
$PhCOCH_2Br$	EtOH	− .93	50	5
$PhCOCH_2Br$	EtOH, 50	+ .27	50	5
$PhCOCH_2Br$	Me_2CO, 90	− .73	50	5
$PhCOCH_2Br$	Me_2CO, 70	− .13	50	5
$PhCOCH_2Br$	Me_2CO, 50	+ .15	50	5
MeBr	Et_3N	+1.85	50	1
MeBr	n-$BuNH_2$	+4.66	50	1
MeBr	C_5H_5N	+3.57	50	1
MeBr	$PhNH_2$	+3.54	50	1
i-BuBr	n-$BuNH_2$	+3.07	50	1
i-BuBr	C_5H_5N	+2.11	50	1
i-BuBr	$PhNH_2$	+2.53	50	1
n-BuBr	Et_3N	−1.14	75	1
n-BuBr	n-$BuNH_2$	+2.72	75	1
n-BuBr	C_5H_5N	+2.12	75	1
n-BuBr	$PhNH_2$	+2.35	75	1
$PhCH_2Cl$	Et_3N	−1.47	50	1
$PhCH_2Cl$	n-$BuNH_2$	+2.70	50	1
$PhCH_2Cl$	C_5H_5N	+1.75	50	1
$PhCH_2Cl$	$PhNH_2$	+2.75	50	1
$(Ph)_2CHCl$	Et_3N	< −10	25	1
$(Ph)_2CHCl$	n-$BuNH_2$	−3.23	25	1
$(Ph)_2CHCl$	C_5H_5N	−3.95	25	1
$(Ph)_2CHCl$	$PhNH_2$	−0.16	25	1
$(Ph)_2CHCl$	MeOH	−0.31	25	7
t-BuBr	EtOH	−1.81	25	8
t-BuBr	EtOH, 90	−0.71	25	6
t-BuBr	EtOH, 60	+1.02	25	6
t-BuBr	Me_2CO, 90	−1.46	25	9
t-BuBr	Me_2CO, 80	−0.52	25	6
t-BuBr	Me_2CO, 70	+ .15	25	9
t-BuCl	Me_2CO, 90	−1.85	25	7
t-BuCl	Me_2CO, 70	+0.13	25	7

[a] See footnote a of Table I. [b] Number after solvent is % by volume based on volumes before mixing with water; when no number is given solvent was anhydrous and pure; Me, Et, Bu, Ph, Ac = CH_3, C_2H_5, C_4H_9, C_6H_5 and CH_3CO. The amine solvents were always 95.2% amine–4.8% benzene based on volumes before mixing.

instead of data for A^0, the equation becomes

$$\log (k/k^0)_A - \log (k/k^0)_{A^{0'}} = (a - \delta)b$$

where

$$\delta = (\log (k/k^0)_{A^{0'}} - \log (k/k^0)_{A^0})/b$$

The minimum, mean and maximum ranges in log $(k/k^0)_{obs}$ values for one compound are 1.0, 3.3 and 6.4 corresponding to variations of 1×10^1, 2×10^3 and 3×10^6 in the observed rate itself. The mean and maximum errors out of 124 log $(k/k^0)_{calc}$ − log $(k/k^0)_{obs}$ values are 0.18 and 0.88 corresponding to factors of 1.52 (for the mean) and 7.6 (for benzhydryl chloride in 90% acetone) in k itself. Measures of fit (Φ) are defined below and listed for typical compounds in Table V; for solvents, Φ = 97% for triethylamine, 97% for water, 95% for formic acid, 63% for acetic acid and 85% for ethanol.

(5) Laura E. Kaiser, Ph.D. thesis, M.I.T., February, 1954.

(6) L. C. Bateman, K. Cooper, E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 925 (1940).

(7) S. Winstein, private communication.

(8) E. D. Hughes, C. K. Ingold, S. Masterman and B. J. McNulty, *J. Chem. Soc.*, 899 (1940).

(9) L. Bateman, M. Church, E. D. Hughes, C. K. Ingold and N. Taher, *ibid.*, 979 (1940).

TABLE III

CONSTANTS FOR COMPOUNDS, $R_1R_2R_3CX$

Compound[a]	No. of reactions	a	R_1—, R_2—, R_3—, X
PicCl	8	−0.42	—C(NO_2)=CH—C(NO_2)= CH—(NO_2)=, Cl
$NO_2PhCOCl$	7	− .37	4-$NO_2C_6H_4$—, O=, Cl
$PhCOCH_2Br$	8	− .04	C_6H_5CO—, H—, H—, Br
MeBr	10	(.00)	H—, H—, H—, Br
PhCOCl	12	+ .06	C_6H_5, O=, Cl
EtBr	5	.15	CH_3—, H—, H—, Br
i-BuBr	4	.16	$(CH_3)_2CH$—, H—, H—, Br
n-BuBr	12	.18	$CH_3CH_2CH_2CH_2$—, H—, H—, Br
$PhCH_2Cl$	8	.19	C_6H_5—, H—, H—, Cl
MePhCOCl	5	.41	4-$CH_3C_6H_4$—, O=, Cl
i-PrBr	5	.42	CH_3—, CH_3—, H—, Br
PhCHClMe	5	.64	C_6H_5—, CH_3, H—, Cl
$(Ph)_2CHCl$	13	.78	C_6H_5—, C_6H_5—, H—, Cl
t-BuBr	7	.93	CH_3—, CH_3—, CH_3—, Br
t-BuCl	15	(1.00)	CH_3—, CH_3—, CH_3—, Cl

[a] See footnote a of Table I.

TABLE IV

CONSTANTS FOR SOLVENTS

Solvent[a]	No. of reactions	b	Dielectric[b] constant	Solvent[a]	No. of reactions	b	Dielectric[b] constant
Et_3N	3	−17.27	3.2	Me_2CO, 80	7	+0.04	30.9
n-$BuNH_2$	5	−10.15	5.3	Me_2CO, 70	7	.42	36.5
C_5H_5N	5	− 9.66	12.4	AcOH	5	.57	9.7
$PhNH_2$	5	− 4.78	7.3	MeOH, 69.5	5	.61	47.3
MeOH	6	− 0.94	33.7	EtOH, 60	4	.88	44.7
EtOH	14	− .74	23.2	Me_2CO, 50	8	1.02	49.5
Me_2CO, 90	7	− .72	24.6	EtOH, 50	8	1.14	51.3
EtOH, 90	4	− .52	28.0	H_2O	4	2.95	79.2
MeOH, 96.7	6	− .51	34.2	HCOOH	6	4.00	58.5
EtOH, 80	15	(0.00)	33.9				

[a] See footnote b of Table II. [b] These constants, measured at or near 20°, were taken from Landolt-Börnstein, "Physikalisch-chemische Tabellen," Julius Springer, Berlin, 1923, Ed. 5, Vol. 2, p. 1035 ff. or "Tables Annuelles de Constantes et Données Numerique," Hermann et Cie, Paris, 1937, Vol. XI, Section 22, pp. 6, 29.

Method of Calculation.—Crude b values were first obtained for solvents in which the rates with both methyl bromide and t-butyl chloride were measured, by use of the equation

$$\log (k/k^0)_{t\text{-BuCl}} - \log (k/k^0)_{MeBr} = b$$

which follows from equation 1 since a = 1.00 for t-BuCl. Crude a values were then determined using equation 1 and any solvent for which b had been obtained. Crude b values were then determined for the other solvents in which methyl bromide was not studied by using the equation

$$\log (k/k^0)_A - \log (k/k^0)_{t\text{-BuCl}} = (a - 1.00)b$$

and any compound A for which a had been obtained.

The values of a and b determined in this way depend on the particular solvents and compounds used in calculating them, since the experimental error is finite and different for each log (k/k^0) value. To minimize the effect of experimental errors, better values of b for all solvents were obtained by the method of least squares from the crude values of a, with equal weighting of all the usable log (k/k^0) values.

$$b \sum_i a_i^2 - \sum_i a_i \left[\log (k/k^0)_{Ai} - \log (k/k^0)_{MeBr}\right] = 0$$

$$b \sum_i (a_i - 1.00)^2 - \sum_i (a_i - 1.00)\left[\log (k/k^0)_{Ai} - \log (k/k^0)_{t\text{-BuCl}}\right] = 0$$

Then better values of a were obtained in the same way by the least-squares method from the better b values.

$$a \sum_j b_j^2 - \sum_j b_j\left[\log (k/k^0)_A - \log (k/k^0)_{MeBr}\right] = 0$$

$$(a - 1.00) \sum_j b_j^2 - \sum_j b_j\left[\log (k/k^0)_A - \log (k/k^0)_{t\text{-BuCl}}\right] = 0$$

These least-squares procedures can be repeated to give still slightly better values of the parameters, but the result proved not worth the effort in the few cases tried. Tables III and IV give the a and b values obtained.

By using the quantity $(\log (k/k^0)_A - \log (k/k^0)_{A^0})$ proportional to a $\Delta\Delta\Delta F^*$, all effects common either to k and k^0 or to A and A^0 are cancelled out. What is left is only a factor a, which appears to be dependent primarily on electron supply to the central carbon, and a factor b, which appears to be dependent primarily on acidity of the solvent and dielectric constant. This equation is limited to simple displacements of similar leaving groups (*e.g.*, chlorides, or chlorides and bromides) from similar sites (*e.g.*, carbon atoms). Nevertheless it is successful in correlating solvolysis of compounds as diverse at *t*-butyl chloride, *n*-butyl bromide and *p*-nitrobenzoyl chloride in solvents as diverse as *n*-butylamine, methanol and anhydrous formic acid.

It is possible that equation 1 approximates

$$\frac{(\Delta E_p^* - \Delta E_p^{*0})_A - (\Delta E_p^* - \Delta E_p^{*0})_{A^0}}{2.303RT} = \frac{\Delta\Delta\Delta E_p^*}{2.303RT}$$

where ΔE_p^* is the difference in potential energy between transition state and ground state in any solvent, and superscript zeros indicate the same for the standard solvent. This would be true if both $\Delta E_z^* - \Delta E_z^{*0}$, where E_z is the zero-point vibrational energy, and $2.303RT \log (Q^*Q^\circ/QQ^{*\circ})$, where Q's are partition functions, were the same for any A under consideration as for A^0.[1,10]

As is commonly done in two-parameter linear free-energy relationships, we consider one parameter (b) as an independent variable, independent of temperature. The other parameter (a) is not as accurate an inverse function of absolute temperature as is ρ in the Hammett equation,[1] but nevertheless probably will not deviate very far from this in practice.

Significance of a and b Values.—Table III compares the value of a with the substituents on the carbon atom at which reaction occurs. Generally, the value of a increases as the electron-supplying ability of the substituents increases. The substituents with nitro groups have the smallest a values; this is expected since nitro groups are electron-attracting. The compounds with the most positive a values bear alkyl or aryl substituents which are electron-donating.

The stepwise replacement of the hydrogens in methyl bromide with methyl groups results in an increase in a. A phenyl group is more effective in increasing the value of a than a methyl group; this may indicate a shift in electron distribution from the phenyl ring toward the reaction site, a resonance effect rather than an inductive effect.

It should be remembered that a may be a function of temperature and the nature of the leaving group in addition to being a function of the polar effects exerted by the substituents on the reaction.

Table IV compares the value of b with dielectric constant of the solvent. Dielectric constant is important in the determination of electrical effects transmitted through a medium. There is a more-or-less general increase in b with increasing dielectric constant, the most notable exception being acetic acid. There seems to be also a trend from basic to acidic solvents as b becomes more positive. The relatively greater acidities of aniline, acetic acid and formic acid in comparison with their neighbors in the table may explain why these compounds have greater b values than their dielectric constants would indicate. It is noted also that as the solvents become more aqueous the b values become greater.

When the product ab is positive the rate of reaction of a given compound in a given solvent relative to the rate in 80% ethanol–20% water is greater than the relative rate for methyl bromide. This condition occurs in the reactions of the strongly nucleophilic solvents (solvents with a negative b) with compounds having strongly electron-withdrawing substituents (compounds with a negative a) and in the reactions of solvents having pronounced electrophilic character (solvents with a positive b) with compounds having electron-supplying substitutents (compounds with a positive a).

Limitations of the Correlation.—To ensure that the zero-point vibrational energies and partition functions will always change in the same way from one solvent to another, the correlation was restricted to compounds with chloride and bromide as leaving groups. By changing the standard compound to a sulfonate ester, a fluoride or a thiocyanate, it may prove possible to correlate the rates of solvolysis of organic sulfonates, fluorides, or thiocyanates. At present there are not enough data to determine the extent of the applicability of equation 1 when it is restricted to other types of leaving groups.

Picryl chloride is less well correlated than the other compounds, possibly because of excessive solvent interaction with the polar nitro groups or because of excessive resonance in the transition state for reaction with the more nucleophilic solvents.

A Measure of Goodness of Fit.—In order to compare the goodness of fit to the experimental data obtained with different quantitative correlations

(10) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 118.

TABLE V

TYPICAL MEASURES OF FIT (Φ)

Equation	Ref.	System	Slope parameters[a]	ϵ	n[b]	Φ, %
$\log (K_B/K_B^0)$	11	$RCOO^- +$ glucose	0.36	0.06	13	77
$\rho\sigma$	12	*m*- and *p*-$ZC_6H_4COOC_2H_5$	2.50	.06	12	90
sn	13	$N + C_2H_5OSO_2C_6H_4CH_3$	0.66	.15	4	83
mY	14	*t*-C_4H_9Br	0.87	.06	7	92
		$(C_6H_5)_2CHCl$	1.13	.57	11	47
		$(C_6H_5)_3CF$[c]	0.47	.90	8	17
		n-C_4H_9Br[c]	.03	.38	8	0
		p-$NO_2C_6H_4COCl$[c]	.02	1.35	8	0
$c_1d_1 + c_2d_2$	3	*t*-C_4H_9Cl	1.00, 1.00	0.25	15	85
		$(C_6H_5)_2CHCl$	1.24, 1.25	.19	9	84
		$(C_6H_5)_3CF$	0.37, 1.12	.25	7	79
		CH_3Br	.80, 0.27	.06	5	93
		n-C_4H_9Br	.77, .34	.05	7	89
		C_6H_5COCl	.81, .52	.23	12	72
		C_6H_5COF	1.36, .66	.11	9	91
		p-$NO_2C_6H_4COCl$	1.09, .21	.07	7	95
ab	1	*t*-C_4H_9Cl	1.00	0.05	14	96
		$(C_6H_5)_2CHCl$	0.78	.36	12	69
		n-C_4H_9Br	.18	.16	11	86
		C_6H_5COCl	.06	.25	11	68
		p-$NO_2C_6H_4COCl$	−0.37	.12	6	85
		$C_6H_5COCH_2Br$	−0.04	.16	7	59
		2,4,6-$(NO_2)_3C_6H_2Cl$	−0.42	.13	7	46

[a] Equal to β, ρ, s, m, (c_1, c_2) and b for equations 12, 13, 14, 15, 3 and 1, respectively. [b] The number of points (n) which equals the number of solvents serving to test the equation is generally one more for equation 15 than for equation 3 or equation 1 because with equation 15 the least squares line was not compelled to run through 80% ethanol; this gives equation 15 an additional point and slightly higher calculated Φ values than if it had been treated similarly to equations 3 and 1. Benzhydryl chloride has only $n = 9$ for equation 3 because the datum for 100% methanol was not known to us when the computations with equation 3 were carried out. [c] Grunwald and Winstein did not expect this equation to apply to these compounds.

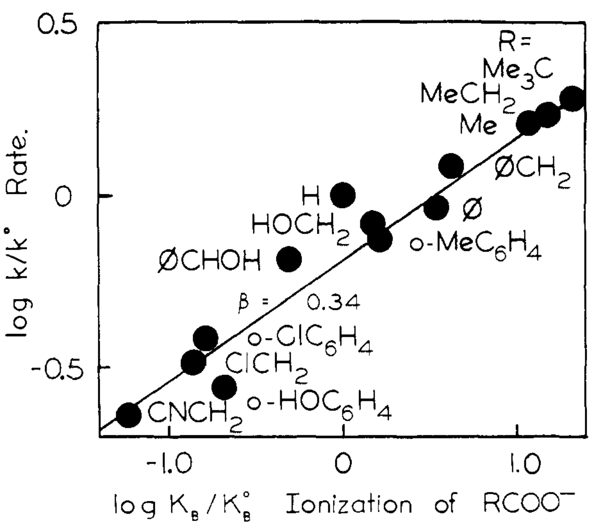

Fig. 1.—Brönsted plot for the mutarotation of glucose by carboxylate anions ($RCOO^-$) in water at 18°.[11]

of rate or equilibrium constants, it is convenient to have an objective measure of fit which will be applicable to them all. This measure should consider not only the absolute errors in the calculations but also the range of the data since an average error of a factor of 1.1 is poor if the observed data vary by only a factor of 1.2 yet an average error of a factor of 2 may be an excellent fit if the experimental data being correlated vary more or less uniformly over a range of 10^6.

A measure of fit which (1) is applicable to any correlation of rate or equilibrium constants, (2) weights all the errors and all the data equally, and (3) is simple to apply is Φ (Phi)

$$\Phi = (1 - (\epsilon/\theta))100\%$$

where ϵ (epsilon) is the average deviation of observed from calculated logarithms (a measure of absolute error), and θ (theta) is the average deviation of observed logarithms from their own mean (a scale factor indicating the range of the data).

$$\epsilon = \frac{1}{n}\sum_n (|\log q_{obs} - \log q_{calc}|)$$

$$\theta = \frac{1}{n}\sum_n (|\log q_{obs} - \frac{1}{n}\sum_n \log q_{obs}|)$$

Here n is the number of points for which ϵ can differ from zero and for which q was observed, and q may be a rate constant (k), an equilibrium constant (K) or a ratio of constants (*e.g.*, k/k^0, where k^0 is the value of k under specified standard conditions). The vertical bars denote absolute magnitude, disregard-

(11) J. N. Brönsted and E. A. Guggenheim, THIS JOURNAL, **49**, 2554 (1927); J. N. Brönsted, *Chem. Revs.*, **5**, 312 (1928); L. P. Hammett, ref. 10, pp. 222–228; H. L. Pfluger, THIS JOURNAL, **60**, 1513 (1938).

(12) L. P. Hammett, ref. 10, pp. 184–198; *Chem. Revs.*, **17**, 125 (1935); *Trans. Faraday Soc.*, **34**, 156 (1938); H. H. Jaffe, *Chem. Revs.*, **53**, 191 (1953); C. G. Swain and W. P. Langsdorf, Jr., THIS JOURNAL, **73**, 2813 (1951); C. T. Hathaway, Ph.D. thesis, M.I.T., July, 1953; R. W. Taft, Jr., THIS JOURNAL, **74**, 2729, 3120 (1952); 4231 (1953); J. D. Roberts and J. A. Yancey, *ibid.*, **73**, 1011 (1951); H. H. Jaffe, *Science*, **118**, 246 (1953).

(13) C. G. Swain and C. B. Scott, THIS JOURNAL, **75**, 141 (1953).

(14) E. Grunwald and S. Winstein, *ibid.*, **70**, 846 (1948); S. Winstein, E. Grunwald and H. W. Jones, *ibid.*, **73**, 2700 (1951).

ing negative signs. Values of Φ extend from +100% for perfect correlation (ϵ = 0) to small or even negative values when there is serious scatter. Values of Φ from 80 to 100% are designated arbitrarily as "excellent," 50–80% as "good," 20–50% as "fair," and less than 20% as "poor," which is generally in accord with subjective evaluation of the corresponding plots by independent observers.

Figure 1 is a plot of one of the oldest linear free-energy relationships, which is included simply to show how much a Φ = 77% correlation scatters. The Brönsted equation implies that the free energy of activation of a base- or acid-catalyzed reaction is a constant fraction of the free energy of ionization of the base or acid. The slope β is also a measure of the fraction of completion of the proton transfer at the transition state.

Table V gives data for typical fits, which vary from "poor" to "excellent."

CAMBRIDGE 39, MASSACHUSETTS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, LOS ANGELES]

Mechanisms of Reaction of Organomercurials.[1] I. Stereochemistry of Electrophilic Displacement on *cis*-2-Methoxycyclohexylneophylmercury by Radio-mercuric Chloride

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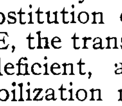
Electrophilic substitution at a saturated carbon atom has been discussed sometimes as analogous to nucleophilic substitution. Possible contrast between the two varieties of substitution, based on electronic and stereoelectronic considerations, is discussed in the present paper. Further, the stereochemistry of electrophilic substitution at a saturated carbon atom has been studied in the case of electrophilic substitution by mercuric chloride on *cis*-2-methoxycyclohexylneophylmercury. The use of radio-mercuric chloride has disclosed the proportions of *cis*-2-methoxycyclohexyl– and neophyl–mercury cleavage. The methoxycyclohexylmercuric chloride derived from the cleavage reaction has been shown, by a sensitive test for the *trans* isomer, to be very pure *cis* material. This result, coupled with the information on the extent of methoxycyclohexyl–mercury bond cleavage in the substitution, shows that substitution on *cis*-2-methoxycyclohexyl proceeds with retention predominating over inversion by a factor of at least 100 to 1. Possible mechanisms for the substitution with retention of configuration are discussed.

Electrophilic substitution at a saturated carbon atom, much less understood than the nucleophilic variety, has been discussed sometimes as analogous to nucleophilic substitution. Thus, Hughes and Ingold,[3] in their 1935 review of substitution, suggested an S_E1–S_E2 classification for electrophilic substitution analogous to S_N1–S_N2 for the nucleophilic case. They suggested a rate sequence, *t*-Bu > *i*-Pr > Et > Me, for S_E2, opposite to the one generally prevailing for S_N2. Also, at that time, they tentatively visualized, for the stereochemical outcome of electrophilic substitution, inversion of configuration in S_E2, as in S_N2,[4] and retention of configuration in S_E1, as in S_N1.[4] Much more recently, Dewar[5] has commented that "cationoid replacements undoubtedly conform to the same general principles as do their anionoid counterparts."

We have been interested in the analogy between electrophilic and nucleophilic substitution at a saturated carbon atom. Just as for nucleophilic substitution, internal or cyclic mechanisms of electrophilic substitution, S_Ei, need to be considered. Also, for the spectrum of possible transition states in S_E2 or S_Ei substitution, we must visualize various degrees of importance of bond formation to the carbon atom undergoing substitution.

Considering stereochemical outcome of S_N2 substitution, the most stable transition state I is attained by trigonal (sp^2) hybridization of orbitals on the central carbon atom, a *p* orbital serving for the partial bonds to the leaving and entering nucleophiles. This arrangement, leading to inverted product, apparently maximizes bonding[6] and minimizes repulsion[7] between electron pairs, of which there are five, in separate bonds. It does not follow that this type of orbital hybridization will be favored also for the transition state in S_E2, involving one less pair of electrons in the five full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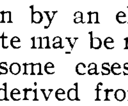
II

or partial bonds to the central carbon atom. Not only is repulsion between separate electron pairs in a transition state of the type II less serious in electrophilic than in nucleophilic substitution, but, in some cases extra stabilization may be associated with this variety of transition state. In electrophilic substitution on carbon by an electrophilic reagent, E, the transition state may be regarded as electron-deficient, and, in some cases at least, extra stabilization may be derived from bonding between the leaving group X and the incoming group E. This is symbolized with the contribution of structure IIIc to the hybrid transition III, or by the summary symbol IV. At any rate, we ap-

(1) Some of the material of this paper was presented at the Organic Reaction Mechanisms Conference, Northwestern University, Evanston, Ill., Aug. 31, 1950.

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(3) E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 244 (1935).

(4) Subsequent work on nucleophilic substitution proved inversion the rule in S_N2. However, a number of possible outcomes of nucleophilic substitution by way of cationic intermediates is possible, depending on the stability and ion pair character of the intermediate, nucleophilic character of the solvent, anchimeric effects, etc.

(5) M. J. S. Dewar, "The Electronic Theory of Organic Chemistry," Oxford University Press, Oxford, 1949, p. 81.

(6) Reference 5, page 64.

(7) E. D. Hughes and C. K. Ingold, *et al.*, *J. Chem. Soc.*, 1252 (1937).