mixed crystals. However, its identity was shown by a kinetic analysis. In 50% acetone–50% water solution it hydrolyzed with a half-life of 980 sec. (*vs.* 960 sec. for an authentic sample of pure trityl acetate, m.p. 87–88°), in a strictly first-order fashion (followed to 88% reaction), and the endpoint (at ten half lives) indicated a quantitative yield of trityl acetate from the trityl fluoride present in the original starting material. Absence of trityl fluoride was shown by titration of the solution for fluoride ion using thorium nitrate and sodium alizarinsulfonate after completion of the solvolysis. As little as 5% trityl fluoride would have been detected by this test.

Although a fourfold change in concentration of acetate ion had no observable effect on the rate when it was in excess over the trityl fluoride, omission of the acetate ion resulted in incomplete acetolysis. Evidently there is a considerable effect of the acetate ion on the position of equilibrium, similar to the effect of pyridine on the methanolysis of trityl chloride in benzene solution.[4a]

Kinetic Measurements.—All of the runs except those in acetic acid were carried out with a cell and technique described previously.[12,16] Since the rate of solvolysis of trityl halides is independent of *p*H, it was possible to follow these reactions by intermittent titration with base. In the 100% ethanol and 80% ethanol–20% water runs, the base used was 0.05*M* sodium ethoxide prepared by dissolving sodium in absolute ethanol. In the 97% methanol–3% water run 0.05 *M* sodium methoxide was used, prepared by dissolving sodium in absolute methanol. In the other runs, 0.05 *M* carbonate-free sodium hydroxide was used. The base solutions were standardized against potassium acid phthalate. Brom thymol blue was used as an indicator in all runs. Identical results were always obtained whether the solution was kept basic or acidic between endpoints. The initial concentration of trityl fluoride was 0.02 *M* in acetic acid and 0.001 *M* in the other solvents. The procedure used may be illustrated by the 40% ethanol–60% water runs: 5 ml. of a fresh solution of trityl fluoride in ethanol (prepared gravimetrically) was added to the cell containing a mixture of 35 ml. of ethanol and 59 ml. of water; since 2 ml. of an aqueous titrating medium was required for the complete solvolysis, the solution was 40% ethanol–60% water at 50% reaction. All percentage compositions reported are by volume before mixing, *i.e.*, deviations from additivity of volumes on mixing were ignored.

It was not possible to use the intermittent titration method (or any other method based on titrating the acid liberated) in the acetic acid–acetic anhydride mixtures because of the very slight difference in acidity between acetic acid and hydrofluoric acid. These runs were followed by quenching 5-ml. aliquots in 50 ml. of benzene, extracting twice with 10-ml. portions of water, separating the aqueous layer, and titrating for fluoride ion with 0.02 *N* thorium nitrate in 0.01 *M* nitric acid using the yellow to orange color change of sodium alizarinsulfonate. No further fluoride ion was extractable by subsequent washing of the benzene layer with water.

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[16] P. D. Bartlett and C. G. Swain, THIS JOURNAL, **71**, 1406 (1949).

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

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

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A four-parameter equation, $\log (k/k^0) = c_1d_1 + c_2d_2$, is tested, where k is the first-order rate constant for solvolysis of any compound in any solvent, k^0 is the corresponding rate constant in a standard solvent (80% ethanol) at the same temperature, c_1 and c_2 are constants depending on only the compound undergoing solvolysis, and d_1 and d_2 are constants depending on only the solvent. All available data capable of serving as a test of the equation were used. Values of c_1 and c_2 are reported for 25 compounds ranging from *p*-nitrobenzoyl chloride to triphenylmethyl fluoride, and values of d_1 and d_2 for 18 solvents ranging from methanol to formic acid. These values were determined from the above equation and 146 observed $\log (k/k^0)$ data by the method of least squares. The mean and maximum ranges in observed rate for a fixed compound are factors of 1.4×10^3 and 7.6×10^6, respectively. The mean and maximum errors in the calculated rate are factors of 1.33 and 4.4.

Many chemical reactions of uncharged substrates (S) in solution appear to involve both a nucleophilic reagent (N) and an electrophilic reagent (E) attacking during, or prior to, the slowest step on the way to products. For these reactions we might expect

$$\log (k/k^0) = sn + s'e \qquad (1)$$

where k is the rate constant with N and E, k^0 is the rate constant with N^0 and E^0 (standard reagents), n measures the nucleophilic reactivity of N, e measures the electrophilic reactivity of E, and s and s' measure the discrimination of S among N and E reagents, respectively.[2] The terms sn and $s'e$ measure nucleophilic and electrophilic driving force.

Equation 1 should apply not only to *concerted* mechanisms, which may be represented by

$$\mathrm{N + S + E \xrightarrow{\mathit{k}} Products}$$

or

$$\mathrm{N + S + E \underset{any\ speed}{\overset{slow}{\rightleftarrows}} I \xrightarrow{fast} Products}$$

such as reaction of pyridine with methyl bromide catalyzed by phenol or mercuric ion in benzene solution,[3] reaction of quaternary ammonium azide with trityl chloride catalyzed by phenol in benzene solution,[4] mutarotation of tetramethylglucose by pyridine and phenol in benzene solution,[5] enolization of acetone by acetate ion and acetic acid in water solution (third-order term),[6] reaction of iodide ion with epichlorohydrin catalyzed by acetic acid in water solution,[7] and cleavage of organosilicon compounds in water solution,[8] but also to mechanisms involving *successive* attacks

$$\mathrm{S + E \overset{\mathit{K}}{\rightleftarrows} I \xrightarrow[slow]{N} Products}$$

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[1] Abstracts of 13th A.C.S. Organic Symposium, Ann Arbor, Michigan, June 17, 1953, pp. 63–69. This work was supported by the Office of Naval Research. Complete experimental data may be found in references 12 and 19.

[2] C. Gardner Swain and Carleton B. Scott, THIS JOURNAL, **75**, 141 (1953).

[3] C. G. Swain and R. W. Eddy, *ibid.*, **70**, 2989 (1948).

[4] C. G. Swain and M. M. Kreevoy, *ibid.*, **77**, 1122 (1955).

[5] C. G. Swain and J. F. Brown, Jr., *ibid.*, **74**, 2534, 2538, 2691 (1952).

[6] H. M. Dawson and E. Spivey, *J. Chem. Soc.*, 2180 (1930).

[7] C. G. Swain, THIS JOURNAL, **74**, 4108 (1952).

[8] F. P. Price, *ibid.*, **69**, 2600 (1947).

or

$$\mathrm{N} + \mathrm{S} \underset{}{\overset{K}{\rightleftharpoons}} \mathrm{I} \xrightarrow[\text{slow}]{\mathrm{E}} \text{Products}$$

provided that the equilibrium constants (K) are small enough so that $[\mathrm{I}] << [\mathrm{S}]$ under all the conditions studied. Equation 1 is most likely to fit well when the reactions compared are similar in respect to solvent, temperature, inert salts and type of atom undergoing displacement (*e.g.*, if all are saturated carbon atoms) and if charged N and E reagents (which are more likely to affect each other's reactivity) are excluded from the comparisons. In reactions with rates proportional to Hammett's acidity function, h_0, either (1) no N is involved in the transition state or (2) the N involved is one previously associated with S in the ground state or (3) s is very low, and the solvent (because of its high concentration) is the only important N. Equation 1 should fail whenever $[\mathrm{I}] > [\mathrm{S}]$, or when S is an anion or cation, or when the reaction is a four-membered cyclic process.

When the electrophilic reagent is held constant, *e.g.*, when water is the solvent and acts as the only important E, we may set $e = 0.00$ for $\mathrm{E} = \mathrm{E}^0$ and

$$\log (k/k^0) = sn \qquad (2)$$

where both k and k^0 are second-order rate constants. One set of n values (and one set of s values) suffices to correlate displacements by water, acetate ion, chloride ion, aniline, hydroxide ion and other N reagents on *carbon* in esters, ethylene oxides, alkyl and acyl halides as S[2]. A different set of n values, *viz.*, $n = \log (K_{\mathrm{B}}/K_{\mathrm{B}^0})$ where K_{B} and K_{B^0} are the basic ionization constants of N and N^0 in water at 25°, is needed to correlate displacements on *hydrogen* or to reduce equation 2 to the Brönsted catalysis law for bases.[2] The differences between these two n scales seem qualitatively to correlate with ΔF_{s}, the free energy of solvation of N. The main reason for the extraordinary nucleophilicity of the ions of heavy atoms (I^-, $\mathrm{O_3SS^-}$) may thus be the ease with which the loosely bound water molecules can be displaced when reaction occurs, relative to the tightly bound ones on small atoms (F^-, $\mathrm{CH_3COO^-}$). Unfortunately there are not yet enough data on free energies of solvation (gas to aqueous solution) to adequately test the equation

$$n = \alpha \log (K_{\mathrm{B}}/K_{\mathrm{B}^0}) + \beta (\Delta F_{\mathrm{s}} - \Delta F_{\mathrm{s}^0})$$

for displacements on carbon. Still different n values are needed to correlate displacements in phosphorus[9] or tin (where n is abnormally high for F^- due to the large per cent. ionic character and strength of the bond forming) or in other solvents than water.

When rates of solvolysis are correlated by equation 1, the solvent is not constant. For this reason we prefer to change the symbols s, n, s' and e to c_1, d_1, c_2 and d_2 to avoid the implication that the solvent parameters are accurate measures of nucleophilic and electrophilic reactivity of the solvent when equation 1 is applied in this manner. A possible approach to obtaining true values of s, n, s' and e would involve diluting each of the solvents with an inert low-dielectric medium so that the experimental log (k/k^0) values could be interpolated to a constant dielectric constant for use in equation 1. We have not done this, but would expect the parameters to have much more obvious and simple physical significance if such a correction were made.

We shall now describe a test of the equation

$$\log (k/k^0) = c_1d_1 + c_2d_2 \qquad (3)$$

where k is the first-order rate constant for solvolysis of any compound in any solvent, k^0 is the corresponding rate constant in a standard solvent at the same temperature, c_1 and c_2 are constants depending on only the compound undergoing solvolysis, and d_1 and d_2 are constants 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 25 compounds.

TABLE I

RATES IN 80% ETHANOL

Compound[a]	$\log_{10} k^0$, sec.$^{-1}$	Temp., °C.	Ref.
$\mathrm{NO_2PhCOCl}$	−1.31	25	12
$\mathrm{NO_2PhCOF}$	−2.00	25	12
PhCOCl	−2.59	25	12
PhCOF	−4.21	25	12
MeCOCl	−2.46	25	12
MePhCOF	−4.67	25	12
MeBr	−5.66	50	13, 14
EtBr	−5.86	50	13, 14
EtOTs	−5.04	50	13
n-BuBr	−5.41[b]	75	15
$\mathrm{PhCH_2Cl}$	−5.65	50	13
$\mathrm{PhCH_2OTs}$	−3.49	25	13
i-PrBr	−5.93	50	13
i-PrOBs	−2.77	70	16
PinOBs	−2.86	70	16
MeOCxOBs	−5.49	50	13
BrCxOBs	−5.15	50	13
PhCHClMe	−3.79	50	17
$\mathrm{(Ph)_2CHCl}$	−2.77	25	18
$\mathrm{(Ph)_2CHF}$	−6.56	25	19
t-BuCl	−5.03	25	20
$\mathrm{(Ph)_3CSCN}$	−2.98[c]	25	19
$\mathrm{(Ph)_3COAc}$	−3.28	25	19
$\mathrm{(Ph)_3COPhNO_2}$	−3.35	25	19
$\mathrm{(Ph)_3CF}$	−3.58	25	19

[a] Ph = $\mathrm{C_6H_5}$ or *p*-substituted $\mathrm{C_6H_4}$; MeOCx = *trans*-2-methoxycyclohexyl; BrCx = *trans*-2-bromocyclohexyl; Pin = pinacolyl; OTs = *p*-toluenesulfonate; OBs = *p*-bromobenzenesulfonate; Me, Et, Pr, Bu = $\mathrm{CH_3}$, $\mathrm{C_2H_5}$, $\mathrm{C_3H_7}$, $\mathrm{C_4H_9}$. [b] Interpolated from a plot of log k *vs.* mole fraction of water. [c] Assumed value. No measurements were made in 80% ethanol.

Table II[10] lists the 146 log (k/k^0) values capable of

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[9] I. Dostrovsky and M. Halmann, *J. Chem. Soc.*, 508 (1953).

[10] The only data knowingly omitted were 6 values on *t*-butyl bromide, which were used in preliminary attempts to fit the equation but were dropped in the course of the Mark IV calculation when they appeared to interfere with convergence of the successive approximation procedure employed. No data in the presence of added salts were available when this calculation was done. The recent discovery that lithium perchlorate in low concentrations can alter the rate of a few solvolyses and not that of others[11] suggests that all the parameters will shift and that the correlation may be poorer when such salts are added.

[11] S. Winstein, E. Clippinger, A. H. Fainberg and G. C. Robinson, THIS JOURNAL, **76**, 2597 (1954).

[12] D. E. Bown, Ph.D. thesis, M.I.T., April, 1953.

serving a check on the equation,[10] *i.e.*, for solvents studied with three or more compounds, or for compounds studied in four or more solvents either at the same temperature or at enough temperatures to permit extrapolation to the common temperature for each compound listed in Table I.

TABLE II

RELATIVE RATES OF SOLVOLYSIS[a]

Compound[b]	Solvent[c]	log (k/k^0)[a]	Ref.
$NO_2PhCOCl$	EtOH, 100	−0.68	12
$NO_2PhCOCl$	Me_2CO, 90	− .91	12
$NO_2PhCOCl$	Me_2CO, 80	− .52	12
$NO_2PhCOCl$	Me_2CO, 70	− .35	12
$NO_2PhCOCl$	Me_2CO, 50	− .12	12
$NO_2PhCOCl$	AcOH, 100	−4.67	12
$NO_2PhCOCl$	HCOOH, 100	−3.37	12
NO_2PhCOF	MeOH, 100	−1.59	12
NO_2PhCOF	MeOH, 96.7	−0.51	12
NO_2PhCOF	MeOH, 69.5	+ .47	12
NO_2PhCOF	EtOH, 100	−1.77	12
NO_2PhCOF	EtOH, 40	+0.51	12
NO_2PhCOF	Me_2CO, 80	−1.07	12
NO_2PhCOF	Me_2CO, 70	−0.64	12
NO_2PhCOF	Me_2CO, 50	− .04	12
NO_2PhCOF	AcOH, 100[d]	−6.37	12
NO_2PhCOF	HCOOH, 100	−4.25	12
PhCOCl	MeOH, 100	+0.22	21
PhCOCl	MeOH, 96.7	+ .33	12
PhCOCl	MeOH, 69.5	+ .87	12
PhCOCl	EtOH, 100	− .52	12
PhCOCl	EtOH, 60	+ .48	12
PhCOCl	EtOH, 50	+ .84	12
PhCOCl	EtOH, 40	+1.30	12
PhCOCl	Me_2CO, 90	−1.18	12
PhCOCl	Me_2CO, 80	−0.72	12
PhCOCl	Me_2CO, 70	− .37	12
PhCOCl	Me_2CO, 50	+ .50	12
PhCOCl	AcOH, 100	−2.39	12
PhCOF	MeOH, 96.7	−0.23	12
PhCOF	MeOH, 69.5	+ .84	12
PhCOF	EtOH, 100	−1.58	12
PhCOF	EtOH, 40	+0.81	12
PhCOF	Me_2CO, 80	−1.19	12
PhCOF	Me_2CO, 70	−0.67	12
PhCOF	Me_2CO, 50	+ .11	12
PhCOF	AcOH, 100[d]	−4.47	12
PhCOF	HCOOH, 100	−1.61	12
MePhCOCl	EtOH, 100	−0.79	21
MePhCOCl	Me_2CO, 80	− .90	12
MePhCOCl	Me_2CO, 50	+ .85	12
MePhCOCl	AcOH, 100	−1.94	12
MePhCOF	Me_2CO, 80	−1.13	12
MePhCOF	Me_2CO, 50	+0.09	12
MePhCOF	AcOH, 100[d]	−3.79	12
MePhCOF	HCOOH, 100	−0.36	12
MeBr	EtOH, 100	− .75	13
MeBr	EtOH, 50	+ .41	13, 22
MeBr	Me_2CO, 50	+ .22	37
MeBr	H_2O, 100	+ .68	13
MeBr	HCOOH, 100[e]	−1.78	13, 24
EtBr	EtOH, 100	−0.77	13, 25
EtBr	EtOH, 50	+ .58	13, 22
EtBr	H_2O, 100	+1.12	13
EtBr	HCOOH, 100[f]	−1.15	13, 25
EtOTs	MeOH, 100	−0.28	13
EtOTs	EtOH, 100	− .57	13
EtOTs	EtOH, 50	+ .37	13
EtOTs	AcOH, 100	−2.38	13
n-BuBr	MeOH, 100[g]	−0.36	15
n-BuBr	MeOH, 96.7[g,h]	− .21	15
n-BuBr	MeOH, 69.5[g,h]	+ .46	15
n-BuBr	EtOH, 100	− .70	15
n-BuBr	EtOH, 90[h]	−0.19	15
n-BuBr	EtOH, 60[h]	+ .27	15
n-BuBr	HCOOH, 100[g]	−1.14	26
$PhCH_2Cl$	MeOH, 100	−0.26	13
$PhCH_2Cl$	EtOH, 100	− .85	13
$PhCH_2Cl$	EtOH, 50	+ .74	13
$PhCH_2OTs$	MeOH, 100	− .29	13
$PhCH_2OTs$	EtOH, 100	− .78	13
$PhCH_2OTs$	AcOH, 100	−2.09	13
i-PrBr	EtOH, 100	−1.02	13
i-PrBr	EtOH, 50	+0.86	13
i-PrBr	H_2O, 100	+1.99	13
i-PrBr	HCOOH, 100	−0.14	13
i-PrOBs	MeOH, 100	− .37	16
i-PrOBs	EtOH, 100	− .81	16
i-PrOBs	AcOH, 100	−1.39	16
i-PrOBs	Ac_2O, 97.5	−3.08	16
PinOBs	MeOH, 100	−0.63	16
PinOBs	EtOH, 100	−1.29	16
PinOBs	AcOH, 100	−0.70	16
PinOBs	Ac_2O, 97.5	−2.08	16
PinOBs	HCOOH[i]	+2.39	16
MeOCxOBs	MeOH, 100	−0.46	13
MeOCxOBs	EtOH, 100	−1.02	13
MeOCxOBs	EtOH, 50	+0.70	13
MeOCxOBs	AcOH, 100	− .97	13, 27
BrCxOBs	MeOH, 100	− .74	13
BrCxOBs	EtOH, 100	−1.42	13
BrCxOBs	EtOH, 50	+1.11	13
BrCxOBs	AcOH, 100	−1.12	13, 27
PhCHClMe	MeOH, 100[j,k]	−0.43	28
PhCHClMe	EtOH, 100[j,m]	−1.50	28
PhCHClMe	Me_2CO, 80[j,n]	−1.12	28
PhCHClMe	AcOH, 100	−1.62	29
$(Ph)_2CHCl$	MeOH, 96.7	−0.07	19

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TABLE II (*Continued*)

Compound[b]	Solvent[c]	log (k/k^0)[a]	Ref.
$(Ph)_2CHCl$	EtOH, 100	−1.51	30
$(Ph)_2CHCl$	EtOH, 90	−0.55	18
$(Ph)_2CHCl$	Me_2CO, 90	−2.57	31
$(Ph)_2CHCl$	Me_2CO, 80	−1.38	31
$(Ph)_2CHCl$	Me_2CO, 70	−0.73	31
$(Ph)_2CHCl$	Me_2CO, 50	+ .98	23
$(Ph)_2CHCl$	AcOH, 100[p]	−2.36	19
$(Ph)_2CHCl$	HCOOH, 83.3	+2.61	19
$(Ph)_2CHF$	EtOH, 50	+1.61	19
$(Ph)_2CHF$	AcOH, 100[p]	+2.11	19
$(Ph)_2CHF$	HCOOH, 83.3	+5.90	19
t-BuCl	MeOH, 100	−1.05	32
t-BuCl	MeOH, 96.7	−0.72	32
t-BuCl	MeOH, 69.5	+1.02	32
t-BuCl	EtOH, 100	−1.98	20
t-BuCl	EtOH, 90	−0.73	20
t-BuCl	EtOH, 60	+1.14	20
t-BuCl	EtOH, 50	+1.60	20
t-BuCl	EtOH, 40	+2.15	20
t-BuCl	Me_2CO, 80	−0.68	20
t-BuCl	Me_2CO, 50	+1.29	33
t-BuCl	H_2O, 100	+3.55	16, 34
t-BuCl	AcOH, 100	−1.64	16
t-BuCl	Ac_2O, 97.5	−3.29	16
t-BuCl	HCOOH, 83.3	+1.50	19
t-BuCl	HCOOH, 100	+2.08	26
$(Ph)_3CSCN$	MeOH, 96.7	−0.30	19
$(Ph)_3CSCN$	MeOH, 69.5	+ .40	19
$(Ph)_3CSCN$	EtOH, 40	+ .56	19
$(Ph)_3CSCN$	Me_2CO, 80	− .28	19
$(Ph)_3CSCN$	Me_2CO, 70	− .05	19
$(Ph)_3CSCN$	Me_2CO, 50	+ .26	19
$(Ph)_3COAc$	MeOH, 96.7	+ .03	19
$(Ph)_3COAc$	MeOH, 69.5	+ .90	19
$(Ph)_3COAc$	EtOH, 60	+ .56	19
$(Ph)_3COAc$	Me_2CO, 80	−1.56	19
$(Ph)_3COAc$	Me_2CO, 50	+0.14	19
$(Ph)_2COPhNO_2$	MeOH, 69.5	+ .83	19
$(Ph)_2COPhNO_2$	EtOH, 40	+1.25	19
$(Ph)_2COPhNO_2$	Me_2CO, 50	+0.37	19
$(Ph)_2COPhNO_2$	AcOH, 100[p]	+ .97	19
$(Ph)_2CF$	MeOH, 96.7	+ .11	19
$(Ph)_2CF$	MeOH, 69.5	+1.50	19
$(Ph)_2CF$	EtOH, 100	−1.73	19
$(Ph)_2CF$	EtOH, 40	+2.02	19
$(Ph)_2CF$	Me_2CO, 70	−1.21	19
$(Ph)_2CF$	Me_2CO, 50	+0.58	19
$(Ph)_2CF$	AcOH, 100[p]	+1.76	19

[a] These are decimal logarithms. For all compounds, log k/k^0 = 0.000 in 80% ethanol by definition. For each compound, the temperature is that given in Table I. [b] Symbols for compounds are explained in footnote *a* of Table I. [c] Number after solvent is % by volume based on volumes before mixing; the residue is water except for 97.5% Ac_2O which is 2.5% AcOH; Me, Et, Ac = CH_3, C_2H_5, CH_3CO. [d] Calculated from data at 80 and 100°. [e] Extrapolated from a higher temperature using ΔE = 20.2 kcal.[35] [f] Extrapolated from a higher temperature using ΔE = 19.8 kcal.[35] [g] Extrapolated from a higher temperature using ΔE = 22.0 kcal.[19] [h] Interpolated from a plot of log *k* *vs.* mole fraction of water. [i] Extrapolated from a lower temperature using ΔE = 27.1 kcal.[36] [j] Unfortunately the values used in these calculations were not the correct ones recorded here but were −1.37, −2.45 and −2.06 for methanol, ethanol and 80% acetone, respectively, which correspond to incorrectly calculated values tabulated by others[16] in the literature. We discovered this error subsequent to completion of the calculation. [k] Extrapolated from a higher temperature using *E* = 21.7 kcal.[35] [m] Extrapolated from a higher temperature using *E* = 21.9 kcal.[35] [n] Extrapolated from a higher temperature using *E* = 21.8 kcal.[35] [p] The datum given was obtained in 99.3% AcOH–0.7% Ac_2O, but is used for 100% AcOH since this compound is relatively little affected by traces of H_2O or Ac_2O.[37]

The data represent a wide range of structural variation. The compounds range from *p*-nitrobenzoyl and methyl to triphenylmethyl and from fluorides to arylsulfonates. Some have strong neighboring group participation and the pinacolyl compound even rearranges. The solvents range from anhydrous alcohols and water to glacial acetic acid and anhydrous formic acid.

Wishing to weight all 146 log (k/k^0) values equally, we chose the condition

$$\Sigma \{\log (k/k^0)_{\text{obs}} - (c_1d_1 + c_2d_2)\}^2 = \text{minimum}$$

to define the best fit. Thus no compound is given more weight than any other. Setting the partial derivative with respect to each of the 25 c_1, 25 c_2, 17 d_1 and 17 d_2 unknown parameters equal to zero gave 84 simultaneous equations. These were solved by an iterative procedure (see method of calculation below) on the Mark IV digital computer of the Harvard Computation Laboratory.

The solution obtained was not unique. To make it unique it was necessary subsequently to impose four conditions (in addition to $d_1 = d_2 = 0.00$ for 80% ethanol). These are in the nature of scale factors or normalization conditions for the calculated parameters and were chosen arbitrarily as follows.

$$c_1 = 3.00\,c_2 \text{ for MeBr}$$
$$c_1 = c_2 = 1.00 \text{ for } t\text{-BuCl}$$
$$3.00\,c_1 = c_2 \text{ for } (Ph)_3CF.$$

Qualitatively these are in the right order because sensitivity to nucleophilic reagents decreases and sensitivity to electrophilic reagents increases in the order methyl bromide, *t*-butyl chloride, trityl fluoride. This choice also makes all the c_1 and c_2 values positive. However, new values (denoted by superscript stars) may be easily calculated for any other choice of the scale factors α and β by use of the equations

$$c_1^* = \alpha c_1 + (1 - \alpha)c_2$$
$$c_2^* = \beta c_1 + (1 - \beta)c_2$$
$$d_1^* = \left(\frac{1 - \beta}{\alpha - \beta}\right) d_1 + \left(\frac{-\beta}{\alpha - \beta}\right) d_2$$
$$d_2^* = \left(\frac{\alpha - 1}{\alpha - \beta}\right) d_1 + \left(\frac{\alpha}{\alpha - \beta}\right) d_2$$
$$d_1^* + d_2^* = d_1 + d_2$$

Table III lists the values of the constants ob-

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TABLE III

VALUES OF COMPOUND AND SOLVENT CONSTANTS

Compound	c_1	c_2	c_1/c_2	Compound	c_1	c_2	c_1/c_2
$NO_2PhCOCl$	1.09	0.21	5.2	*i*-PrOBs	0.63	0.48	1.33
NO_2PhCOF	1.67	.49	3.4	MeOCxOBs	.57	.57	1.00
PhCOCl	0.81	.52	1.6	BrCxOBs	.80	.87	0.92
PhCOF	1.36	.66	2.1	PinOBs	.76	.87	0.86
MePhCOCl	0.82	.65	1.3	PhCHClMe	1.47	1.75	.84
MePhCOF	1.29	.80	1.6	$(Ph)_2CHCl$	1.24	1.25	.99
MeBr	0.80	.27	(3.0)	$(Ph)_2CHF$	0.32[a]	1.17[a]	.27[a]
EtBr	.80	.36	2.2	*t*-BuCl	(1.00)	(1.00)	(1.00)
EtOTs	.65	.24	2.7	$(Ph)_3CSCN$	0.19	0.28	0.69
n-BuBr	.77	.34	2.2	$(Ph)_3COAc$	2.19[b]	.77[b]	. . .
$PhCH_2Cl$	.74[a]	.44[a]	1.7[a]	$(Ph)_3COPhNO_2$	0.18	.59	.31
$PhCH_2OTs$	.69[a]	.39[a]	1.8[a]	$(Ph)_3CF$	.37	1.12	(.33)
i-PrBr	.90	.58	1.5				

Solvent	d_1	d_2	$d_1 - d_2$	Solvent	d_1	d_2	$d_1 - d_2$
MeOH, 100	−0.05	−0.73	+0.7	Me_2CO, 90	−0.53[c]	−1.52[c]	+ 1.0[e]
MeOH, 96.7	− .11	− .05	−0.1	Me_2CO, 80	− .45	−0.68	+ 0.2
MeOH, 69.5	− .06	+1.32	−1.4	Me_2CO, 70	− .09[e]	− .75[e]	+ 0.7[e]
EtOH, 100	− .53	−1.03	+0.5	Me_2CO, 50	− .25	+ .97	− 1.2
EtOH, 90	− .01[c]	− .54[c]	+ .5[c]	H_2O, 100	− .44[d]	+4.01[d]	− 4.5[d]
EtOH, 80	(.00)	(.00)	(.00)	AcOH, 100	−4.82	+3.12	− 7.9
EtOH, 60	− .22[d]	+1.34[d]	−1.6[d]	Ac_2O, 97.5	−8.77[c]	+5.34[c]	−14.1[c]
EtOH, 50	+ .12	+1.33	−1.2	HCOOH, 83.3	−4.44[c]	+6.26[c]	−10.7[c]
EtOH, 40	− .26	+2.13	−2.4	HCOOH, 100	−4.40	+6.53	−10.9

[a] Somewhat doubtful because based on only three log (k/k^0) values. [b] Based on only five log (k/k^0) values for very similar media; none was an absolute alcohol or contained over 50% water or any acetic acid or formic acid. [c] Based on only three compounds. [d] Based on only four compounds. [e] Based on aromatic compounds only, hence may give poor predictions for aliphatic compounds.

tained. The values in parentheses are the ones arbitrarily assigned. Values based on very limited data are indicated by superscript letters referring to explanatory notes.

The ratio c_1/c_2 is a convenient single number to characterize the reactivity of a compound. Compounds which discriminate relatively more highly among nucleophilic reagents than among electrophilic reagents tend to have high values for this ratio. As expected, this ratio decreases from *p*-nitro to *p*-methyl and in the order methyl, ethyl, isopropyl, *t*-butyl, benzhydryl, trityl.

The difference $d_1 - d_2$ is a convenient single number to characterize the reactivity of a solvent. The most nucleophilic solvents have the highest values for this difference, with the difference decreasing in the order anhydrous alcohols, acetone–water and alcohol–water mixtures, water, glacial acetic acid, anhydrous formic acid.

It must nevertheless be admitted that some of the individual c_1, c_2, d_1 and d_2 values are surprising. For example, it seems odd that c_1 increases in the order ethyl bromide (0.80), isopropyl bromide (0.90), *t*-butyl bromide (1.00). The ratio c_1/c_2 decreases only because of an even larger increase in c_2.

Figure 1 shows the correlation for several typical compounds using these compound and solvent constants. Table IV lists some measures of fit.[38] The compound with the largest ϵ (mean error in log $k_{\text{calc.}}$) is *t*-butyl chloride and for it our measure of fit,[38] Φ, is typical and excellent, *viz.*, 85%. The largest individual error is for benzoyl chloride in methanol and corresponds to a factor of 4.4 in k. The mean ϵ for all compounds is 0.124 (factor of 1.33 error in k). For typical solvents ϵ is 0.12 for methanol (n = 12), 0.22 for 50% acetone (n = 13), 0.07 for acetic acid (n = 18), and 0.04 for formic acid (n = 10). Thus the fit is about as good for the extreme compounds and solvents studied as for the ones of intermediate reactivity.

TABLE IV

MEASURES OF FIT[38] FOR CERTAIN COMPOUNDS

Compound	n	ϵ	Φ, %
$NO_2PhCOCl$	7	0.07	95
NO_2PhCOF	10	.15	90
PhCOCl	12	.23	72
PhCOF	9	.11	91
MeBr	5	.06	93
n-BuBr	7	.05	89
$(Ph)_2CHCl$	9	.19	84
t-BuCl	15	.25	85
$(Ph)_3CF$	7	.25	79

Discussion.—The results are compared with those using other equations in the following paper.[38] The correlation is particularly gratifying for *p*-nitrobenzoyl chloride and triphenylmethyl fluoride, which gave almost random scatter plots[19] of log $(k/k^0)_{\text{obs.}}$ *vs.* log $(k/k^0)_{\text{calc.}}$ when using the equation log $(k/k^0) = mY$.

Acknowledgment.—We are greatly indebted to Professor Howard H. Aiken and the Air Force for making the Harvard Mark IV digital computer available, and especially to Mr. Peter F. Strong and Mr. J. Orten Gadd, Jr., of the Harvard Computation Laboratory for setting up and solving this mathematical problem on the computer. Their abbreviated description of the procedure is given below.

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(38) C. G. Swain, D. C. Dittmer and L. E. Kaiser, THIS JOURNAL, **77**, 3737 (1955).

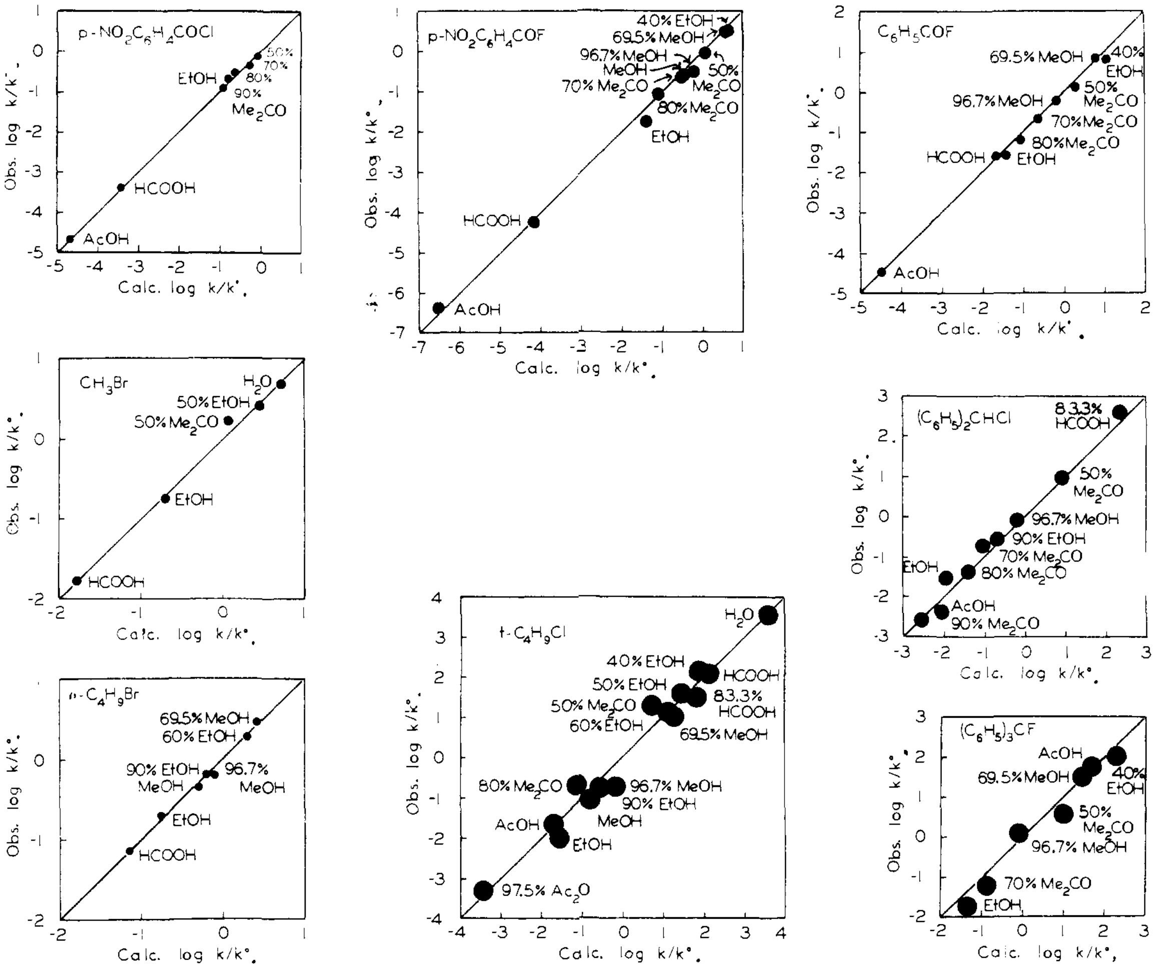

Fig. 1.—Correlation of rates of solvolysis for eight typical compounds.

Method of Calculation

In this problem it is required to find the best values of a_i, b_i, c_j, d_j to represent a given matrix of the form $E_{ij}Z_{ij}$ by the scalar product

$$Z_{ij} \doteq a_i c_j + b_i d_j, \quad i = 1,2, \ldots, m$$
$$j = 1,2, \ldots, n$$

Not all possible elements Z_{ij} are given; the elements E_{ij} are introduced to form an existence matrix such that $E_{ij} = 1$ if the corresponding Z_{ij} is given and $E_{ij} = 0$ otherwise.

To obtain a least squares fit, it is required that the quantity

$$\epsilon^2 = \sum_i \sum_j E_{ij}(Z_{ij} - a_i c_j - b_i d_j)^2$$

be minimum. From this it follows that

$$\frac{\partial}{\partial a_i}(\epsilon^2) = \frac{\partial}{\partial b_i}(\epsilon^2) = \frac{\partial}{\partial c_j}(\epsilon^2) = \frac{\partial}{\partial d_j}(\epsilon^2) = 0$$

for all i and j. Carrying out the differentiations one obtains a system of $2(m + n)$ non-linear simultaneous equations as

$$a_i \Sigma_j E_{ij} c_j^2 + b_i \Sigma_j E_{ij} c_j d_j = \Sigma_j E_{ij} c_j Z_{ij} \qquad (1)$$
$$a_i \Sigma_j E_{ij} c_j d_j + b_i \Sigma_j E_{ij} d_j^2 = \Sigma_j E_{ij} d_j Z_{ij} \qquad (2)$$
$$c_j \Sigma_i E_{ij} a_i^2 + d_j \Sigma_i E_{ij} a_i b_i = \Sigma_i E_{ij} a_i Z_{ij} \qquad (3)$$
$$c_j \Sigma_i E_{ij} a_i b_i + d_j \Sigma_i E_{ij} b_i^2 = \Sigma_i E_{ij} b_i Z_{ij} \qquad (4)$$

If approximations to the values of c_j and d_j be given, equations 1 and 2 can be solved simultaneously to give approximate values of a_i and b_i. Then equations 3 and 4 can be solved to give new approximations to the values of c_j and d_j. This is a simple process since, for a given value of i, equations 1 and 2 are just a pair of linear simultaneous equations involving a_i and b_i as unknowns, and a similar remark applies to equations 3 and 4.

Although equations 1, 2, 3 and 4 may be used as an iterative process to obtain a solution of the problem it was decided to employ an extrapolation process[39] in order to decrease the time required to obtain the answer. Let the sets of numbers a_i, b_i, c_j and d_j obtained after the n-th iteration form the vector V_n. Let

$$V_{n+1} - V_n = D_n$$

Now ϵ^2 may be written as

$$\epsilon^2 = f(V_{n+1})$$

since ϵ^2 is a function of the variables which form the components of V_n. One may calculate

$$f_0 = f(V_{n+1})$$
$$f_1 = f(V_{n+1} + hD_n)$$
$$f_2 = f(V_{n+1} + 2hD_n)$$

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[39] The principle on which this process is based was suggested by Dr. R. E. Clapp.

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.

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[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

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

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 $A^{0\prime}$ are used

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(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.