CORRELATION OF SOLVOLYSIS RATES

by

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Abstract

An equation has been proposed to correlate the rates of solvolysis of twenty organic compounds in eighteen solvents.

$$\log (k/k_o) = sn + s'e \qquad (6)$$

In this equation, k and k_o are the first-order rate constants for solvolysis in any solvent and in the standard solvent, respectively; n and e represent the nucleophilic and electrophilic character of the solvent, respectively; and s and s' measure the susceptibility of the compound to nucleophilic and electrophilic attack, respectively. The compounds range from methyl bromide to triphenylmethyl fluoride and the solvents include ethanol - water, methanol - water, acetone - water, acetic anhydride - acetic acid, and formic acid - acetone mixtures.

The mean probable error for the 106 rates calculated from equation 6 is a factor of 1.28 and the mean variation in rates for the twenty compounds is a factor of 10^3.

No support has been found for the hypothesis that two essentially different types of transition states are involved in solvolyses of organic compounds. Neither is any support apparent in this work for the hypothesis that all compounds which have at least as great a tendency as t-butyl chloride to ionize into a carbonium ion react by way of identical transition states.

The data are more consistent with the hypothesis that

all solvolyses occur by way of one type of transition state in which both a nucleophilic and an electrophilic solvent molecule are involved. Only quantitative variations in this transition state are necessary to account for the experimental facts.

INTRODUCTION

Classification of Reaction Mechanisms.- Many reactions in organic chemistry are classified as polar displacement reactions. They can be expressed stoichiometrically by equation 1.

$$Y\!: + RX \longrightarrow RY + :X \qquad (1)$$

Y: and :X may be neutral or negatively charged. Two general mechanisms have been written for such processes; one has been called S_N1 (Substitution, Nucleophilic, of the 1st order), unimolecular,[1] solvolytic, or polymolecular.[2] In this mechanism a preliminary, rate-determining ionization is thought to be

$$RX \xrightarrow{\text{slow}} R^+ + X^-$$

$$R^+ + Y\!: \xrightarrow{\text{fast}} RY$$

followed by a fast, product-controlling step. It has been recognized[2,3] that solvent molecules or added electrophilic reagents solvate the leaving group, and it has been thought that much of the driving force[4] for the reaction comes from

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(1) E. D. Hughes, C. K. Ingold, and C. S. Patel, J. Chem. Soc., 526 (1933); E. D. Hughes, and C. K. Ingold, ibid., 244 (1935); Nature, 132, 933 (1933); E. D. Hughes, Trans. Faraday Soc., 37 611 (1941); I. Dostrovsky, E. D. Hughes, and C. K. Ingold, J. Chem. Soc., 173 (1946).

(2) J. Steigman and L. P. Hammett, J. Am. Chem. Soc., 59, 2536 (1937); N. T. Farinacci and L. P. Hammett, J. Am. Chem. Soc., 59, 2542 (1937); 60, 3097 (1938).

(3) L. Bateman, E. D. Hughes, and C. K. Ingold, J. Am. Chem. Soc., 60, 3080 (1938).

(4). M. G. Evans and M. Polanyi, Trans. Faraday Soc., 34, 11 (1938).

this solvation.[2] This type of mechanism is thought to occur with tertiary (and some secondary) aliphatic halides, e.g., t-butyl chloride, or especially with halides which on ionization leave a carbonium ion which can be greatly stabilized by resonance. Examples of these are allyl, benzhydryl, and trityl carbonium ions. The evidence for such a mechanism includes the absence of increase in rate of hydrolysis upon addition of bases or other highly nucleophilic species,[5,6] the "mass-law" effect[6] and the high degree of racemization associated with the hydrolyses of optically active halides.[2,7]

The second mechanism has been called $\underline{S}_{\underline{N}}2$ (Substitution Nucleophilic of the 2nd order).[8] It is usually applied to primary (and sometimes secondary) halides and is characterized by second-order kinetics with highly nucleophilic species,[8] and by absence of racemization in the hydrolysis of optically active halides.[9] The $\underline{S}_{\underline{N}}2$ mechanism is thought to involve a direct, synchronous displacement of the leaving group by the entering group, and a transition state in which five atoms

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(5) A. M. Ward, J. Chem. Soc., 445 (1927).

(6) L. Bateman, M. Church, E. D. Hughes, C. K. Ingold, and N. Taher, J. Chem. Soc., 979 (1940).

(7) E. D. Hughes, C. K. Ingold, and A. D. Scott, J. Chem. Soc., 1201 (1937); W. von E. Doering, and H. Zeiss, Abstracts of Paper, 117th Meeting American Chemical Society, April, 1950, p.7L, W. von E. Doering and A. Streitweiser, Jr., Abstracts of Papers, 119 Meeting American Chemical Society, April, 1951 p.45M.

(8) W. Hanhart and C. K. Ingold, J. Chem. Soc., 997 (1927); J. Gleave, E. D. Hughes, and C. K. Ingold, ibid., 236 (1935).

(9) E. D. Hughes and U. G. Shapiro, J. Chem. Soc., 1192 (1937); E. D. Hughes, C. K. Ingold, and S. Masterman, ibid, 1196 (1937).

have at least partial covalent bonds to the central carbon atom.

On the other hand, there is some evidence that all these polar displacements may proceed via one type of transition state with only quantitative differences between different compounds. In benzene solution where the solvent is inert, both trityl chloride and methyl bromide give third-order kinetics.[10] Furthermore, ρ, the reaction constant in the Hammett equation[11] for correlating the effects of m-and p-substituents on rates and equilibria shows no evidence of grouping into two classes, as might be expected if the reactions involved two distinct types of rate-determining steps. Also, there is evidence that many, if not all, acid - base catalyzed reactions involve both an electrophilic and a nucleophilic reagent.[12] Lastly, it has recently been proposed[13] that the rates of solvolysis of secondary halides may be discussed more profitably in terms of one intermediate mechanism than of the simultaneous operation of both $\underline{S}_N1$ and $\underline{S}_N2$ mechanisms.

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(10) C. G. Swain, J. Am. Chem. Soc., 70, 1119 (1948); C. G. Swain and R. Eddy, ibid, 70, 2989 (1948).

(11) L. P. Hammett, "Physical Organic Chemistry" McGraw-Hill Book Co., Inc., New York, N. Y., 1940, Chapter VII.

(12) C. G. Swain, J. Am. Chem. Soc., 72, 4578 (1950).

(13) S. Winstein, E. Grunwald, and H. W. Jones, J. Am. Chem. Soc., 73, 2700 (1951).

Previous Correlations of Solvolysis Rates.- Solvolyses, or reactions with the (generally hydroxylic) solvent are fairly typical displacement reactions. In equation 2, R' may be

$$RX + R'OH \longrightarrow ROR' + HX \qquad (2)$$

alkyl, acyl, or hydrogen. By using widely different solvents, major changes in the reactants may be made. In general, the rates of these reactions are convenient for measurement. The rates of reactions are closely related to the driving forces, and therefore to the mechanisms. For these reasons, and also since many data are already available in the literature, the correlation of rates of solvolysis is an attractive and important problem.

A correlation has been proposed[14] for hydrolyses in water - dioxane, water - tetrahydrofuran, water - ethylene glycol dimethyl ether, or water - diethylene glycol dimethyl ether mixtures. Over limited ranges of water concentration the data were correlated by equation 3, where k is the first

$$\log k = \log a + m \log \epsilon \qquad (3)$$

order rate constant, ϵ is the dielectric constant, and a and m are constants. This relation fails both in highly aqueous mixtures and in highly non-aqueous mixtures. Furthermore, it is clear that it is not applicable to other solvents.

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(14) H. Bohme and W. Schurhoff, Chem. Ber., 84, 28 (1951).

For example, solvolysis of many compounds is more rapid in acetic acid than in ethanol, yet the dielectric constants are 9.7 and 25.8, respectively.

Other proposals that should be mentioned are those concerned with correlating the rates of solvolysis of t-butyl chloride in ethanol - water and methanol - water mixtures in terms of simultaneous bimolecular[15,16] or termolecular[17] reactions with water or alcohol. The bimolecular equations could not correctly predict the ratio of alcohol to ether in the product,[18] and the termolecular equation had so many disposable parameters that its predictions were not significant.

An equation similar to the bimolecular equations just mentioned has been proposed[19] for the solvolyses of n-butyl bromide in ethanol - water and methanol - water mixtures which predicts both the rates and product ratios if molarities are used to obtain Henry's Law constants for n-butyl bromide. If mole fractions are used, the equation will fit the rates, but not the products.[20]

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(15) A. R. Olson and R. S. Halford, J. Am. Chem. Soc., 59, 2644 (1937).

(16) P. D. Bartlett, J. Am. Chem. Soc., 61, 1630 (1939).

(17) S. Winstein, J. Am. Chem. Soc., 61, 1635 (1939).

(18) L. C. Bateman, E. D. Hughes, and C. K. Ingold, J. Chem. Soc. 881 (1938).

(19) M. L. Bird, E. D. Hughes, and C. K. Ingold, J. Chem. Soc., 255 (1943).

(20) E. Grunwald and S. Winstein, J. Am. Chem. Soc., 70, 846 (1948).

By far the most extensive and successful correlation in the literature is that of Grunwald and Winstein.[13,20] These investigators were able to correlate the rates of solvolysis of t-butyl chloride, t-butyl bromide, α-methylallyl chloride, pinacolyl p-bromobenzenesulfonate, neopentyl bromide, trans-2-bromocyclohexyl p-bromobenzenesulfonate, and trans-2-methoxycyclohexyl p-bromobenzenesulfonate in ethanol - water, methanol - water, acetone - water, and acetic acid - acetic anhydride mixtures, as well as in pure formic acid by means of equation 4. In this equation, k is the first-order rate

$$\log k/k_o = mY \qquad (4)$$

constant for solvolysis of any compound in any solvent, k_o is the first-order rate constant for solvolysis of that compound in a standard solvent (80% ethanol - 20% water), m is a parameter characteristic of the compound, and Y is a parameter characteristic of the solvent. By defining m as unity for a standard compound (t-butyl chloride), Y was determined for all solvents, and thus m could be calculated for all other compounds.

Since the free energy of activation is proportional to the logarithm of the rate constant, equation 4 implies a linear relation between free energies of activation, where

$$F^{\ddagger} - F_o^{\ddagger} = cY \qquad (5)$$

$F^{\ddagger}$ and $F_o^{\ddagger}$ are the free energies of activation in any solvent and in the standard solvent, respectively, and c is a proportionality factor.

Classifications of Reaction Mechanisms in Borderline Cases.-

In addition to the S_N1 - S_N2 classification mentioned above, a second classification has recently been made.[13] The compounds whose rates were well correlated by equation 4 had been considered to solvolyze by the S_N1 mechanism. Compounds whose solvolyses had been considered borderline under the S_N1 - S_N2 classification correlated less well. Compounds usually considered to solvolyze by the S_N2 mechanism correlated poorly with equation 4. It was therefore proposed that this equation be used as a criterion for determining the sort of mechanism which was followed in the solvolysis of a compound, and that those compounds whose rates were well correlated be termed Limiting (in mechanism), signifying that no covalent interaction of solvent with carbon existed in the transition state. Those compounds whose rates were not well correlated were termed Nucleophilic (in mechanism), signifying that to a greater or lesser extent some covalent interaction between carbon and a nucleophilic solvent molecule exists in the transition state.

RESULTS AND DISCUSSION

The Present Approach.- As noted above, equation 4 fails badly when applied to compounds having less tendency to ionize and more tendency to undergo attack by nucleophilic reagents than t-butyl chloride (those compounds considered to solvolyze by the $\underline{S}_N2$ mechanism or considered borderline under the $\underline{S}_N1$ - $\underline{S}_N2$ classification). These compounds included methyl, ethyl, i-propyl, and benzyl halides and sulfonate esters. It had also been found[20] to fail when applied to compounds having a greater tendency to ionize. Benzhydryl chloride and α-phenylethyl chloride were observed to react in acetone - water mixtures at a rate about one tenth of that predicted by equation 4.

It has now been found (Table I and Figs. 1 - 2) that equation 4 does not describe adequately the behavior of triphenylmethyl (trityl) acetate, trityl fluoride, trityl p-nitrophenyl ether, or benzhydryl fluoride. It has also been found that the failure of equation 4 for benzhydryl chloride is not limited to acetone - water mixtures (Fig 1).

The deviations between calculated and observed rates for these trityl and benzhydryl compounds are large, factors of ten to one hundred in several cases. Moreover, the deviations are quite regular. Observed rates in formic acid, acetic acid, methanol - water mixtures, and highly aqueous ethanol - water mixtures are greater than those calculated from equation 4 and m-values obtained from the least-squares lines through plots of the data. Observed rates in acetone - water mixtures are smaller than those calculated, and those in highly non-aqueous acetone - water mixtures deviate the most.

It will be noted that those solvents which would be expected to favor ionization most, give consistently faster rates than predicted . Since these benzhydryl and trityl compounds, on ionization, all form carbonium ions with greater resonance stabilization than the t-butyl ion, it appears that the failure of equation 4 for this type of compound may be quite general. This suggests that in mechanism as well as structure, the compounds which were correlated by equation 4 may be intermediate.

If both a nucleophilic and electrophilic reagent are necessary for polar displacements, then any correlation of rates of solvolysis which is designed to work over large changes in the structure of both solvent and compound must take these changing nucleophilicities and electrophilicities into account. Different solvents will be able to perform these two tasks with varying efficiencies. For example, acetic acid is more electrophilic than nucleophilic; on the other hand, ethanol is more nucleophilic than electrophilic.

Furthermore, different compounds will be affected in different manners by a change in nucleophilic or electrophilic power of the solvent. For example, it may be expected that triphenylmethyl halides will be strongly dependent on

TABLE I

SOLVOLYSIS RATES AT 25.0°

Compound	Solvent[a]	k_1, sec.$^{-1}$	log k_1
Benzhydryl chloride	CH_3COOH	7.45×10^{-6}	-5.13
	83.3% $HCOOH$ - 16.7% CH_3COCH_3	0.693	-0.16
	96.7% CH_3OH	1.47×10^{-3}	-2.83
Triphenylmethyl fluoride	C_2H_5OH	4.88×10^{-6}	-5.31
	80% C_2H_5OH	2.61×10^{-4}	-3.58
	40% C_2H_5OH	2.74×10^{-2}	-1.56
	96.7% CH_3OH	3.39×10^{-4}	-3.47
	69.5% CH_3OH	8.28×10^{-3}	-2.08
	70% CH_3COCH_3	1.60×10^{-5}	-4.80
	50% CH_3COCH_3	9.83×10^{-4}	-3.01
	CH_3COOH	1.51×10^{-2}	-1.82
Triphenylmethyl acetate	80% C_2H_5OH	5.27×10^{-4}	-3.28
	60% C_2H_5OH	1.9×10^{-3}	-2.72
	96.7% CH_3OH	5.6×10^{-4}	-3.25
	69.5% CH_3OH	4.2×10^{-3}	-2.38
	80% CH_3COCH_3	1.45×10^{-5}	-4.84

TABLE I (cont.)

Compound	Solvent[a]	k_1, sec.$^{-1}$	log k_1
Triphenylmethyl thiocyanate	40% C_2H_5OH	3.8×10^{-3}	-2.42
	96.7% CH_3OH	5.2×10^{-4}	-3.28
	69.5% CH_3OH	2.6×10^{-3}	-2.58
	80% CH_3COCH_3	5.5×10^{-4}	-3.26
	70% CH_3COCH_3	9.3×10^{-4}	-3.03
Benzhydryl fluoride	80% C_2H_5OH	2.78×10^{-7}	-6.56
	50% C_2H_5OH	1.12×10^{-5}	-4.95
	CH_3COOH	3.58×10^{-5}	-4.45
	83.3% HCOOH - 16.7% CH_3COCH_3	0.222	-0.65
Triphenylmethyl p-nitrophenyl ether	80% C_2H_5OH	4.49×10^{-4}	-3.35
	40% C_2H_5OH	7.89×10^{-3}	-2.10
	69.5% CH_3OH	3.04×10^{-3}	-2.52
	50% CH_3COCH_3	1.06×10^{-3}	-2.97
	CH_3COOH	4.17×10^{-3}	-2.38
t-Butyl chloride	83.3% HCOOH - 16.7% CH_3COCH_3	2.92×10^{-4}	-3.53

[a] Where only part of the solvent is specified, the rest is water.

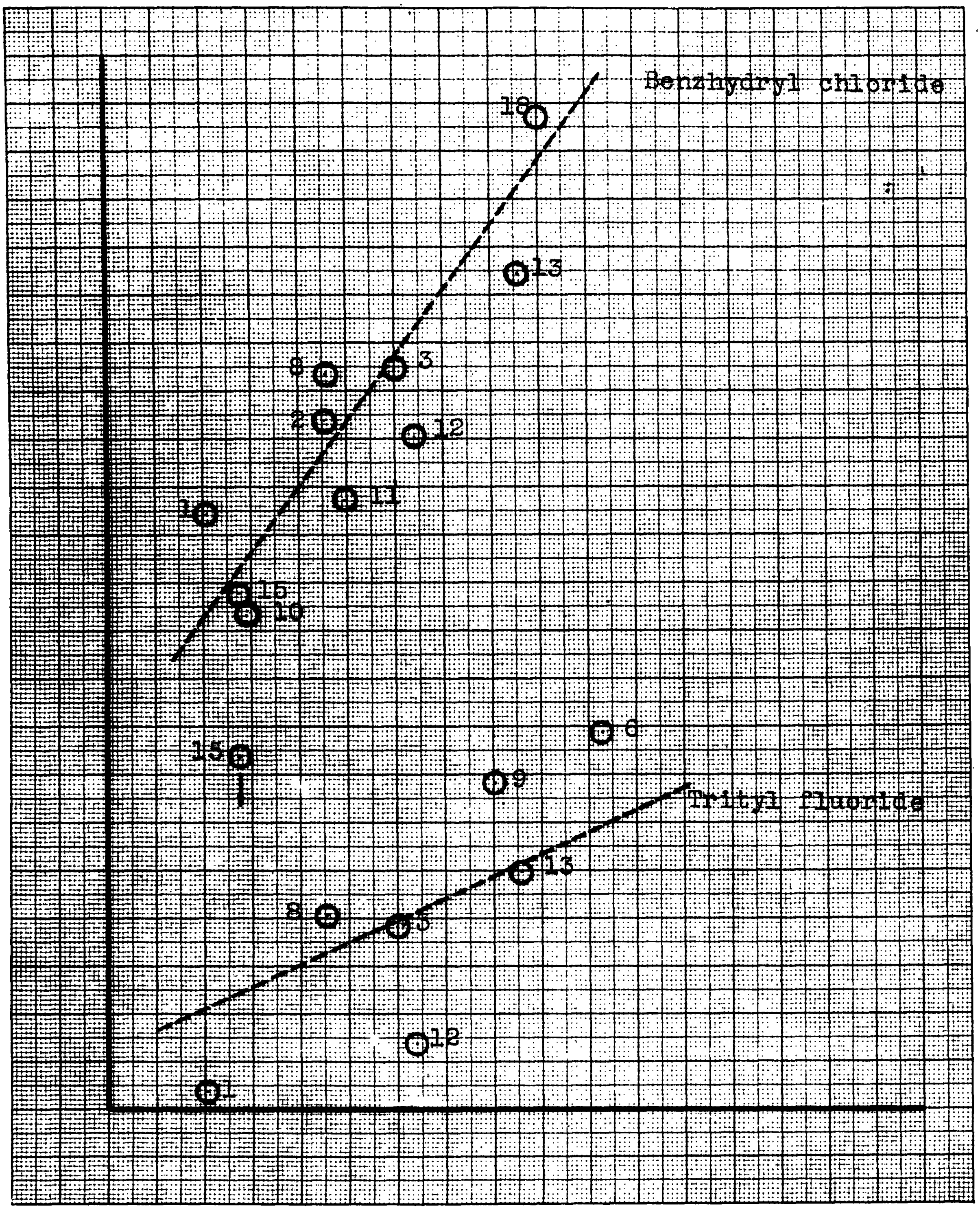

Fig 1 - Plot of log k/k_o vs. Y for two compounds. For identification of solvents see footnote c p. 37.

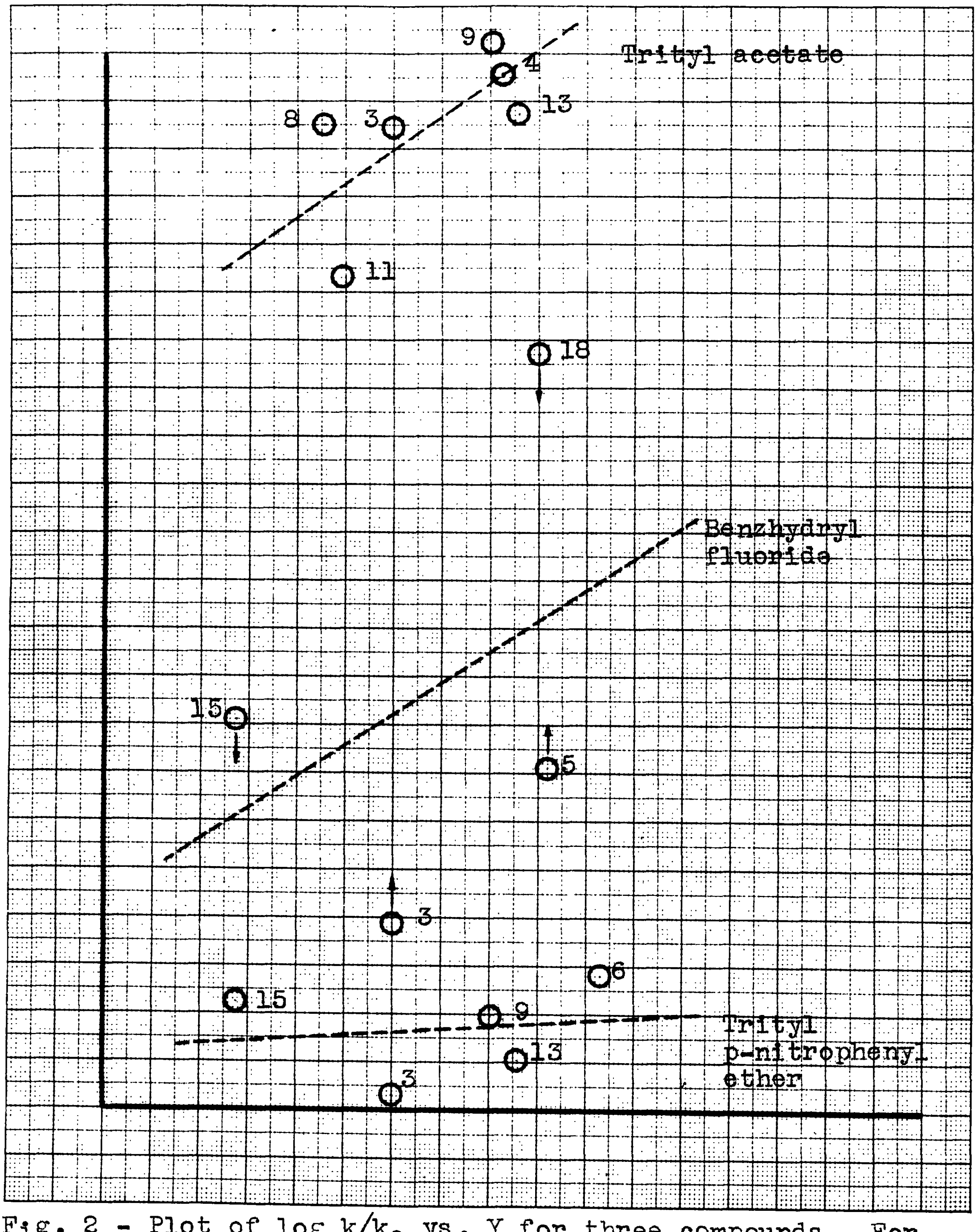

Fig. 2 - Plot of log k/k_0 vs. Y for three compounds. For identification of solvents see footnote c p. 37.

electrophilicity, but only weakly dependent on nucleophilicity. This is primarily because of their great ability to distribute a positive charge on the central carbon by resonance. On the other hand, methyl halides will be expected to show relatively little dependence on electrophilicity and much greater dependence on nucleophilicity. This is shown by the relatively slow rate exhibited in their reactions with silver ion,[21] and the relatively fast rate with phenoxide ion.[22]

We have then, at least four factors which seem likely to affect the relative rates of solvolysis, and these are expressed in equation 6. In this equation, k and k_o have

$$\log (k/k_o) = sn + s'e \qquad (6)$$

the same significance as in equation 4; n and e are constants representing the nucleophilicity and electrophilicity of the solvent, respectively; and s and s' are constants representing the susceptibility of the compound to changes in nucleophilicity and electrophilicity, respectively. Since the ratio k/k_o is unity in the standard solvent (80% ethanol - 20% water), n and e are defined as unity for this solvent.

Equation 6 is equivalent to equation 7, where $F^{\ddagger}$ and

$$F^{\ddagger} + F^{\ddagger}_o = an + a'e \qquad (7)$$

$F^{\ddagger}_o$ have the same significance as in equation 5; n and e have the same significance as in equation 6; and a and a'

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(21) K. Burke and F. Donnan, J. Chem. Soc., 85, 555 (1904).

(22) D. Segaller, J. Chem. Soc., 103, 1154, 1421 (1913); 105, 106, 113 (1914).

are proportional to s and s' in equation 6. Equation 7 assigns all changes in free energies of activation with solvent to the four factors mentioned above: nucleophilicity of the solvent and susceptibility of the compound to nucleophilic attack, and electrophilicity of the solvent and susceptibility to electrophilic attack. The degree of success of equation 6 in correlating rates is a measure of the validity of equation 7.

Data available from the literature are collected in Table II. Data are included for all compounds for which rates in four or more solvents have been measured at a single temperature. Data are included for all solvents in which rates for three or more compounds have been reported. In one solvent, 90% acetone - 10% water, only two compounds have been reported.

In Tables III and IV the number of solvents in which data are available, s, s', s/s', r (the mean deviation of the logarithm of the calculated rates), and the temperature at which the data were obtained, are listed for 20 compounds. In Tables V and VI values of n and e are tabulated for 18 solvents. In Figs. 3-16 the logarithm of the relative rates calculated from equation is plotted against the logarithm of the experimental relative rates for the 20 compounds. The deviations of calculated log (k/k_0) from observed log (k/k_0) are listed in Tables VII and VII A.

TABLE II

SOLVOLYSIS RATES FROM THE LITERATURE

Compound	Solvent[a]	k_1, $sec.^{-1}$	log k_1	Ref.	Temp.(°C.)
α-Phenylethyl chloride	C_2H_5OH	$5.87x10^{-7}$	-6.23	20, 7	50.0
	80% C_2H_5OH	$1.64x10^{-4}$	-3.79	5	50.0
	CH_3OH	$7.06x10^{-6}$	-5.15	20, 7	50.0
	80% CH_3COCH_3	$1.44x10^{-6}$	-5.84	20, 7	50.0
	CH_3COOH	$3.9x10^{-6}$	-5.41	2	50.0
t-Butyl bromide	C_2H_5OH	$5.69x10^{-6}$	-5.24	20, 29	25.0
	90% C_2H_5OH	$7.14x10^{-5}$	-4.15	30	25.0
	80% C_2H_5OH	$3.63x10^{-4}$	-3.44	30	25.0
	60% C_2H_5OH	$3.76x10^{-3}$	-2.42	30	25.0
	90% CH_3COCH_3	$1.27x10^{-5}$	-4.90	6	25.0
	80% CH_3COCH_3	$1.10x10^{-4}$	-3.96	20, 30	25.0
	70% CH_3COCH_3	$5.15x10^{-4}$	-3.29	6	25.0
Benzyl p-toluenesulfonate	C_2H_5OH	$5.33x10^{-5}$	-4.27	13	25.0
	80% C_2H_5OH	$3.24x10^{-4}$	-3.49	13	25.0
	CH_3OH	$1.67x10^{-4}$	-3.78	13	25.0
	CH_3COOH	$2.61x10^{-6}$	-5.58	13	25.0

TABLE II (cont.)

Compound	Solvent[a]	k_1, $sec.^{-1}$	log k_1	Ref.	Temp.(°C.)
Isopropyl bromide	C_2H_5OH	$1.12x10^{-7}$	-6.95	13	50.0
	80% C_2H_5OH	$1.18x10^{-6}$	-5.93	13	50.0
	50% C_2H_5OH	$8.45x10^{-6}$	-5.07	13	50.0
	H_2O	$1.16x10^{-4}$	-3.94	13	50.0
	HCOOH	$8.6x10^{-7}$	-6.07	13	50.0
Ethyl p-toluenesulfonate	C_2H_5OH	$2.46x10^{-6}$	-5.61	13	50.0
	80% C_2H_5OH	$9.23x10^{-6}$	-5.03	13	50.0
	50% C_2H_5OH	$2.18x10^{-5}$	-4.66	13	50.0
	CH_3OH	$4.83x10^{-6}$	-5.32	13	50.0
	CH_3COOH	$3.83x10^{-8}$	-7.42	13	50.0
Ethyl bromide	C_2H_5OH	$2.37x10^{-7}$	-6.63	35	55.0
	80% C_2H_5OH	$1.39x10^{-6}$	-5.86	30	55.0
	50% C_2H_5OH	$5.25x10^{-6}$	-5.28	13	55.0
	H_2O	$1.83x10^{-5}$	-4.74	13	55.0
	HCOOH[b]	$9.8x10^{-8}$	-7.01	31	55.0
Triphenylmethyl thiocyanate	50% CH_3COCH_3	$1.92x10^{-3}$	-2.72	38	25.0

TABLE II (cont.)

Compound	Solvent[a]	k_1, sec.$^{-1}$	log k_1	Ref.	Temp.(°C)
Benzyl chloride	C_2H_5OH	3.14×10^{-7}	-6.50	13	50.0
	80% C_2H_5OH	2.22×10^{-6}	-5.65	13	50.0
	50% C_2H_5OH	1.22×10^{-5}	-4.91	13	50.0
	CH_3OH	1.23×10^{-6}	-5.91	13	50.0
t-Butyl chloride	C_2H_5OH	9.70×10^{-8}	-7.01	20	25.0
	90% C_2H_5OH	1.73×10^{-6}	-5.76	26	25.0
	80% C_2H_5OH	9.24×10^{-6}	-5.03	26	25.0
	60% C_2H_5OH	1.27×10^{-4}	-3.90	26	25.0
	50% C_2H_5OH	3.67×10^{-4}	-3.44	26	25.0
	40% C_2H_5OH	1.29×10^{-3}	-2.89	26	25.0
	CH_3OH	8.20×10^{-7}	-6.09	20, 15	25.0
	96.7% CH_3OH	1.75×10^{-6}	-5.76	15	25.0
	69.5% CH_3OH	9.75×10^{-5}	-4.01	15	25.0
	80% CH_3COCH_3	1.94×10^{-6}	-5.71	26	25.0
	50% CH_3COCH_3	1.82×10^{-4}	-3.74	39	25.0
	H_2O	3.3×10^{-2}	-1.48	20, 28	25.0
	CH_3COOH	2.13×10^{-7}	-6.67	20	25.0
	HCOOH	1.1×10^{-3}	-2.96	20, 27	25.0
	97.5%$(CH_3CO)_2O$- 2.5% CH_3COOH	4.77×10^{-9}	-8.32	20	25.0

TABLE II (cont.)

Compound	Solvent[a]	k_1 sec.$^{-1}$	log k_1	Ref.	Temp.(°C)
Methyl bromide	C_2H_5OH	3.93×10^{-7}	-6.41	13	50.0
	80% C_2H_5OH	2.19×10^{-6}	-5.66	13	50.0
	50% C_2H_5OH	5.66×10^{-6}	-5.25	13	50.0
	H_2O	1.05×10^{-5}	-4.98	13	50.0
	HCOOH[c]	3.65×10^{-8}	-7.44	31	50.0
	50% CH_3COCH_3	$3.65\times10^{\cancel{-4}\,-6}$	-5.44	38	50.0
trans-2-Bromo-cyclohexyl p-bromo-benzenesulfonate	C_2H_5OH	2.67×10^{-7}	-6.57	13	50.0
	80% C_2H_5OH	7.02×10^{-6}	-5.15	13	50.0
	50% C_2H_5OH	9.12×10^{-5}	-4.04	13	50.0
	CH_3OH	1.28×10^{-6}	-5.89	13	50.0
	CH_3COOH	5.28×10^{-7}	-6.28	13, 34	50.0
trans-2-Methoxy-cyclohexyl p-bromo-benzenesulfonate	C_2H_5OH	3.11×10^{-7}	-6.51	13	50.0
	80% C_2H_5OH	3.25×10^{-6}	-5.49	13	50.0
	50% C_2H_5OH	1.61×10^{-5}	-4.79	13	50.0
	CH_3OH	1.12×10^{-6}	-5.95	13	50.0
	CH_3COOH	3.46×10^{-7}	-6.46	13, 34	50.0
Triphenylmethyl acetate	50% CH_3COCH_3	7.2×10^{-4}	-3.14	38	25.0

TABLE II (cont.)

Compound	Solvent[a]	k_1, $sec.^{-1}$	log k_1	Ref.	Temp.(°C.)
Benzhydryl chloride	C_2H_5OH	$5.30x10^{-5}$	-4.28	32	25.0
	90% C_2H_5OH	$4.90x10^{-4}$	-3.31	33	25.0
	80% C_2H_5OH	$1.72x10^{-3}$	-2.76	33	25.0
	90% CH_3COCH_3	$4.60x10^{-6}$	-5.34	6	25.0
	80% CH_3COCH_3	$7.24x10^{-5}$	-4.14	6	25.0
	70% CH_3COCH_3	$3.20x10^{-4}$	-3.49	6	25.0
	50% CH_3COCH_3	$1.65x10^{-2}$	-1.78	38	25.0
Isopropyl p-bromobenzenesulfonate	C_2H_5OH	$2.64x10^{-4}$	-3.58	20	70.0
	80% C_2H_5OH	$1.70x10^{-3}$	-2.77	20	70.0
	CH_3OH	$7.31x10^{-4}$	-3.14	20	70.0
	CH_3COOH	$6.94x10^{-5}$	-4.16	20	70.0
	97.5%$(CH_3CO)_2O$- 2.5% CH_3COOH	$1.42x10^{-6}$	-5.85	20	70.0
Pinacolyl p-bromobenzenesulfonate	C_2H_5OH	$7.04x10^{-5}$	-4.15	20	70.0
	80% C_2H_5OH	$1.38x10^{-3}$	-2.86	20	70.0
	CH_3OH	$3.21x10^{-9}$	-3.49	20	70.0
	CH_3COOH	$2.74x10^{-4}$	-3.56	20	70.0
	97.5%$(CH_3CO)_2O$- 2.5% CH_3COOH	$1.16x10^{-5}$	-4.94	20	70.0
	CH_3COOH	$6.95x10^{-7}$	-6.16	36	25.0
	HCOOH	$8.58x10^{-4}$	-3.07	36	25.0

TABLE II (Cont.)

Compound	Solvent[a]	k_1, sec.$^{-1}$	log k_1	Ref.	Temp.(°C.)
n-Butyl bromide	C_2H_5OH	7.8×10^{-7}	-6.11	19	75.1
	90% C_2H_5OH[e]	2.51×10^{-6}	-5.60	19	75.1
	80% C_2H_5OH[e]	3.89×10^{-6}	-5.41	19	75.1
	60% C_2H_5OH[e]	7.24×10^{-6}	-5.14	19	75.1
	CH_3OH[d]	1.70×10^{-6}	-5.77	19	75.1
	96.7% CH_3OH[d,e]	2.42×10^{-6}	-5.62	19	75.1
	69.5% CH_3OH[d,e]	1.13×10^{-5}	-4.95	19	75.1
	HCOOH[d]	2.82×10^{-7}	-6.55	37	75.1

[a] Where only part of the solvent is specified, the rest is water

[b] Extrapolated from a higher temperature using

$= 19.8$ kcal.[13]

[c] Extrapolated from a higher temperature using

$= 20.2$ kcal.[13]

[d] Extrapolated from higher or lower temperatures using

$= 22.0$ kcal.

[e] Interpolated from a plot of log k vs. mole fraction water

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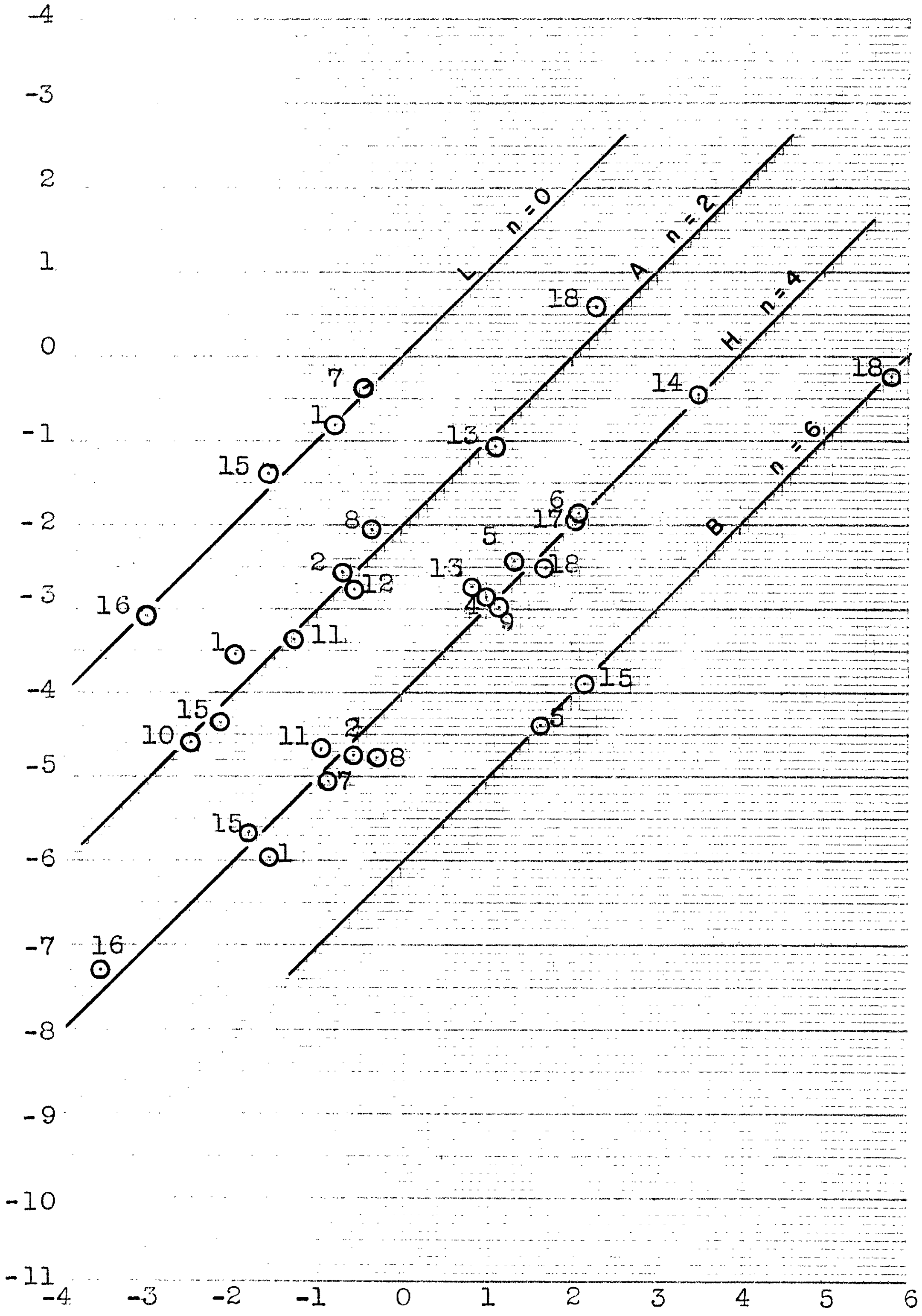

Fig. 3 .- n + Log k/k_o(obsd.) vs. log k/k_o (calcd.) from Whirlwind I Constants. For identification of solvents and compounds see p. 37.

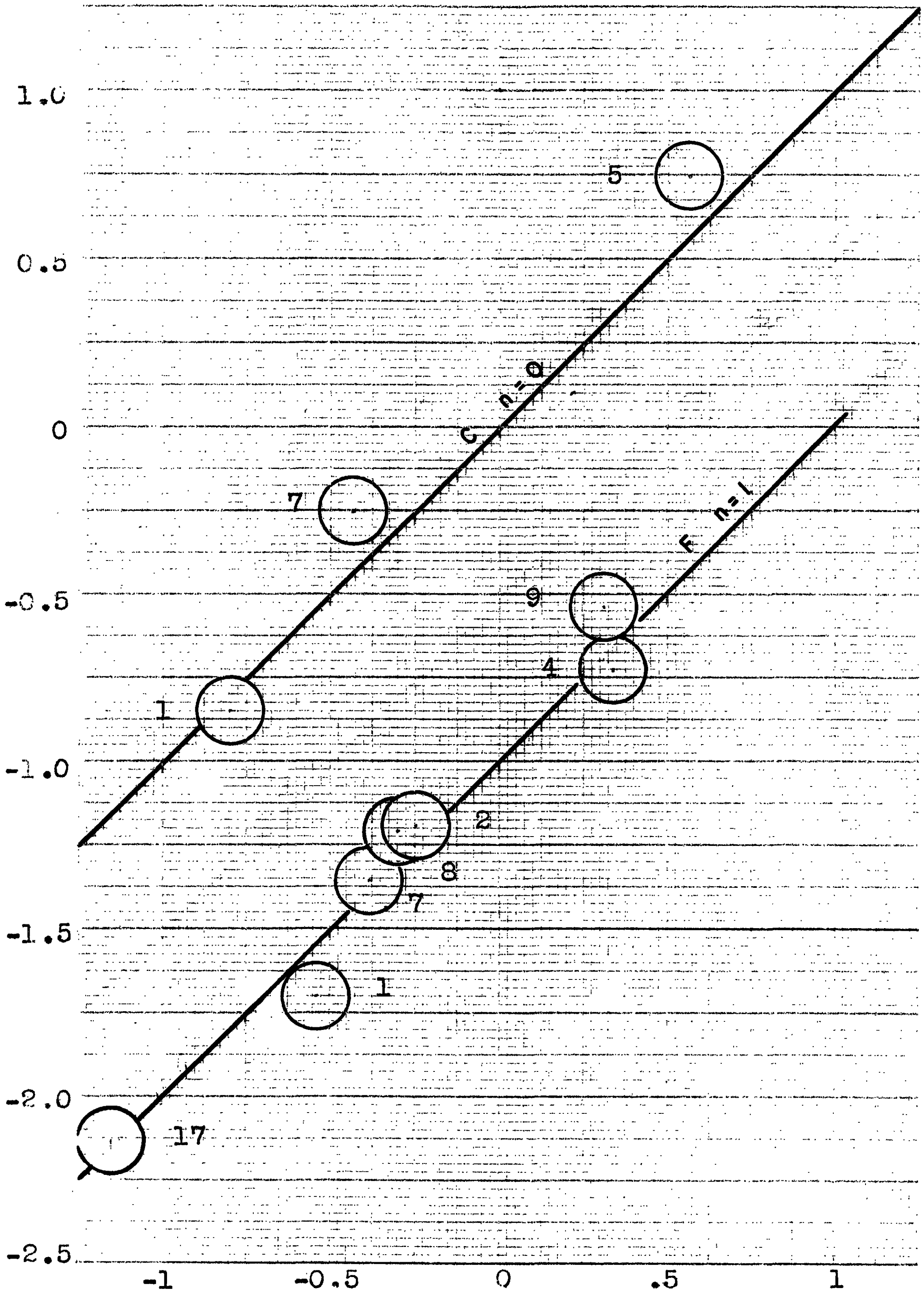

Fig. 4 .- n+Log k/k_o (obsd.) vs. log k/k_o (calcd.) from Whirlwind I Constants. For identification of solvents and compounds see p. 37.

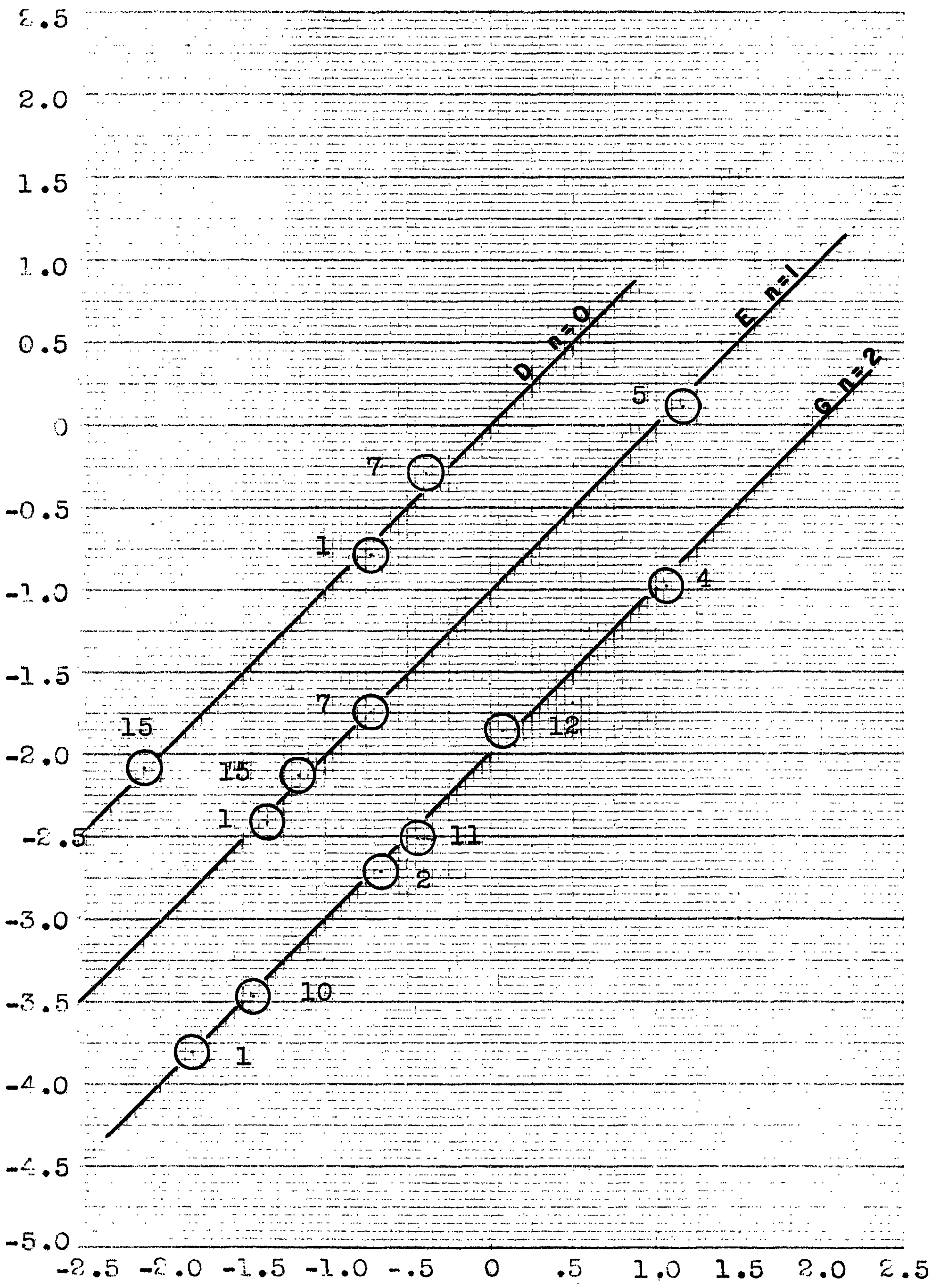

Fig. 5 .- n+Log k/k_o (obsd.) vs. log k/k_o (calcd.) from Whirlwind I Constants. For identification of solvents and compounds see p. 37.

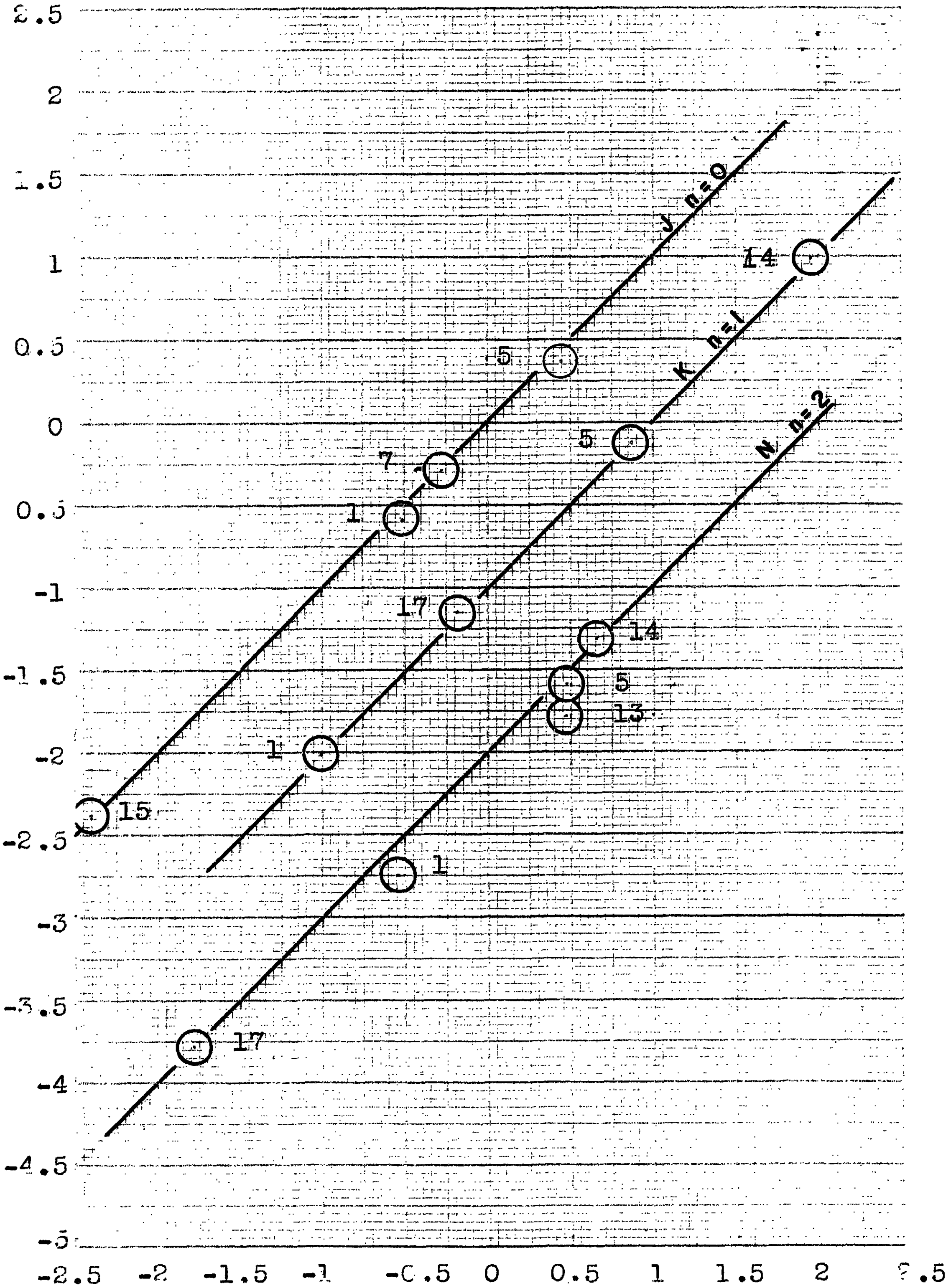

Fig. 6 .- n + Log k/k_o (obsd.) vs. log k/k_o (calcd.) from Whirlwind I Constants. For identification of solvents and compounds see p. 37.

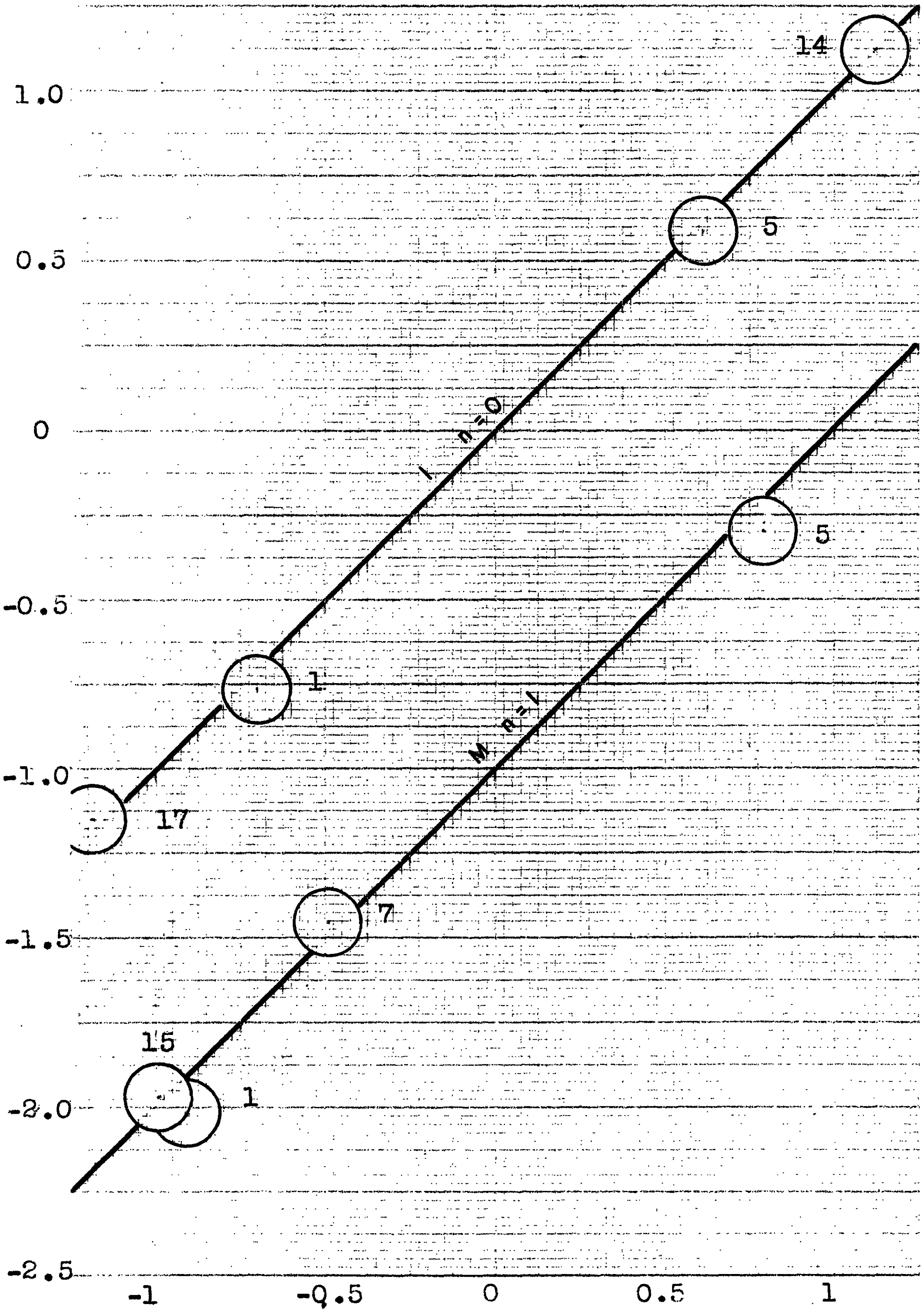

Fig. 7 .- n+Log k/k$_o$ (obsd.) vs. log k/k$_o$ (calcd.) from Whirlwind I Constants. For identification of solvents and compounds see p. 37.

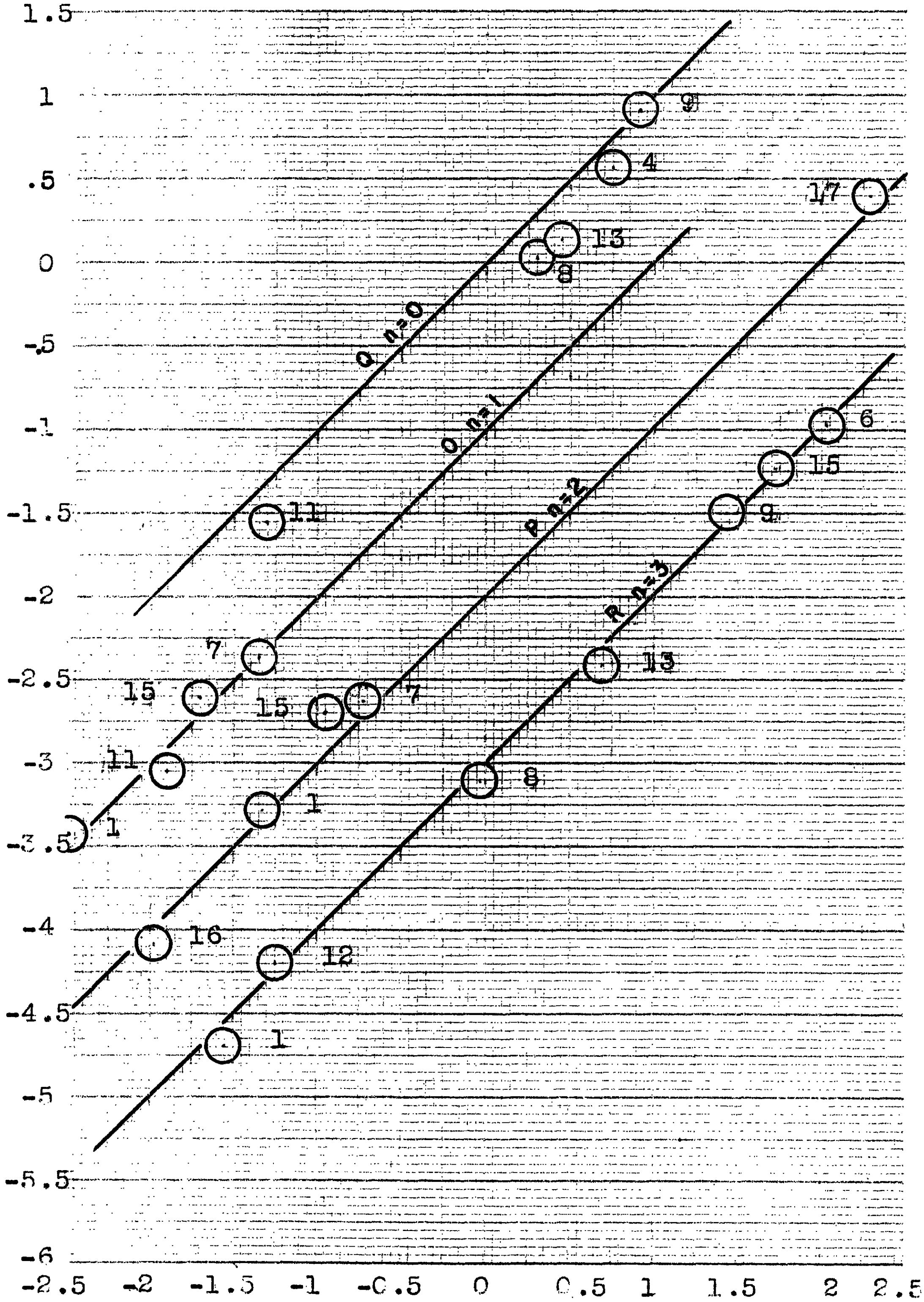

Fig. 8 .- $n + \text{Log } k/k_0$ (obsd.) vs. log k/k_0 (calcd.) from Whirlwind I Constants. For identification of solvents and compounds see p. 37.

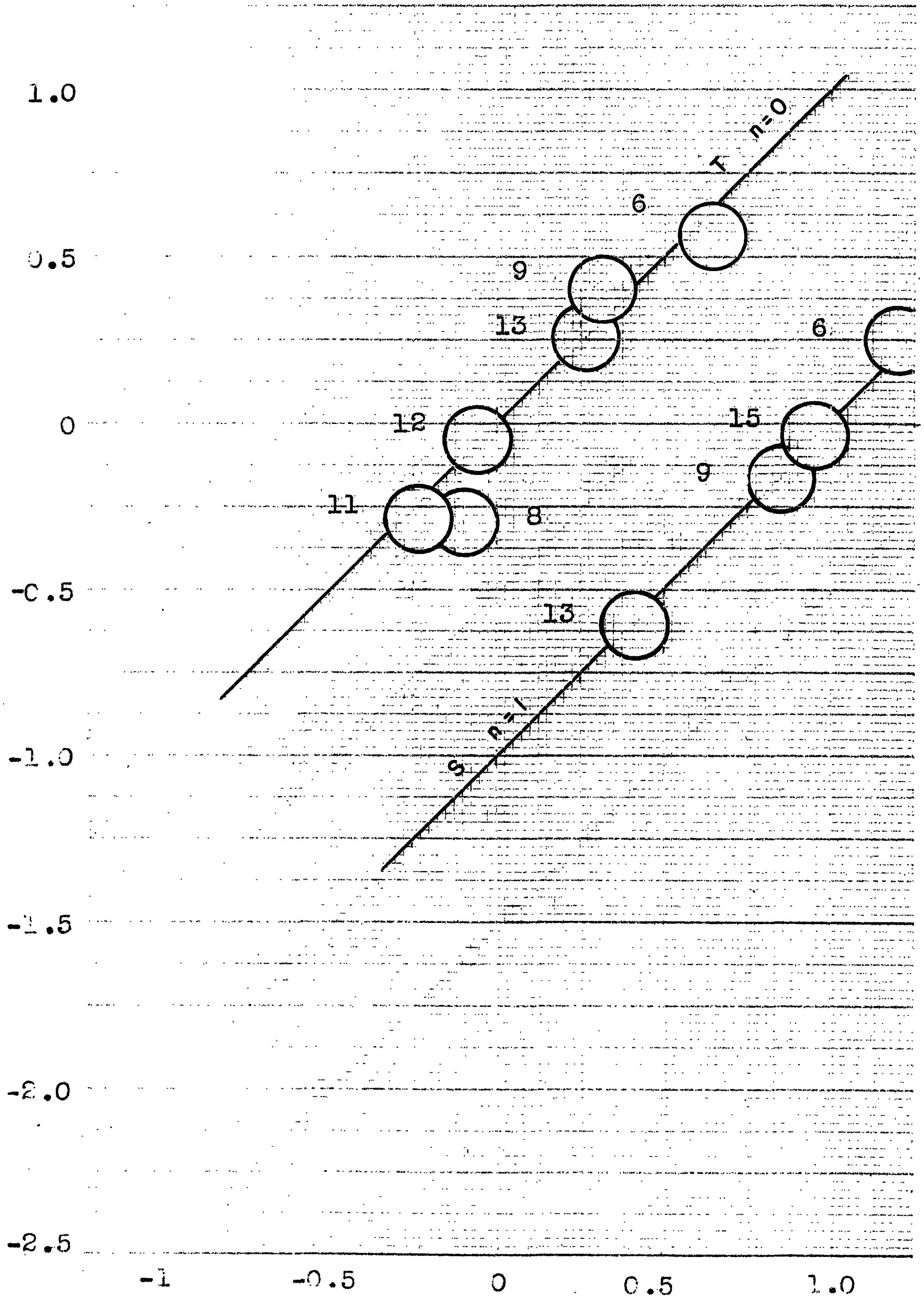

Fig. 9 .- n + Log k/k_o (obsd.) vs. log k/k_o (calcd.) from Whirlwind I Constants. For identification of solvents and compounds see p. 37.

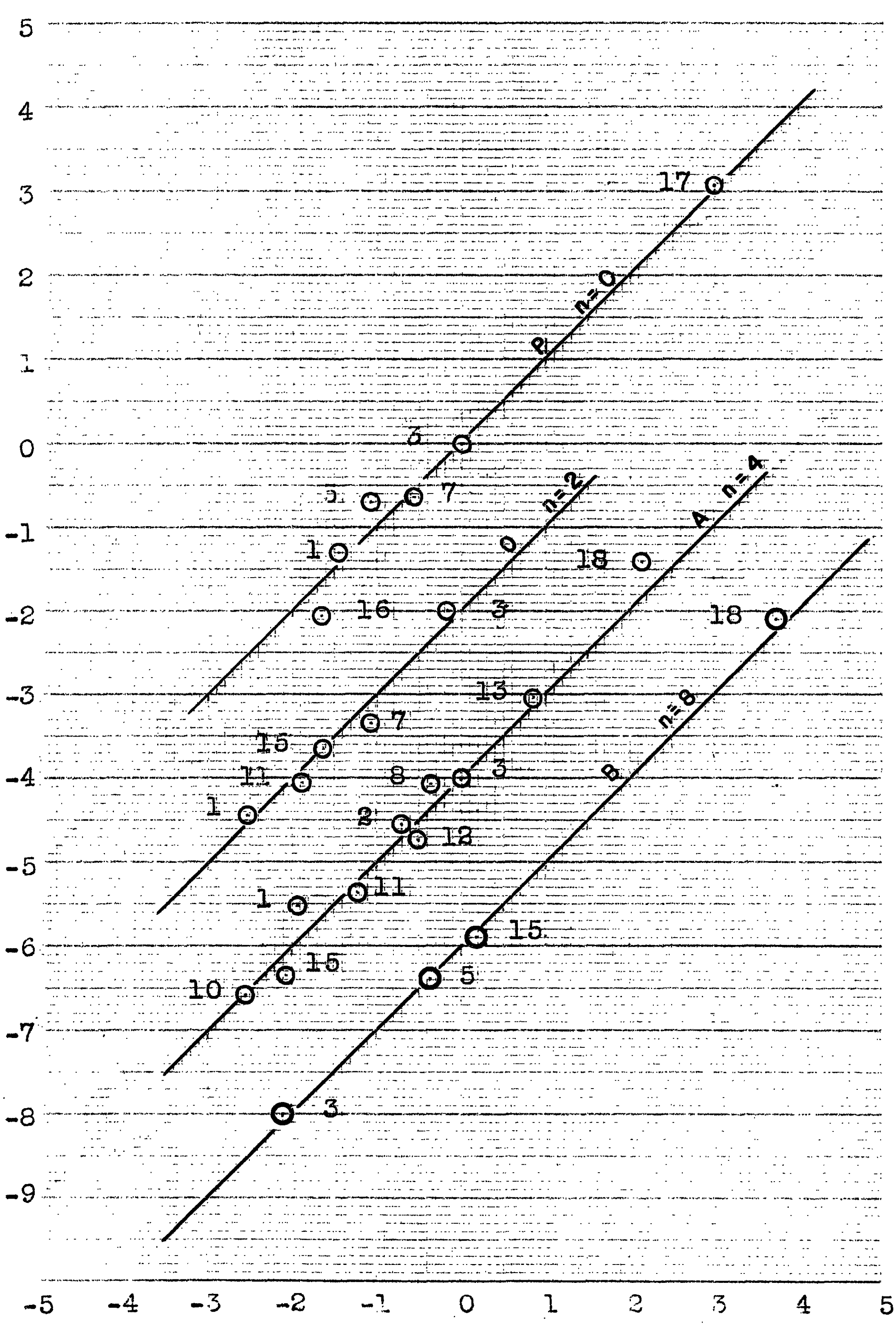

Fig. 10 .- Log. k/k_o (obsd.)+n vs. log k/k_o (calcd.) from Trial and Error Constants. Add 2 to abscissa of Compound B. For identification of solvents and compounds see p. 37.

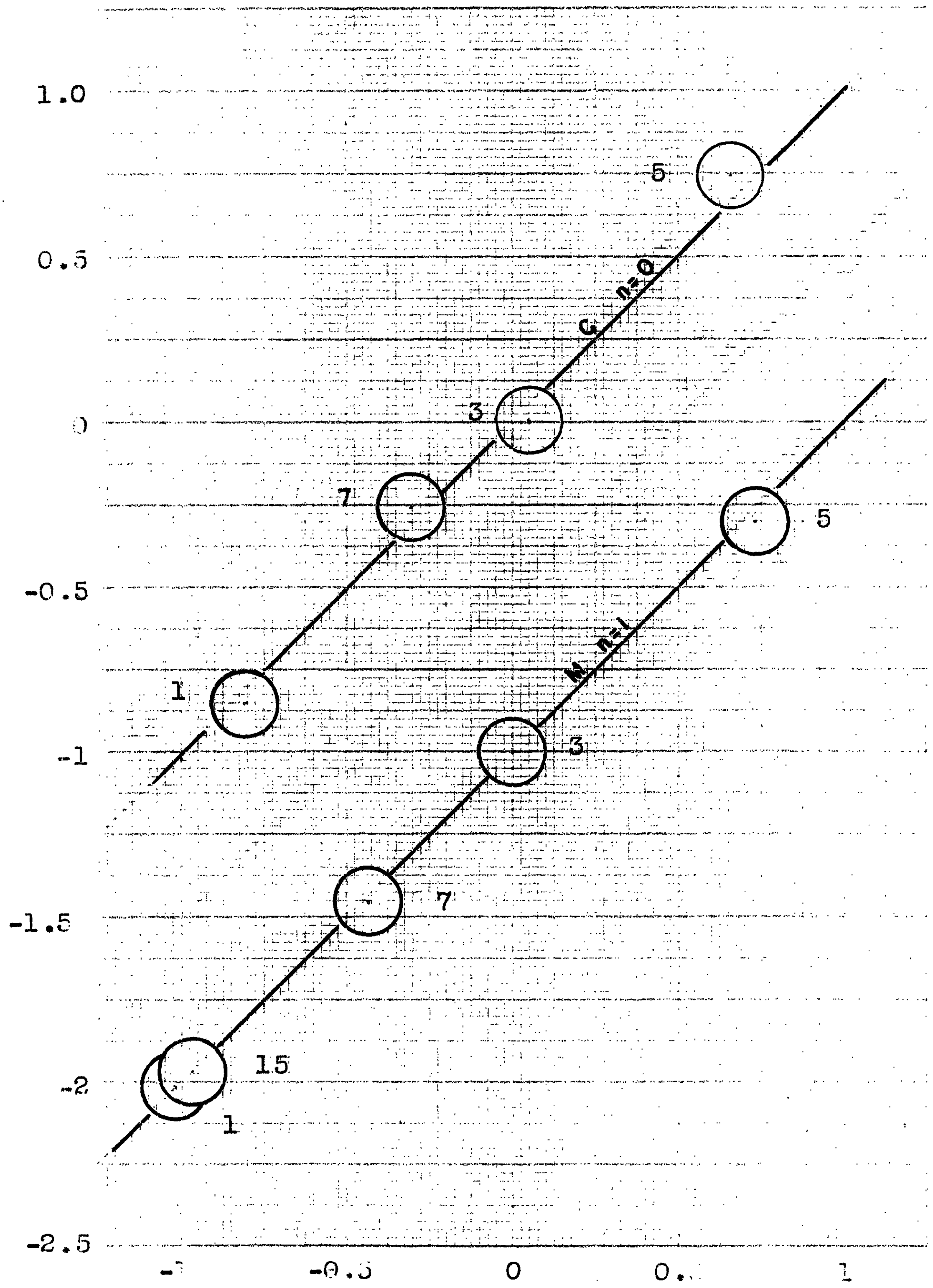

Fig. 11 .- $n + \log k/k_o$ (obsd.) vs. $\log k/k_o$ (calcd.) from Trial and Error Constants. For identification of solvents and compounds see p. 37.

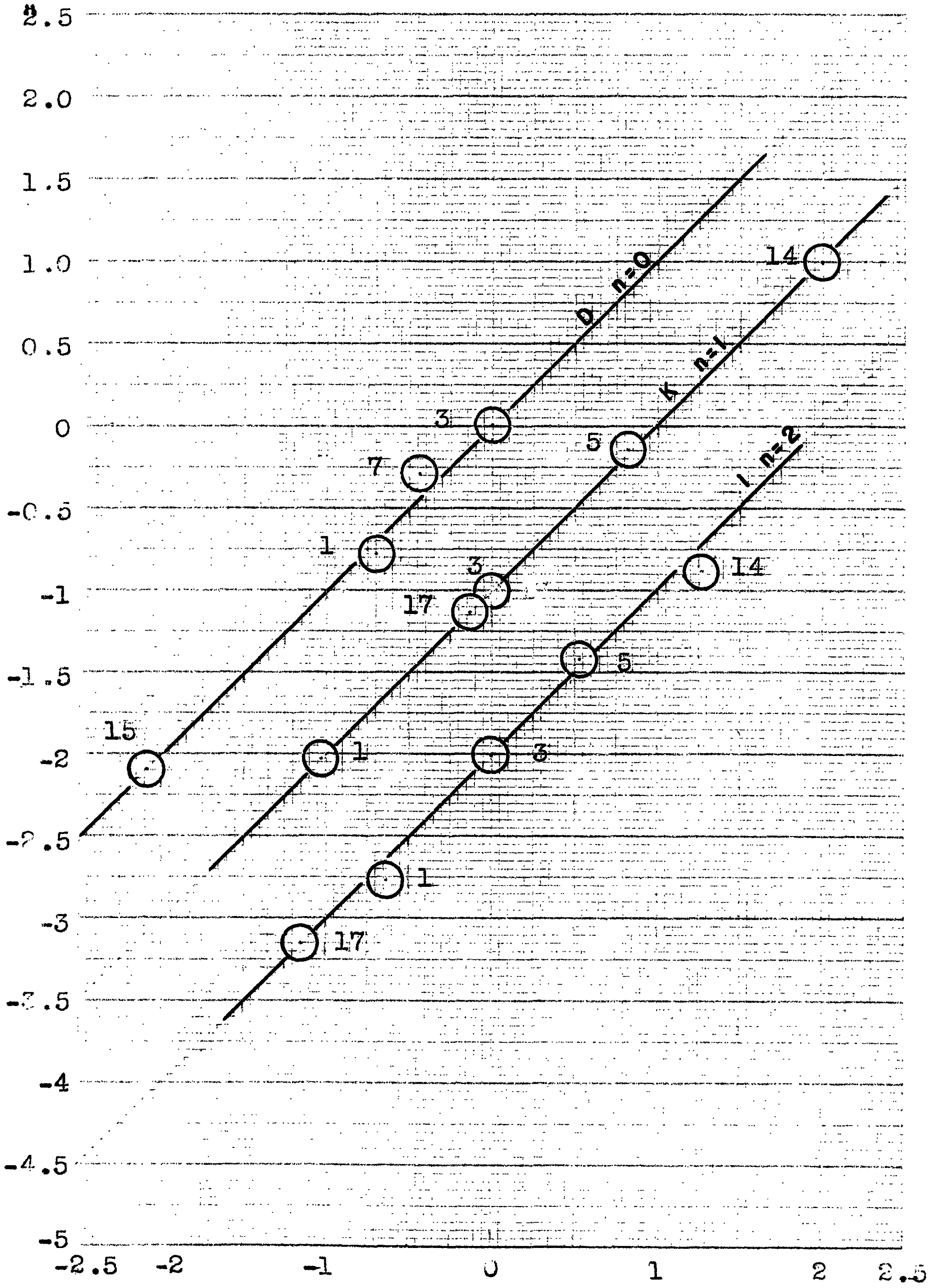

Fig. 12 -- $n +$ Log k/k_o (obsd.) vs. log k/k_o (calcd.) from Trial and Error Constants. For identification of solvents and compounds see p. 37.

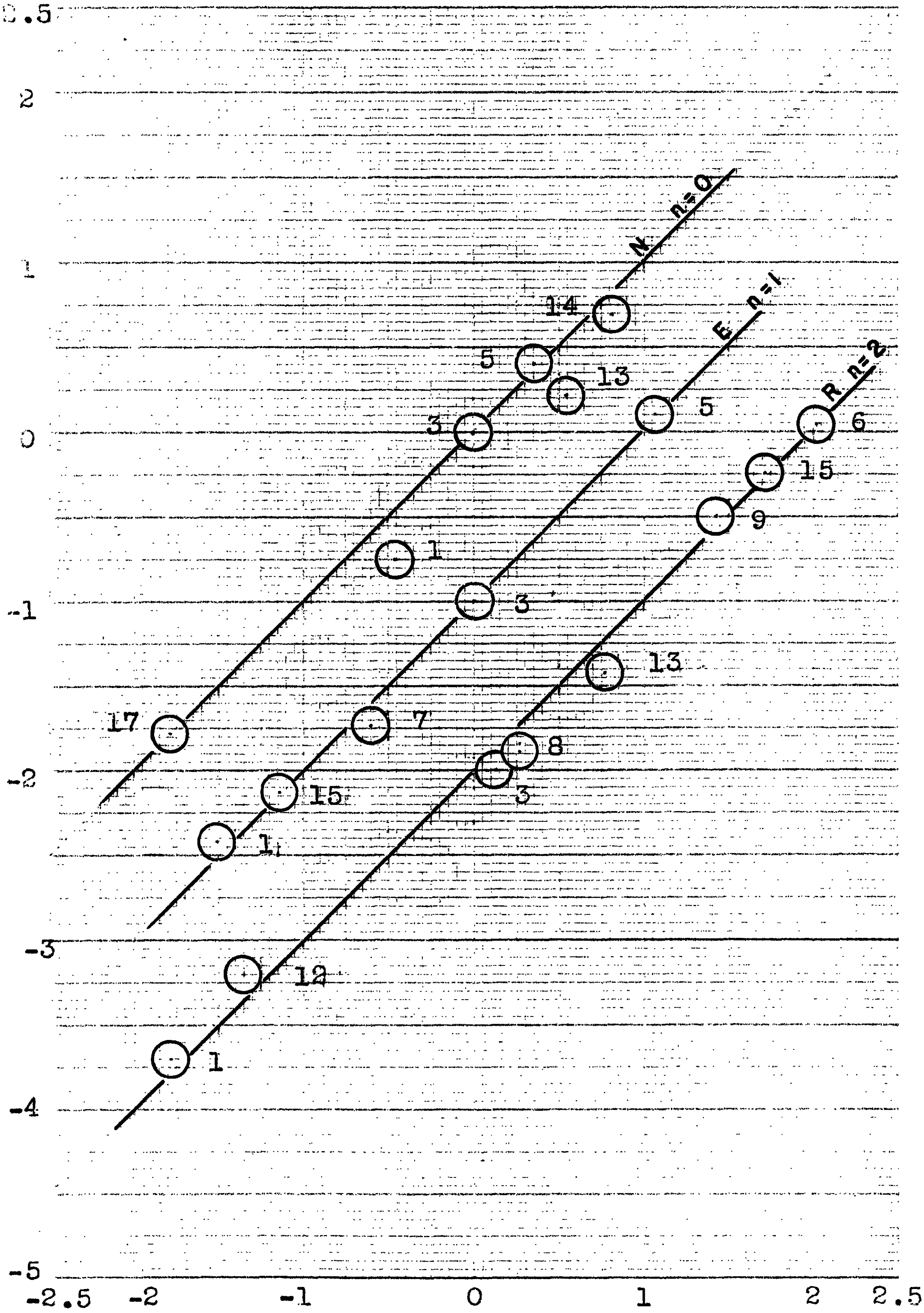

Fig. 13 .- $n + \text{Log } k/k_o$ (obsd.) vs. $\log k/k_o$ (calcd.) from Trial and Error Constants. For identification of solvents and compounds see p. 37.

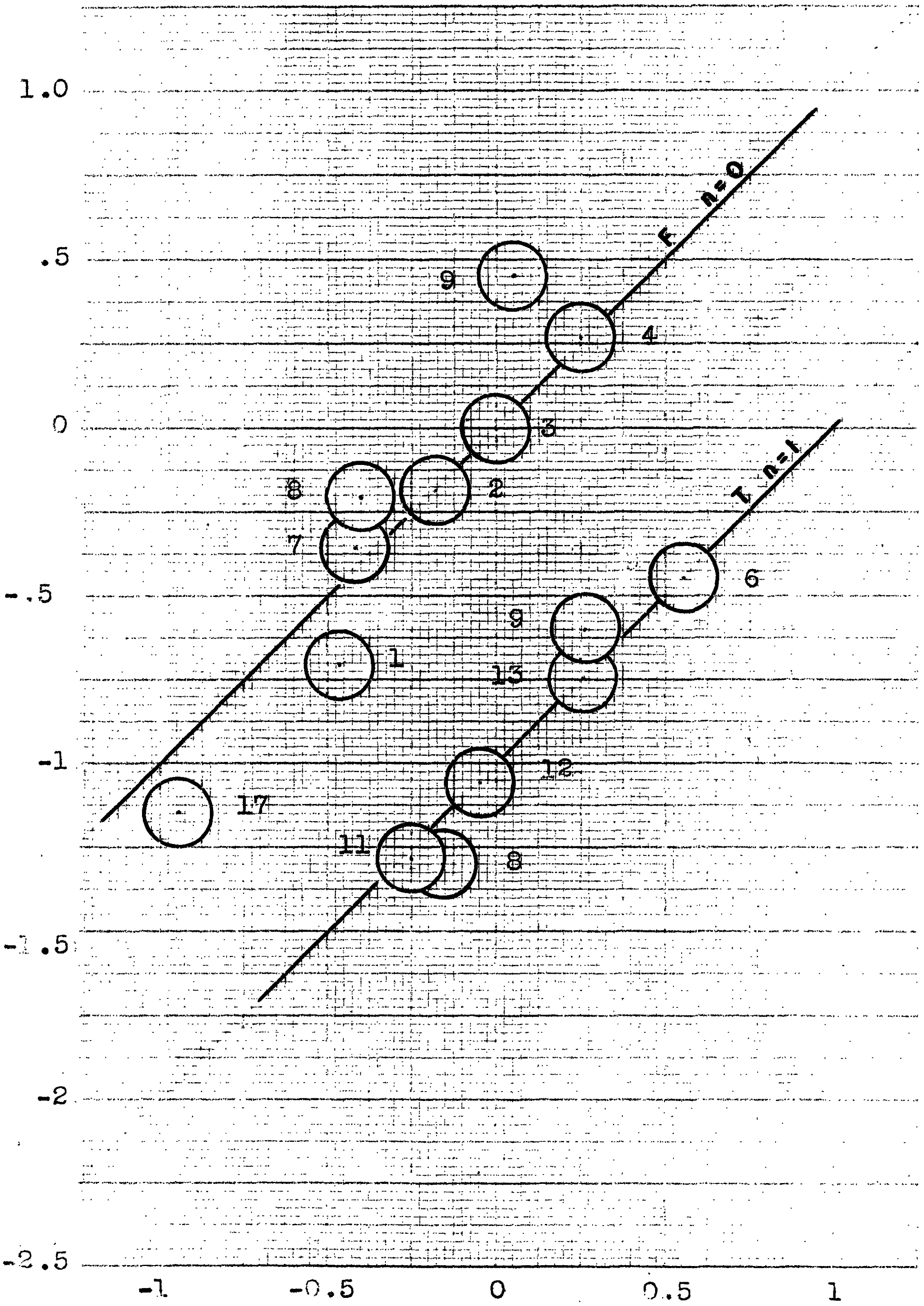

Fig. 14 .- n + Log. k/k_o (obsd.) vs. log k/k_o (calcd.) from Trial and Error Constants. For identification of solvents and compounds see p. 37.

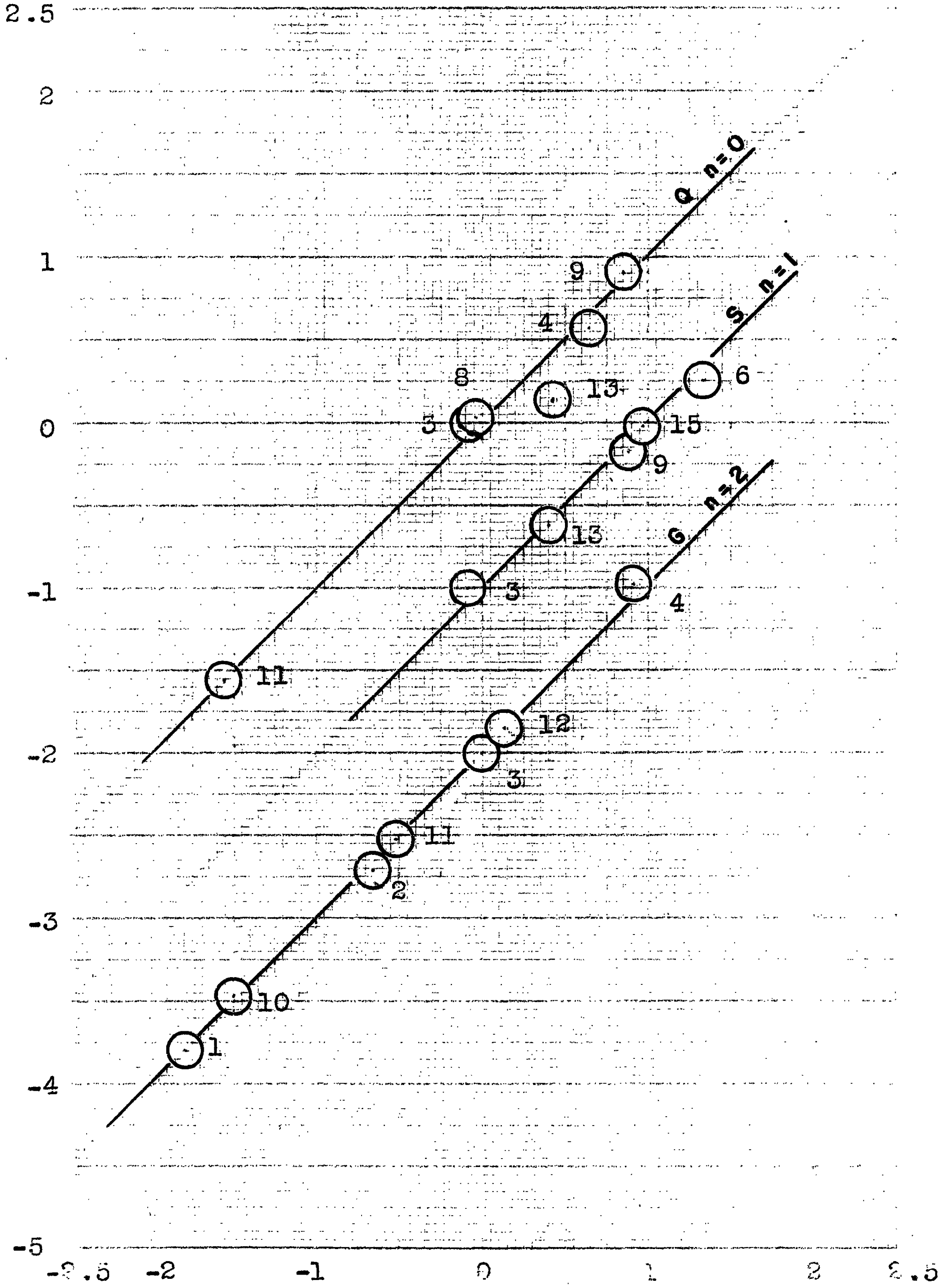

Fig. 15 .-- n + Log k/k_o (obsd.) vs. log k/k_o (calcd.) from Trial and Error Constants. For identification of solvents and compounds see p. 37.

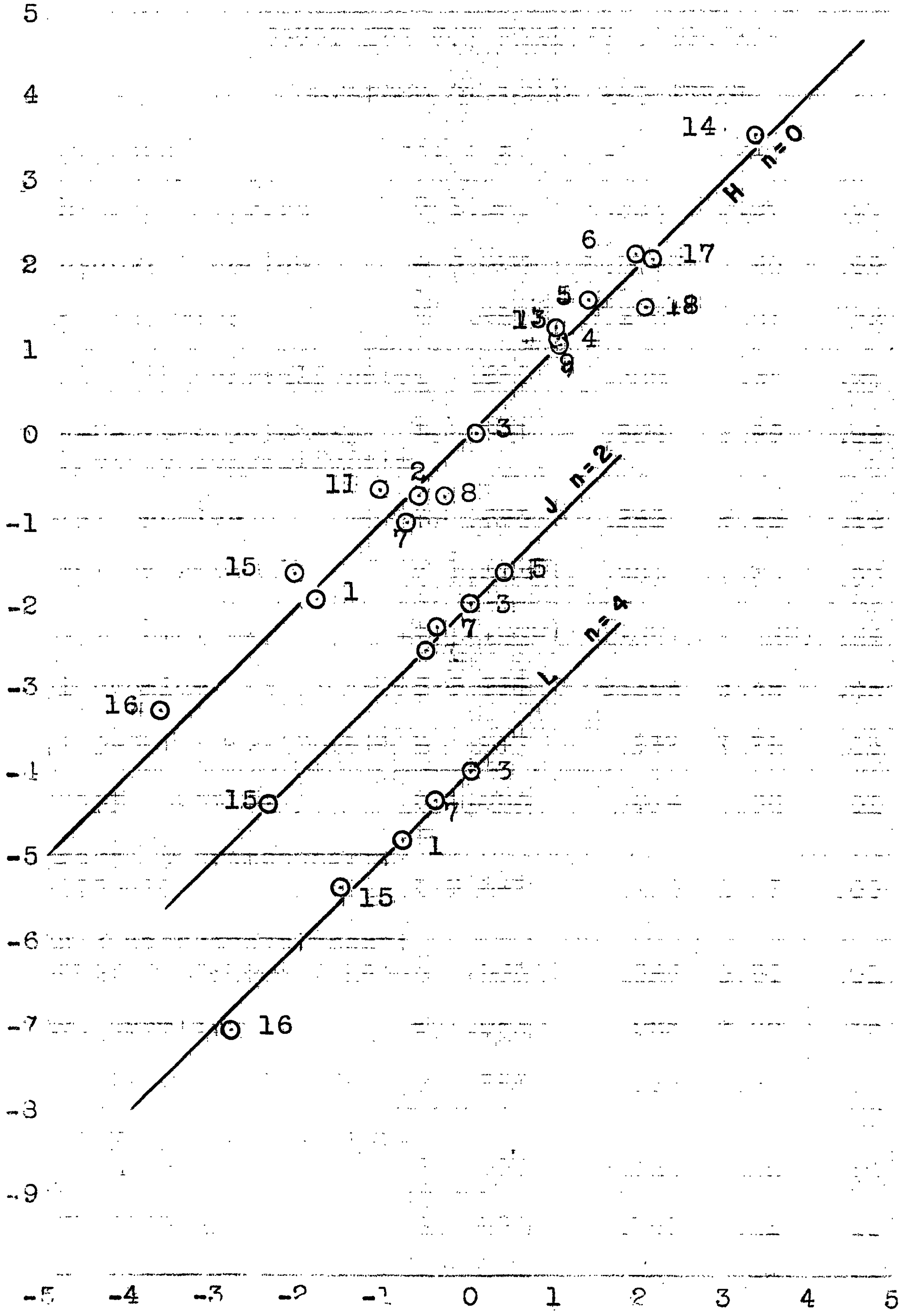

Fig. 16 .- n + Log. k/k_o (obsd.) vs. log k/k_o (calcd.) from Trial and Error Constants. For identification of solvents and compounds see p. 37.

TABLE III

CONSTANTS FOR VARIOUS COMPOUNDS

OBTAINED BY TRIAL AND ERROR

Compound	no.	s	s'	s/s'	r	Temp., °C
Benzhydryl chloride	9	1.000	1.023	0.97	0.21	25.0
Benzhydryl fluoride	4	0.328	1.304	.25	.09	25.0
Benzyl chloride	4	.421	0.459	.91	.06	50.0
Benzyl p-toluenesulfonate	4	.623	.380	1.64	.06	25.0
trans-2-Bromocyclohexyl p-bromobenzenesulfonate	5	.691	.804	0.89	.06	50.0
n-Butyl bromide	8	.695	.263	2.63	.14	75.1
t-Butyl bromide	7	1.373	.965	1.55	.03	25.0
t-Butyl chloride	16	(1.000)	(1.000)	(1.00)	.24	25.0
Ethyl bromide	5	0.968	0.395	2.45	.06	55.0
Ethyl p-toluenesulfonate	5	.667	.292	2.28	.04	50.0
Isopropyl bromide	5	1.023	.614	1.66	.01	50.0
Isopropyl p-bromobenzenesulfonate	5	0.547	.433	1.27	.09	70.0
trans-2-Methoxycyclohexyl p-bromobenzenesulfonate	5	.505	.544	0.93	.01	50.0
Methyl bromide	6	.943	.263	3.59	.13	50.0
-Phenylethyl chloride	5	.996	1.222	0.81	.14	50.0
Pinacolyl p-bromobenzenesulfonate	6	.653	0.760	.86	.18	70.0
Trityl acetate	6	.305	.749	.41	.10	25.0
Trityl fluoride	8	.286	1.003	.29	.10	25.0
Trityl p-nitrophenyl ether	5	.244	0.760	.32	.05	25.0
Trityl thiocyanate	6	.358	.298	1.20	.05	25.0

TABLE IV

CONSTANTS FOR VARIOUS COMPOUNDS OBTAINED BY WHIRLWIND I

	Compound	no.	s	s'	s/s'	r	Temp., °C
A	Benzhydryl chloride	9	1.241	1.273	0.97	0.22	25.0
B	Benzhydryl fluoride	4	0.330	1.319	.25	.05	25.0
C	Benzyl chloride	4	.421[a]	0.526[a]	.80[a]	.12[a]	50.0
D	Benzyl p-toluenesulfonate	4	.727	.429	1.69	.06	25.0
E	trans-2-Bromocyclohexyl p-bromobenzenesulfonate	5	.788	.880	0.89	.04	50.0
F	n-Butyl bromide	8	.928	.381	2.43	.08	75.1
G	t-Butyl bromide	7	1.656	1.099	1.51	.05	25.0
H	t-Butyl chloride	16	(1.000)	(1.000)	(1.00)	.21	25.0
I	Ethyl bromide	5	0.957	0.394	2.43	.03	55.0
J	Ethyl p-toluenesulfonate	5	.706	.285	2.48	.04	50.0
K	Isopropyl bromide	5	1.014	.610	1.66	.02	50.0
L	Isopropyl p-bromobenzenesulfonate	5	0.651	.492	1.32	.09	70.0
M	trans-2-Methoxycyclohexyl p-bromobenzenesulfonate	5	.574	.588	0.98	.06	50.0
N	Methyl bromide	6	.946	.279	3.39	.11	50.0
O	-Phenylethyl chloride	5	1.352	1.636	0.83	.08	50.0
P	Pinacolyl p-bromobenzenesulfonate	6	0.741	0.880	.84	.12	70.0
Q	Trityl acetate	6	.211[b]	.731[b]	.29[b]	.21[b]	25.0
R	Trityl fluoride	8	.274	1.097	.25	.08	25.0
S	Trityl p-nitrophenyl ether	5	.178	.648	.27	.03	25.0
T	Trityl thiocyanate	6	.342	.293	1.16	.06	25.0

TABLE IV (Cont.)

[a] The value of s obtained by Whirlwind I was -10.5. Since a negative s has no physical significance the s and s' listed were obtained by trial and error. They are thought to be reasonable but should be considered only provisional. The mean deviation using the Whirlwind I values($s = -10.48$; $s' = 1.84$) is 0.04.

[b] The value of s obtained by Whirlwind I was -0.4. The values listed should be considered only provisional[a]. The mean deviation using the Whirlwind I values ($s = -0.402$; $s' = 0.544$) is 0.15.

TABLE V

CONSTANTS FOR VARIOUS SOLVENTS OBTAINED BY TRIAL AND ERROR

Solvent	n	e
1 Ethanol	0.05	-1.92
2 90% Ethanol - 10% water	.00	-0.68
3 80% Ethanol - 20% water	.00	.00
4 60% Ethanol - 40% water	.00	.96
5 50% Ethanol - 50% water	.00	1.33
6 40% Ethanol - 60% water	.00	1.88
7 Methanol	-.48	-0.34
8 96.7% Methanol - 3.3% water	-.71	.34
9 69.5% Methanol - 30.5% water	-.48	1.44
10 90% Acetone - 10% water	2.14	-4.58
11 80% Acetone - 20% water	1.42	-2.56
12 70% Acetone - 30% water	1.42	-1.88
13 50% Acetone - 50% water	0.43	0.51
14 Water	-.10	3.42
15 Acetic acid	-5.22	3.08
16 97.5% Acetic anhydride - 2.5% acetic acid	-10.78	7.08
17 Formic acid	-3.42	5.47
18 83.3% Formic acid - 16.7% acetone	-3.32	5.34

TABLE vi

CONSTANTS FOR VARIOUS SOLVENTS

OBTAINED BY WHIRLWIND I

	Solvent	n	e
1	Ethanol	-0.166	-1.383
2	90% Ethanol - 10% water	-.075	-0.479
3	80% Ethanol - 20% water	(.000)	(.000)
4	60% ethanol - 40% water	-.094	1.096
5	50% Ethanol - 50% water	.141	1.193
6	40% Ethanol - 60% water	.321	1.770
7	Methanol	-.106	-0.735
8	96.7% Methanol - 3.3% water	-.342	.053
9	69.5% Methanol - 30.5% water	-.230	1.373
10	90% Acetone - 10% water	1.320	-3.268
11	80% Acetone - 20% water	1.171	-2.136
12	70% acetone - 30% water	0.968	-1.383
13	50% Acetone - 50% water	.328	0.541
14	Water	-.471	3.973
15	Acetic acid	-4.485	2.694
16	97.5% Acetic anhydride - 2.5% Acetic acid	-8.009	4.478
17	Formic acid	-3.526	5.563
18	83.3% Formic acid - 16.7% acetone	-3.595	5.299

TABLE VII

DEVIATIONS OF LOGARITHMS OF RATES CALCULATED FROM TRIAL AND ERROR CONSTANTS FROM LOGARITHMS OF OBSERVED RATES[a]

Compound[b]	Solvent[c]																	
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
A	-.39	-.15	.00	-	-	-	-	-.29	-	.03	.17	.22	-.11	-	.29	-	-	-.46
B	-	-	-.10	-	.03	-	-	-	-	-	-	-	-	-	.08	-	-	-.14
C	.04	-	.05	-	-.08	-	-.05	-	-	-	-	-	-	-	-	-	-	-
D	.08	-	.00	-	-	-	-.14	-	-	-	-	-	-	-	.00	-	-	-
E	-.09	-	.00	-	-.04	-	.14	-	-	-	-	-	-	-	-.01	-	-	-
F	.23	.01	.00	-.02	-	-	-.06	-.19	-.41	-	-	-	-	-	-	-	.20	-
G	.02	.05	.00	-.10	-	-	-	-	-	-.04	.00	-.01	-	-	-	-	-	-
H	.17	.11	.06	-.11	-.20	-.20	-.30	.42	.00	-	-.40	-	-.29	-.17	-.44	-.35	.04	.58
I	.13	-	.00	-	-.05	-	-	-	-	-	-	-	-	.14	-	-	.00	-
J	.05	-	.00	-	.02	-	-.11	-	-	-	-	-	-	-	.00	-	-	-
K	-.01	-	.00	-	-.04	-	-	-	-	-	-	-	-	.01	-	-	.00	-
L	.01	-	.00	-	-	-	-.04	-	-	-	-	-	-	-	-.14	.24	-	-
M	.00	-	.00	-	.03	-	.03	-	-	-	-	-	-	-	.00	-	-	-
N	.29	-	.00	-	-.06	-	-	-	-	-	-	-	.32	.13	-	-	.00	-
O	-.08	-	-.18	-	-	-	.29	-	-	-	.16	-	-	-	.00	-	-	-

TABLE VII (Cont.)

Compound[b]	Solvent[c] 1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
P	-.14	-	.00	-	-	-	.06	-	-	-	-	-	-	-	-.37	.42	.09	-
Q	-	-	-.08	.08	-	-	-	-.07	-.05	-	.00	-	.29	-	-	-	-	-
R	-.08	-	.13	-	-	-.01	-	.15	-.07	-	-	-.15	.19	-	-.04	-	-	-
S	-	-	-.09	-	-	.09	-	-	.05	-	-	-	.02	-	.00	-	-	-
T	-	-	-[d]	-	-	.00	-	.14	-.14	-	.03	.00	.00	-	-	-	-	-

[a] A positive deviation indicates that the calculated rate is faster than the observed rate.

[b] A = Benzhydryl chloride; B = Benzhydryl fluoride; C = Benzyl chloride; D = Benzyl p-toluenesulfonate; E = trans-2-Bromocyclohexyl p-bromobenzenesulfonate; F = n-Butyl bromide; G = t-Butyl bromide; H = t-Butyl chloride; I = Ethyl bromide; J = Ethyl p-toluenesulfonate; K = Isopropyl bromide; L = Isopropyl p-bromobenzenesulfonate; M = trans-2-Methoxycyclohexyl p-bromobenzenesulfonate; N = Methyl bromide; O = -Phenylethyl chloride; P = Pinacolyl p-bromobenzenesulfonate; Q = Trityl acetate; R = Trityl fluoride; S = Trityl p-nitrophenyl ether; T = Trityl thiocyanate.

[c] 1 = Ethanol; 2 = 90% Ethanol - 10% water; 3 = 80% Ethanol - 20% water; 4 = 60% Ethanol - 40% water; 5 = 50% Ethanol - 50% water; 6 = 40% Ethanol - 60% water; 7 = Methanol; 8 = 96.7% Methanol - 3.3% water; 9 = 69.5% Methanol - 30.5% water; 10 = 90% Acetone - 10% water; 11 = 80% Acetone - 20% water; 12 = 70% Acetone - 30% water; 13 = 50% Acetone - 50% water; 14 = Water; 15 = Acetic acid; 16 = 97.5% Acetic anhydride - 2.5% acetic acid; 17 = Formic acid; 18 = 83.3% Formic acid - 16.7% acetone.

[d] No data are available in this solvent for trityl thiocyanate. Log k_o was assumed to be -2.98.

TABLE VII A

DEVIATIONS OF LOGARITHMS OF RATES CALCULATED FROM WHIRLWIND I CONSTANTS FROM LOGARITHMS OF OBSERVED RATES[a]

Compound[b]	Solvent[c]																	
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
A	-.45	-.15	.00	-	-	-	-	.29	-	.10	.11	.17	.12	-	.23	-	-	-.31
B	-	-	.00	-	.01	-	-	-	-	-	-	-	-	-	-.04	-	-	-.11
C	-.05	-	.00	-	.17	-	-.17	-	-	-	-	-	-	-	-	-	-	-
D	.07	-	.00	-	-	-	-.10	-	-	-	-	-	-	-	-.02	-	-	-
E	.08	-	.00	-	-.05	-	.01	-	-	-	-	-	-	-	-.03	-	-	-
F	.16	-.06	.00	.06	-	-	-.01	-.09	-.15	-	-	-	-	-	-	-	-.01	-
G	-.01	.05	.00	.04	-	-	-	-	-	.02	.08	-.08	-	-	-	-	-	-
H	.43	.18	.00	-.13	-.26	-.05	.22	.44	.12	-	-.29	-	-.42	-.05	-.15	-.24	-.03	-.20
I	.07	-	.00	-	.07	-	.01	-	-	-	-	-	-	-	-.01	-	-	-
J	.07	-	.00	-	.03	-	-	-	-	-	-	-	-	.00	-	-	-.03	-
K	.01	-	.00	-	.01	-	-	-	-	-	-	-	-	-.04	-	-	-.04	-
L	.02	-	.00	-	-	-	-.06	-	-	-	-	-	-	-	-.20	-.07	-	-
M	.11	-	.00	-	.07	-	-.03	-	-	-	-	-	-	-	-.02	-	-	-
N	.21	-	.00	-	.06	-	-	-	-	-	-	-	.24	-.02	-	-	.00	-
O	-.05	-	.00	-	-	-	.01	-	-	-	.15	-	-	-	-.10	-	-	-

TABLE VII A (Cont.)

Compound[b]	Solvent[c]																	
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
P	-.05	-	.00	-	-	-	-.10	-	-	-	-	-	-	-	-.25	.09	-.10	-
Q	-	-	.00	.19	-	-	-	.26	.01	-	.30	-	.31	-	-	-	-	-
R	.14	-	.00	-	-	.00	-	-.15	-.06	-	-	-.05	.11	-	-.04	-	-	-
S	-	-	.00	-	-	-.05	-	-	.02	-	-	-	.03	-	-.02	-	-	-
T	-	-	.00[d]	-	-	.07	-	.20	-.08	-	.05	-.02	.01	-	-	-	-	-

[a,b,c,d] See corresponding footnotes in Table VII

TABLE VIII

LOGARITHMS OF RELATIVE RATES

Solvent^{c}

Compound^{b}	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
A	-1.52	-0.55	0.00	-	-	-	-	-0.07	-	-2.58	-1.38	-0.73	0.98	-	-2.37	-	-	2.60
B	-	-	.00	-	1.61	-	-	-	-	-	-	-	-	-	2.11	-	-	5.91
C	-0.85	-	.00	-	0.74	-	-0.26	-	-	-	-	-	-	-	-	-	-	-
D	-0.78	-	.00	-	-	-	-0.29	-	-	-	-	-	-	-	-2.09	-	-	-
E	-1.42	-	.00	-	1.11	-	-.74	-	-	-	-	-	-	-	-1.13	-	-	-
F	-0.70	-0.19	.00	0.27	-	-	-.36	-.21	0.46	-	-	-	-	-	-	-	-1.14	-
G	-1.80	-.71	.00	1.02	-	-	-	-	-	-1.46	-0.52	.15	-	-	-	-	-	-
H	-1.98	-.73	.00	1.13	1.59	2.14	-1.06	-.73	1.02	-	-.68	-	1.29	3.55	-1.64	-3.29	2.07	1.50
I	-0.77	-	.00	-	0.58	-	-	-	-	-	-	-	-	1.12	-	-	-1.15	-
J	-.58	-	.00	-	.37	-	-0.29	-	-	-	-	-	-	-	-2.39	-	-	-
K	-1.02	-	.00	-	.86	-	-	-	-	-	-	-	-	1.99	-	-	-0.14	-
L	-0.81	-	.00	-	-	-	-.37	-	-	-	-	-	-	-	-1.39	-3.08	-	-
M	-1.02	-	.00	-	.70	-	-.46	-	-	-	-	-	-	-	-0.97	-	-	-
N	-0.75	-	.00	-	.41	-	-	-	-	-	-	-	0.22	0.68	-	-	-1.78	-
O	-2.44	-	.00	-	-	-	-1.36	-	-	-	-2.05	-	-	-	-1.62	-	-	-
P	-1.29	-	.00	-	-	-	-0.63	-	-	-	-	-	-	-	-0.70	-2.08	2.39	-

TABLE VIII (Cont.)

Compound[b]	Solvent[c]																	
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Q	-	-	0.00	0.56	-	-	-	0.03	0.90	-	-1.56	-	0.14	-	-	-	-	-
R	-1.70	-	.00	-	-	2.03	-	.11	1.50	-	-	-1.20	.57	-	1.76	-	-	-
S	-	-	.00	-	-	1.25	-	-	0.83	-	-	-	.38	-	0.97	-	-	-
T	-	-	a	-	-	0.56	-	-.30	.40	-	-0.28	-0.05	.26	-	-	-	-	-

[a] The value of -2.98 was assumed for log k_o

[b,c] See corresponding footnotes in Table VII

The mean deviation[23] in log k/k_o for the 106 reactions available is 0.108 corresponding to a factor of 1.28 , for compounds ranging from methyl bromide to trityl fluoride in ethanol - water, methanol - water, acetone - water, acetic acid - acetic anhydride, and formic acid - acetone mixtures. No deviation is as large as a factor of three. It is felt that this fit is quite satisfactory, considering the wide range of solvents, of compounds and of rates covered. The rates for some compounds vary by five or six powers of ten over the range of solvents investigated, the mean variation being three powers of ten. The largest mean deviation for any compound is a factor of 1.66 for benzhydryl chloride, for which the total variation in rates is more than five powers of ten.

For comparison, the mean deviation for the same reactions using equation 4 is a factor of 2.34 and the largest mean deviation is a factor of 76 for benzhydryl fluoride. Further, 14 of the 20 compounds have mean deviations in excess of a factor of two, and 8 have mean deviations in excess of a factor of three. The largest error for any reaction is a factor of 575 for benzhydryl fluoride in 83.3% formic acid - 16.7% acetone.

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(23) R. Livingston, "Physico Chemical Experiments", MacMillan Co., New York, N. Y., 1948, p. 29.

The n, e, s, and s' values listed in Tables III and V were obtained in the following manner. The reasonable (cf. Appendix B) approximation was made that water - ethanol mixtures are all of similar nucleophilicity and differ mainly in electrophilic character. (A similar assumption has been made by Winstein[13].) If this is true, then equation 6 degenerates to

$$\log (k/k_o) = s'e$$

in ethanol - water mixtures, since n = 0 for 80% ethanol - 20% water and hence for all ethanol - water mixtures. By assigning s' = 1.00 for ethyl p-toluenesulfonate the e values for ethanol - water mixtures listed in Table IX were calculated.

TABLE IX

PROVISIONAL VALUES OF e FOR ETHANOL - WATER MIXTURES

Solvent	e
Ethanol	-0.58
80% Ethanol - 20% water	0.00
50% Ethanol - 50% water	0.37

From n = 0.0 and these e values, s' values for most of the other compounds could be calculated from the data for ethanol - water solutions (Table X). Values of e for other ethanol - water mixtures could be calculated from the s' value of 3.86 for t-butyl chloride (Table XI). From these values, s' could be calculated (Table XII) for trityl acetate and trityl p-nitrophenyl ether (for which rate constants are not available in the solvents listed in Table IX).

TABLE X

PROVISIONAL VALUES OF s' FOR SEVERAL COMPOUNDS

Compound	s'
Benzhydryl chloride	2.42
Benzhydryl fluoride	4.35
Benzyl chloride	1.73
Benzyl p-toluenesulfonate	1.34
trans-2-Bromocyclohexyl p-bromobenzenesulfonate	2.72
n-Butyl bromide	1.21
t-Butyl bromide	3.10
t-Butyl chloride	3.86
Ethyl bromide	1.45
Ethyl p-toluenesulfonate	1.00
Isopropyl bromide	2.04
Isopropyl p-bromobenzenesulfonate	1.40
trans-2-Methoxycyclohexyl p-bromobenzenesulfonate	1.82
Methyl bromide	1.15
α -Phenylethyl chloride	4.21
Pinacolyl p-bromobenzenesulfonate	2.22
Trityl fluoride	2.98

TABLE XI

PROVISIONAL VALUES OF e FOR ETHANOL - WATER MIXTURES

Solvent	e
90% Ethanol - 10% water	-0.19
60% Ethanol - 40% water	.29
40% Ethanol - 60% water	.55

TABLE XII

PROVISIONAL VALUES OF s'

Compound	s'
Trityl p-nitrophenyl ether	2.27
Trityl acetate	1.93

By assigning n = 1.00 and e = 1.00 to acetic acid, values of s listed in Table were obtained.

TABLE XIII

SOME PROVISIONAL VALUES OF s

Compound	s
Benzhydryl chloride	4.79
Benzhydryl fluoride	2.24
Benzyl p-toluenesulfonate	3.43
trans-2-Bromocyclohexyl p-bromobenzenesulfonate	3.85
t-Butyl chloride	5.50
Ethyl p-toluenesulfonate	3.39
Isopropyl p-bromobenzenesulfonate	2.79

TABLE XIII (Cont.)

Compound	s
trans-2-Methoxycyclohexyl p-bromobenzenesulfonate	2.79
α-Phenylethyl chloride	5.83
Pinacolyl p-bromobenzenesulfonate	2.92
Trityl fluoride	1.24
Trityl p-nitrophenylether	1.30

By use of the s and s' values provisionally assigned to t-butyl chloride and pinacolyl p-bromobenzenesulfonate, n and e for methanol could be calculated provisionally to be 0.05 and -0.35, respectively. By use of these n and e values and the s' values listed in Table X , s could be calculated for the compounds in Table XIII . These provisional s and s' values are not all reasonable ones. For example, s/s' for benzyl chloride is larger than s/s' for n-butyl bromide, indicating that nucleophilic driving forces are more important for benzyl chloride, cf. p. 56. This is not in accord with the expectation that nucleophilic attack should be less important for compounds which can form more stable carbonium ions.

In a similar fashion, values of s for all the other compounds may be calculated. From these s values and the s' values in Table X , n and e values could be obtained for all other solvents. These s, s', n, and e values were then adjusted to give the best fit of the data. The final values are collected in Tables III and V . It is seen that these values are, on the whole, more reasonable than the provisional values. For example, s/s' is now smaller for benzyl chloride than for n-butyl bromide.

The constants listed in Tables IV and VI were obtained by a method of least squares. If $\sum_{ij} (Z_{ij} - s_i n_j - s_i' e_j)^2$, where i refers to the compound and j to the solvent, and Z_{ij} is $\log k_{ij}/k_i^o$, is minimized with respect to s_i we obtain a set of equations

$$\sum_j Z_{ij} n_j = s_i \sum_j n_j^2 + s_i' \sum_j n_j e_j$$

Similarly if the expression is minimized with respect to s_i' we obtain a set of equations

$$\sum_j Z_{ij} e_j = s_i \sum_j n_j e_j + s_i' \sum_j e_j^2$$

If a set of n and e values are assumed then these two sets of equations may be solved to give a set of **s** and **s'** values which minimize the expression <u>for the set of n and e values assumed</u>.

Now if the expression is minimized with respect to n_j and then e_j, we obtain a set of equations

$$\sum_i Z_{ij} s_i = n_j \sum_i s_i^2 + e_j \sum_i s_i s_i'$$

$$\sum_i Z_{ij} s_i' = n_j \sum_i s_i s_i' + e_j \sum_i s_i^2$$

With the use of the s and s' values just obtained, these equations may be solved for a set of n and e values which minimize the expression $\sum_{ij} (Z_{ij} - s_i n_j - s_i e_j)^2$ for the set of s and s' values used.

The digital computer, Whirlwind I, was utilized to perform the calculations just outlined. A detailed description of the program used, and a brief discussion of the computer and programming for it, are given in Appendix C.

After 19 of the iterations described above, the set of n, e, s, and s' values listed in Tables IV and VI were obtained. Carrying this procedure out 1800 more iterations gave a somewhat better fit of the data (a mean deviation in k of a factor of 1.22 vs. a factor of 1.28), but a few of the values had become much less reasonable. Since the procedure had not converged after 1800 iterations (as judged from plots of the n and e against number of iterations), the more reasonable set of values has been used. It was not possible to carry the method out past 1800 iterations because a prohibitively large amount of computer time was being used. There was no definite indication that even another 1800 iterations would lead to convergence. Furthermore, no reliable criterion for convergence, except lack of change after a very large number of further iterations, was available.

The set of n and e values used to start the procedure is in Tables III and IV.

<u>Comparison of the two sets of constants</u>. Tables III and IV, VII and VII A show that the constants derived by Whirlwind I give a better fit of the data for several compounds. The fit is significantly better for n-butyl bromide α-phenylethyl chloride, and pinacolyl p-bromobenzenesulfonate; and significantly poorer for benzyl chloride and trityl acetate (the compounds for which s and s' were assigned by trial and error, cf. footnotes to Table IV.). The mean deviation for all the reactions is also lower (a factor of 1.28 vs a factor of 1.35) using the constants obtained by Whirlwind I. In view of the better fit and the greater objectivity of the method, the constants obtained by Whirlwind I are to be preferred over those obtained by trial and error and have been used throughout this thesis.

Comparison of the s/s' values in Tables III and V shows a remarkable similarity in the two sets of ratios, the average difference being less than 6%. Comparison of the individual s and s' values shows less similarity, but even here only a small proportion of the numbers have been changed significantly. Both s and s' for n-butyl bromide were increased by Whirlwind I and these values are to be preferred, since they are nearer to the values for ethyl bromide and also give a significantly better fit of the data. Both s and s' for α-phenylethyl chloride were also increased by Whirlwind I and these values give a better fit of the data as noted above. The s value for trityl p-nitrophenyl ether was decreased by Whirlwind I and the already good fit was improved somewhat. The value of s for trityl acetate in Table III is larger than the value in Table IV.

Comparison of the trial-and-error set of n and e (Table V) and the Whirlwind I set (Table VI) shows several major changes. Some of these, such as the constants for 90% acetone - 10% water and for 97.5% acetic anhydride - 2.5% acetic acid, may be ascribed to the small amount of data available for fixing the paramaters. In some cases, i.e., 96.7% methanol - 3.3% water, 70% acetone - 30% water, and pure water, the Whirlwind I values give better agreement with the data. In other cases, i.e., ethanol, methanol, and acetic acid, the agreement is not significantly different.

It will be noted that in both Table III and Table IV, s and s' for t-butyl chloride are set at 1.000. This was done after all the constants had been assigned, and no greater weight was given to t-butyl chloride than to any other compound.

Inspection of Tables III and IV shows that data at temperatures between 25° and 75° has been correlated. Since $\log k/k_0$ must be inversely proportional to the absolute temperature, then either s and s' or n and e must also be inversely proportional to the absolute temperature. It is convenient to define n and e as temperature independent. This means that the s and s' values listed are valid only at the temperature listed. If it is desired to calculate relative rates at a different temperature the relation

$$\frac{s'}{s_2} = \frac{s'}{s'_2} = \frac{T_2}{T_1}$$

may be used to calculate the new s and s'.

Although the major variations in rate appear to be well correlated by equation 6 , some of the deviations of calculated from observed rates are definitely outside experimental error. Further refinements in the theory might account for these variations, but it is not felt that sufficient data is available to warrant such a treatment. Nevertheless, some speculation may be made concerning the nature of these effects. It has been assumed that s and s' are entirely independent of n and e. This may not be quite true. For example, in the presence of a strongly electrophilic reagent some compounds may show less dependence on the nucleophilicity of the solvent. Furthermore, all compounds need not exhibit this property to the same degree.

It should be pointed out that the n values listed in Tables III and IV are not strictly comparable with those obtained by Scott[38] for the correlation of rates in one solvent with added nucleophilic reagents. Changing the solvent not only changes the nucleophilic and electrophilic species, it also makes massive changes in such factors as dielectric constant and activity coefficients of both reactants and transition-states. An example of the effect of changing activity coefficients may be seen in the solvolysis of t-butyl chloride. It has been shown[20] that the rate constants for solvolysis of t-butyl chloride in acetone - water, methanol - water, and ethanol - water mixtures (but not in pure ethanol) are well correlated by the equation,

$$\log k = 1.232 \log H - 9.811$$

where H is the Henry's Law constant for t-butyl chloride, and is proportional to the activity coefficient. This equation fails for pure ethanol as well as for acetic acid - acetic anhydride mixtures. Furthermore, the Bronsted Rate Law

$$\text{velocity} = k \prod C_i \frac{\prod f_i}{f_x}$$

shows immediately that unless changes in activity coefficients of reactants are balanced by similar changes in activity coefficients of the transition-state, the velocity of the reaction will be affected by medium changes.

Since equation 6 does not contain these factors explicitly, they must be implicit in n and e. Now Scott was not concerned with changes in solvent, so the n values he obtained do not contain this implicit dependence on dielectric constant, activity coefficients, etc. It must be emphasized, therefore, that no meaningful comparison of the two sets of n values can be made.

This implicit dependence of n and e on factors other than nucleophilicity and electrophilicity of individual molecules is quite likely responsible for some of the deviations of calculated from observed rates. As mentioned above, further refinement of the treatment might eliminate these errors, but sufficient data to warrant this are not available.

Further Significance of Equation 6 . It may be shown[40] that the Bronsted Catalysis Law[11] may be derived from equation 6 If the catalysis of a reaction by various bases is being studied, then s, s' and e are constant and only n is being varied.

$$\log k/k_o = sn + \text{constant} \qquad (8)$$

$$\log k = sn + C$$

This is the same form as the Bronsted Catalysis Law for bases, equation 9 , if n is proportional to log K_b. Similarly, if the nucleophilic agent remains the same,

$$\log k_c = x \log K_b + C \qquad (9)$$

and various acids are used as electrophilic agents, the Bronsted Catalysis Law for acids, equation 10 , results, if e is proportional to log K_a.

$$\log k/k_o = s'e + \text{constant}$$

$$\log k = s'e + C$$

$$\log k = x \log Ka + C \qquad (10)$$

If the electrophilic agent is kept the same and various nucleophilic reagents are added, equation 8 is obtained. Now if rates with two different nucleophilic reagents are compared we obtain

$$\log (k_1/k_2) = s(n_1 - n_2)$$

$$\log (k_1/k_2) = sn'$$

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(40) C. G. Swain and C. B. Scott, J. Am. Chem. Soc., 74, 0000 (1952).

(where $n' = n_1 - n_2$). This is the same form of equation used by Scott[38] to correlate rates of reaction of a series of nucleophilic reagents with a series of compounds.

Significance of s and s'.- The quantity s/s' seems to be a measure of the relative importance of nucleophilic and electrophilic attack in influencing the relative rates of a compound, but it must be emphasized that these ratios have significance only relative to other s/s' values. Methyl bromide has s/s' = 3.39, indicating that the first term in equation 6 contributes relatively greatly to the right hand side of the equation. This is consistent with the evidence mentioned above that nucleophilic attack exerts a greater influence than electrophilic attack on the rates of reaction of methyl halides. A steady decrease in the quantity s/s' is observed over the series methyl bromide, ethyl bromide, isopropyl bromide, t-butyl bromide. This is in agreement with much evidence[24] that a decreasing susceptibility to nucleophilic attack exists over this series. For trityl derivatives, s/s' is quite low, averaging 0.49. This agrees with the qualitative prediction made above that trityl derivatives should be more susceptible to electrophilic than nucleophilic attack. In general, it is seen that those compounds which are expected to show the greater dependence on nucleophilicity have the higher s/s'; but a few inconsistencies are apparent.

It will be noted from Table IV that there is no evidence for grouping the compounds into two discrete classes according to values of s, s', or s/s'. Such a grouping might be expected

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(24). Ref. 11, p. 152.

if two separate transition-states, e.g., of the $\underline{S}_N1$[1-3] and $\underline{S}_N2$[8] types existed for solvolyses. Furthermore, no evidence is seen for a Limiting mechanism[13], with a transition-state which is identical for t-butyl halides and all other compounds which have greater tendencies to ionize. Rather, a smooth gradation from methyl bromide to trityl derivatives more closely approximates the data of Table IV.

Significance of n and e.- The large positive e values and large negative n values for carboxylic acids are in agreement with the generally accepted[20] observation that such solvents are very favorable to processes requiring electrophilic attack, and very unfavorable to processes requiring nucleophilic attack. As mentioned above, the approximation that e is constant in ethanol - water mixtures seems a good one. Methanol - water mixtures are seen to be more electrophilic than nucleophilic; while the reverse is true for relatively non-aqueous acetone - water mixtures.

The one value in Table VI that at first glance does not appear reasonable is the e-value for 97.5% acetic anhydride - 2.5% acetic acid. The problem is not simple, because acetic acid is highly dimerized and polymerized[25], but one would not expect that addition of acetic anhydride to dry acetic acid would make the solvent more electrophilic.

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(25) M. I. Batuer, Compt, rend. acad. sci. U.R.S.S., 52, 401 (1946); 53, 317, 507 (1946.

Consideration of Other Possible Equations.- The question arises whether or not it is possible to correlate the rates of all these compounds by assuming that some or all of them react simultaneously by two different mechanisms. Part of the t-butyl chloride molecules, for example, might follow one path and the rest another. If this is true it might be possible to sort out the fractions reacting by each path. These fractions should conform to conclusions previously reached[1] on the hypothesis of a duality of mechanism, e.g., that solvolysis of t-butyl chloride is chiefly $\underline{S}_N1$, at least in acetic acid and the more highly aqueous of the water - alcohol and water - acetone mixtures.

If trityl fluoride reacts entirely by the $\underline{S}_N1$ mechanism and n-butyl bromide entirely by the $\underline{S}_N2$ mechanism then it might be possible to set up a quantitative scale for solvents based on these compounds, which would measure the tendency for $\underline{S}_N1$ and $\underline{S}_N2$ reactions to occur. Such a set is recorded in Table XIV. The Y_1 values are based on trityl fluoride. They are defined by equation 11. The Y_2 values are based on

$$Y_1 = \log k - \log k_{80\%\text{ ethanol}} \qquad (11)$$

$$Y_2 = \log k - \log k_{80\%\text{ ethanol}} \qquad (12)$$

n-butyl bromide and are defined by equation 12. The new equations for the rate of solvolysis in any medium are then

$$\log (k_1/k_1{}^{o}) = m_1Y_1$$

$$\log (k_2/k_2{}^{o}) = m_2Y_2$$

where the two equations represent, respectively, the $\underline{S}_N1$ and $\underline{S}_N2$ contributions to the total rate. For purposes of evaluating m_1 for t-butyl chloride, k, the observed first-order rate constant, was set equal to k_1 for both acetic acid and 40% ethanol - 60% water; k_1 could then be calculated for all other solvents. To evaluate m_2, k_2 was set equal to the observed first-order rate constant minus the calculated k_1 for ethanol and for 80% ethanol - 20% water, and k_2 was calculated for the other solvents.

It is clear from Table XIV that useful predictions are not made under the assumption that trityl fluoride reacts entirely by the $\underline{S}_N1$ mechanism, n-butyl bromide entirely by the $\underline{S}_N2$ mechanism, and compounds intermediate in structure by both mechanisms. Although the agreement of calculated and observed rates is fair, it is necessary to assume that in all solvents other than 40% ethanol - 60% water and acetic acid, less than .00004% of the observed rate is due to an $\underline{S}_N1$ reaction. Furthermore, Table XV shows that a similar calculation indicates nearly one-fourth of the rate of isopropyl bromide in 50% ethanol - 50% water to be due to an $\underline{S}_N1$ reaction, whereas less than 0.000001% of the reaction of t-butyl chloride in this medium is calculated to occur by the $\underline{S}_N1$ mechanism. Thus a secondary halide shows more tendency to undergo an $\underline{S}_N1$ reaction than a tertiary halide, in contradiction to

TABLE XIV

SOLVOLYSIS OF t-BUTYL CHLORIDE AT 25.0°

Solvent[a]	Y_1	Y_2	$k_{obsd.}$, sec.$^{-1}$	$k_1$calc., sec.$^{-1}$	k_2 calc., sec.$^{-1}$	k_1/k
C_2H_5OH	-1.73	-0.70	$9.70x10^{-8}$	$3.8x10^{-58}$	$(9.70x10^{-8})$	0.000
80% C_2H_5OH	0.00	0.00	$9.24x10^{-6}$	$6.3x10^{-33}$	$(9.24x10^{-6})$	0.000
96.7% CH_3OH	0.11	-0.21[b]	$1.75x10^{-6}$	$2.14x10^{-31}$	$2.40x10^{-6}$	0.000
60% C_2H_5OH	1.18[b]	0.27[b]	$1.27x10^{-4}$	$7.10x10^{-16}$	$5.38x10^{-5}$	0.000
50% C_2H_5OH	1.43[b]	0.51[b]	$3.67x10^{-4}$	$3.47x10^{-12}$	$2.57x10^{-4}$	0.000
69.5% CH_3OH	1.50	0.46[b]	$9.75x10^{-5}$	$3.55x10^{-11}$	$1.86x10^{-4}$	0.000
CH_3COOH	1.76	-	$2.13x10^{-7}$	$(2.13x10^{-7})$	-	1.000
40% C_2H_5OH	2.02	-	$1.29x10^{-3}$	$(1.29x10^{-3})$	-	1.000

[a] Where a portion of the solvent is not specified, it is water.

[b] Interpolated

TABLE XV

SOLVOLYSIS OF ISOPROPYL BROMIDE AT 75.1°

Solvent[a]	Y_2	$k_{obsd.}$, sec.$^{-1}$	k_1[b], sec.$^{-1}$	k_2 calc., sec.$^{-1}$	k_1/k
C_2H_5OH	-0.70	$1.12x10^{-7}$	-	$(1.12x10^{-7})$	(0.000)
80% C_2H_5OH	0.00	$1.18x10^{-6}$	-	$(1.18x10^{-6})$	(0.000)
50% C_2H_5OH	0.51[c]	$8.45x10^{-6}$	$1.99x10^{-6}$	$6.46x10^{-6}$	0.237

[a] That part of the solvent not specified is water

[b] $k_1 = k_{obsd.} - k_2$ calc.

[c] Interpolated

numerous investigations by other workers.[21,27]

One other hypothesis might suffice to correlate the rates of these compounds. It is at least conceivable that all the compounds solvolyze with a significant fraction of the reaction proceeding by each mechanism in some solvents. If this is true, then it should be possible to set up sets of Y_1 and Y_2 values based on two hypothetical compounds reacting by pure $\underline{S}_N1$ and $\underline{S}_N2$ mechanism. With the help of some very reasonable assumptions such a hypothesis may also be shown to lead to quite unreasonable conclusions.

If it is assumed that the reactions of both t-butyl chloride and trityl fluoride in acetic acid and in 40% ethanol - 60% water and of trityl fluoride in 69.5% methanol - 30.5% water occur by the $\underline{S}_N1$ mechanism to the extent of at least 99% then it may be calculated that less than 0.000002% of the reaction of t-butyl chloride in 50% ethanol - 50% water occurs by the $\underline{S}_N1$ mechanism. Even if it is assumed that only 1% of the reaction of t-butyl chloride in 40% ethanol - 60% water is by the $\underline{S}_N1$ mechanism, less than 0.0004% of the reaction of t-butyl chloride in 50% ethanol - 50% water is calculated to occur by $\underline{S}_N1$. The assumption that smaller proportions of the reaction of trityl fluoride occur by $\underline{S}_N1$ in the partly aqueous media leads to even more incongrous results. Then if n-butyl bromide is assumed to react entirely by the $\underline{S}_N2$ mechanism in ethanol - water mixtures containing 50% ethanol or more, and if isopropyl bromide reacts entirely by the $\underline{S}_N2$ mechanism in 80% ethanol - 20% water and in pure ethanol, it is once more found that nearly one-fourth of the reaction of isopropyl bromide in 50% ethanol - 50% water is by the $\underline{S}_N1$ route. The anomaly of isopropyl bromide showing a greater tendency than t-butyl chloride to undergo $\underline{S}_N1$ reactions is thus calculated once again. It is concluded that the assumption that all these compounds react simultaneously by both mechanisms does not lead to useful or reasonable conclusions.

Another possible method for correlation of these rates is the use of an equation involving only three parameters. Three such simple equations are shown. Such equations may also be shown to be inadequate by use of the fact that in

$$\log (k/k_o) = a + b + c \qquad (13)$$

$$\log (k/k_o) = a + bc \qquad (14)$$

$$\log (k/k_o) = abc \qquad (15)$$

the standard solvent, $\log (k/k_o) = 0$. Equation 13 is inadequate because all three parameters must either be functions of the solvent alone or of both the solvent and the compound. If the former is the case then equation 13 is only equation 4 with $\underline{m}$ equal to unity for all compounds. If the latter is true then it is really a four (or more) parameter equation.

The first term of equation 14 must likewise be a function either of just the solvent or of both the solvent and the compound. If the former is true, then equation 14 is merely equation 6, with either s or s' equal to unity for all compounds. No evidence is to be found in Table III that such a condition satisfies the experimental facts. Quite the contrary, both s and s' vary widely as the structure of the compound is changed. If the first term in equation 14 is a function of both solvent and compound, then this is really a four-parameter equation.

If any of the parameters of equation 15 are functions of both solvent and compound then it is a four or more parameter equation. If each is a function only of solvent or of compound, then equation 15 reduces to equation 4. Thus it appears that at least four parameters are needed to correlate the existing data.

Experimental

1. Solvents

Ethanol.- U. S. I. absolute ethanol was used. For runs in absolute ethanol, it was dried[41] by addition of excess sodium metal followed by refluxing for at least four hours with an amount of ethyl formate (Eastman Pure) more than equivalent to the water present and less than equivalent to the sodium added. Distillation yielded ethanol containing less than 0.01% water by Robertson's paraffin oil test.[41]

Acetone.- Mallinkrodt reagent grade acetone was dried over Drierite and distilled before use.

Methanol.- Mallinkrodt reagent grade methanol was used without further purification.

Acetic acid.- Dry acetic acid was prepared from Mallinkrodt reagent (dichromate test) glacial acetic acid. by refluxing for at least two hrs with an amount of Baker's reagent acetic anhydride equivalent to three or four times the amount of water present, and then distilling. The concentration of acetic anhydride in the acetic acid prepared in this fashion was determined.[42] by addition of a known excess of anthranilic acid and was always about 0.1%.

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(41) G. R. Robertson, "Laboratory Practice of Organic Chemistry", MacMillan Co., New York, N. Y., 1943, pp. 178, 296.

(42) S. Kilpi, Chem. Abstracts, 35, 2445 (1945).

After allowing the reaction between anthranilic acid and acetic anhydride to be completed, the excess was back - titrated with standard perchloric acid in acetic acid, using brom phenol blue as indicator.

Formic acid.- Baker and Adamson 98 - 100% reagent formic acid was used without further purification.

All solvent compositions are % by volume before mixing.

2. Other Materials

Sodium Acetate.- Anhydrous sodium acetate was prepared by fusing Mallinkrodt reagent grade sodium acetate trihydrate and drying for three hours at 140°.

Potassium Acid Phthalate.- Mallinkrodt reagent grade potassium acid phthalate was used without further purification.

Sodium Formate.- Merck reagent grade sodium formate was used without further purification.

Sodium Hydroxide.- Carbonate-free sodium hydroxide solutions were prepared by filtration of 50% aqueous sodium hydroxide (to remove sodium carbonate) followed by dilution to the proper volume with boiled distilled water.

Sodium Ethoxide.- Sodium ethoxide in absolute ethanol was prepared by dissolving the required amount of shiny sodium in absolute ethanol.

Sodium Methoxide.- "Sodium methoxide" in 97% methanol - 3% water for use in runs 192 and 193 was prepared by addition of the required amounts of methanol and water to a carbonate-free aqueous solution of sodium hydroxide.

Trityl fluoride was prepared according to a method devised by Dr. Robert Ehrenfeld. Trityl chloride (37g., 0.132 mole) was placed in a nickel crucible and gaseous hydrogen fluoride was led in by a copper tube through a hole in the cover. The solid quickly turned to a yellow-brown solution. After 20 min., the excess hydrogen fluoride was evaporated, 20 ml. of benzene was added, the solution re-evaporated and allowed to cool, and the resulting solid recrystallized from anhydrous ether at -70°, yielding 23g. (62%) trityl fluoride, m.p. 101.3-102.0° The purity, as judged from acid liberated on quantitative hydrolysis, varied from 85% - 95% in different preparations. Repeated crystallizations did not give higher purities. Kinetic analysis showed that less than 0.5% of trityl chloride was present, and it was assumed that the impurity was triphenylcarbinol. The m.p. did not depend strongly on the amount of triphenylcarbinol present (cf. Table XVI).

Benzhydryl fluoride was prepared from diphenyldiazomethane[43] and hydrogen fluoride. Benzophenone hydrazone (39.2g., 0.200 moles), 44.0g (0.203 mole) yellow mercuric oxide, and 200 ml. petroleum ether were shaken mechanically

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(43)L. I. Smith and K. L. Howard, Org. Syntheses, 24, 53 (1944).

TABLE XVI

MELTING POINTS OF MIXTURES OF TRITYL FLUORIDE AND TRIPHENYLCARBINOL

% $(C_6H_5)_3COH$	m.p., °C
14.0	105.2 - 106.3
19.0	106.0 - 111.1
27.8	107.0 - 112.0
36.2	111.4 - 132.9
45.0	116 - 133.4
53.5	125 - 142.9
62.1	113 - 136.8
70.8	116 - 149.8
79.4	147.6 - 156.0
100.0	163.4 - 164.2

until only a small amount of solid remained. The red solution was filtered and dried over anhydrous sodium sulfate. An anhydrous solution of hydrogen fluoride in ethyl ether was added in small portions until bubbling ceased and the solution had turned pale yellow. The cloudy liquid was evaporated at room temperature and 300 ml. benzene added. The benzene solution was extracted rapidly with water, 5% sodium carbonate solution, water, 10% nitric acid, and water. After drying over sodium sulfate, the benzene was removed at room temperature and the remaining straw-colored liquid distilled, b.p. 88 - 100° (0.3 mm.); yield 20.6 g. (54.8%). After two more distillations it had b.p. 86 - 90° (0.29 mm.). Anal. Calcd. for $C_{13}H_{11}F$: C,83.8; H,5.9. Found: C,84.1; H,6.18. Equiv. wt. from quantitative solvolysis, 181; calcd. for $C_{13}H_{11}F$, 186. It was stored in a polyethylene bottle in a desiccator, but the faintly yellow liquid had turned red after standing for two days. The apparatus used in distilling this compound should be scrupulously dry, and the material should be re-extracted as above immediately before distillation to avoid extensive decomposition.

Trityl p-nitrophenyl ether was prepared from 21.3 g (0.0764 mole) trityl chloride and 18.8 g. (0.0764 mole) silver p-nitrophenolate in 80 ml. dry dioxane. The red silver salt was added in portions to the dioxane solution of trityl chloride which was stirred with a magnetic stirrer without cooling. Considerable heat was evolved and the reaction appeared to be complete in a few minutes. After stirring for 30 min., 15 ml. dry benzene was added and the solution was filtered to remove silver salts. The filtrate was concentrated to 40 ml. and dilutedwith 70 ml. dry hexane. Cooling and shaking induced crystallization. Yield after one more recrystallization from benzene- hexane was 26 g. (89.3%). Two more recrystallizations from benzene gave material with m.p. 156.5 - 157.5°. Anal. Calcd. for $C_{25}H_{19}O_3N$: C,78.74; 4.99. Found: C,78.42; H,5.17.

Trityl 2,4-dinitrophenyl ether was prepared by adding 47.2 g. (0.162 mole) silver 2,4-dinitrophenolate to 40 g. (0.143 mole) trityl chloride in 125 ml. dry dioxane and stirring for 24 hr. At the end of this time the solution was filtered and the precipitate of silver chloride washed with dry benzene. The filtrate and washings were concentrated to 90 ml. and diluted with 60 ml. dry hexane. Cooling and shaking produced crystals. Yield after one more recrystallization from benzene-hexane was 55 g. (90%). After another recrystallization from benzene-hexane and one recrystallization from benzene the material had m.p. 174.5° (dec.). Anal. Calcd. for $C_{25}H_{18}O_5N_2$: c,70.42; H,4.23. Found: C,70.44; H,4.34. This compound proved to react too rapidly for convenient measurement.

Trityl chloride was prepared according to Org. Syntheses.[44]

Benzhydryl chloride was prepared according to Gilman and Kirby[45] from benzhydrol and thionyl chloride.

Benzhydrol was prepared according to Org. Syntheses.[46]

All b.p. are uncorrected; all m.p. are corrected.

3. Kinetic Measurements

All kinetics on trityl fluoride except those in acetic acid were obtained by the intermittent titration method.[47] The method may be illustrated by Run 8. Trityl fluoride (48.0 mg.) was dissolved as rapidly as possible in 10 ml. methanol. At zero time, a 5 ml. portion was added to 64.5 ml. methanol plus 29.5 ml. water at 30.06° and the solution thoroughly mixed with an air stirrer. Two cc. of an aqueous solution was used in titrating, so the composition at 50% reaction was 69.5% acetone - 30.5% water. Since the solution had been previously adjusted to neutrality using brom thymol blue as indicator, the amount of base necessary to restore neutrality at any time is a measure of the amount of acid produced by the reaction at that time. Thus buret readings and times at which the indicator changes color are recorded

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(44) W. E. Bachmann, Org. Syntheses, 23, 100 (1943).

(45) H. Gilman and J. E. Kirby, J. Am. Chem. Soc., 48, 1733 (1926).

(46) F. Y. Wiselogle and H. Sonneborn, III, Coll. Vol. I, 90 (1932).

(47) R. A. Peters and E. Walker, Biochem. J., 17, 260 (1923).

in Table XXII. Previous tests had showed that addition of 5 ml. of methanol to 65 ml. methanol - 30 ml. water causes only a negligible rise in temperature. The cell in which these reactions were carried out has been described previously.[48]

The trityl fluoride runs in acetic acid were followed by quenching 5 ml. aliquots in 50 ml. benzene, extracting the benzene twice with 10 ml. portions of water, and titrating the combined extracts for fluoride ion with thorium nitrate solution, using sodium alizarinsulfonate as indicator. The end-point in this titration is poor, and the results are therefore not very accurate.

Kinetic measurements on trityl thiocyanate were carried out by the intermittent titration method in the same fashion described for trityl fluoride.

Kinetic measurements on trityl acetate in methanol - water and acetone - water mixtures were also performed by the intermittent titration method. For the runs in ethanol - water mixtures, the reaction was followed by quenching 10 ml. aliquots in 20 ml. ethyl ether. These runs were carried out in the presence of excess base, so extraction of the ether layer with water and titration of the remaining base afforded a measure of the extent to which reaction had proceeded.

Kinetic measurements on benzhydryl chloride in 96.7%

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(48) C. G. Swain, R. Esteve, and R. Jones, J. Am. Chem. Soc., 71, 965 (1949).

methanol - 33% water were performed by the intermittent titration method. Those in acetic acid were carried out in the presence of excess potassium acid phthalate (a strong base in acetic acid) and followed by direct titration of 10 ml. aliquots with standard perchloric acid in acetic acid. The kinetic measurements on benzhydryl chloride in 83.3% formic acid - 16.7% acetone were performed by quenching 10 ml. aliquots in 50 ml. ether, extracting the ether twice with 25 ml. portions of water, and titrating the combined water layers for chloride ion using the Volhard method.

The kinetic measurements on t-butyl chloride in 83.3% formic acid - 16.7% acetone were carried out in the same manner as those on benzhydryl chloride.

Kinetic measurements on benzhydryl fluoride in ethanol - water mixtures were carried out in the presence of excess base. Since these reactions were run at higher temperatures, the sealed-ampoule technique was used. At known times ampoules were removed from the constant-temperature bath, cooled under the tap, opened, and titrated for remaining base. The runs in acetic acid and 83.3% formic acid - 16.7% acetone required a rather laborious method. Aliquots (10 ml.) were quenched in 25 ml. chloroform. The chloroform was extracted with water, 10% sodium carbonate solution, and water. The chloroform layer (containing the unreacted benzhydryl fluoride) was evaporated to dryness on the steam cone. The residue was taken up in ethanol. Sufficient water and aqueous sodium hydroxide were added to make the solution 70% ethanol - 30% water, and the solution sealed off in a soft glass test-tube. The amount of sodium hydroxide added was more than equivalent to the benzhydryl fluoride present. After 10 hr. at 100° the tubes were cooled, opened, and titrated for fluoride ion with thorium nitrate using sodium alizarinsulfonate as indicator.

Kinetic measurements on trityl p-nitrophenyl ether were performed by spectrophotometric analysis for sodium p-nitrophenolate, using the peak at 399 mμ. Two spectrophotometers were used. For runs in 40% ethanol - 60% water, 69.5% methanol - 30.5% water, and 50% acetone - 50% water the reaction was carried out in the cell of a Cary Recording Quartz Spectrophotometer, Model 11MS. Sufficient sodium hydroxide was present to maintain at least 99.9% of the liberated p-nitrophenol in the form of the sodium salt. In the runs in 80% ethanol - 20% water the reaction was followed by quenching 10 ml. aliquots in 25 ml. ethyl ether, extracting the sodium p-nitrophenolate with dilute aqueous sodium hydroxide, making the aqueous layers up to 100 ml. and analyzing for sodium p-nitrophenolate on a Beckman Quartz Spectrophotometer, Model DU. Sufficient sodium hydroxide was present to maintain at least 99.9% of the p-nitrophenol in the form of its sodium salt. The runs in acetic acid were done in the same fashion, except that 1 ml. aliquots were used, and that sufficient 50% aqueous sodium hydroxide to more than neutralize the acetic acid was added to the water layer before extraction. Since small, but perhaps real, deviations from Beer's law were observed (cf. Table XVII), a working curve was prepared, and concentrations of sodium p-nitrophenolate were determined from this.

Temperature control was ± 0.1° in all runs except Runs 20, 21, 23, 198, 199, 200, and 206, where it was ± 0.5°.

TABLE XVII

EXTINCTION COEFFICIENTS OF SODIUM p-NITROPHENOLATE

$NaOC_6H_4NO_2$, M. x 10^6	Extinction Coefficient x 10^{-4}
100	1.79
50	1.80
25	1.84
10	1.86
5.0	1.95

TABLE XVIII

RUN 4. SOLVOLYSIS OF 1.035×10^{-3} M. TRITYL FLUORIDE IN 80% ETHANOL - 20% WATER AT 29.93°

Time, sec.	0.0566 M. $NaOC_2H_5$, ml.	HF liberated, % of 1.035×10^{-3}M.
0	0.000	0.0
103	.074	4.0
195	.140	7.6
272	.190	10.4
357	.240	13.1
446	.290	15.8
552	.340	18.6
623	.390	21.3
717	.440	24.0
817	.490	26.7
918	.540	29.5
1023	.590	32.2
1132	.640	35.0
1251	.690	37.7
1378	.740	40.4
1505	.790	43.2
1640	.840	45.9
1783	.890	48.7
1936	.940	51.3
2094	.990	54.1
2274	1.040	56.9
2465	1.090	59.7
2590	1.140	62.2
2870	1.190	65.0
3090	1.240	67.8
3345	1.290	70.4
3610	1.340	73.2
3910	1.390	76.0
4260	1.440	78.8
4960	1.543	84.3
5350	1.590	87.0
24000	1.830	100.0

$k_1 = 3.68 \times 10^{-4}$ sec.$^{-1}$

TABLE XIX

RUN 5. SOLVOLYSIS OF 1.053×10^{-3} M. TRITYL FLUORIDE IN 80% ETHANOL - 20% WATER AT 29.90°

Time, sec.	0.0566 M. $NaOC_2H_5$, ml.	HF liberated, % of 1.053×10^{-3}M.
0	0.000	0.0
40	.010	0.5
63	.045	2.4
132	.095	5.1
207	.145	7.8
267	.195	10.5
343	.245	13.2
424	.295	15.8
505	.345	18.5
589	.395	21.2
754	.495	26.6
848	.545	29.3
951	.595	31.9
1057	.645	34.6
1163	.695	37.3
1275	.745	40.0
1384	.795	42.7
1512	.845	45.4
1637	.895	48.1
1780	.947	50.9
1917	.995	53.4
2075	1.045	56.1
2250	1.095	58.9
2422	1.145	61.6
2615	1.195	64.2
2830	1.245	66.9
3030	1.295	69.6
3284	1.347	72.4
3525	1.395	75.0
3790	1.445	77.7
4115	1.495	80.3
24000	1.862	100.0

$k_1 = 3.98 \times 10^{-4}$ sec.$^{-1}$

TABLE XX

RUN 6. SOLVOLYSIS OF 8.13×10^{-4} M. TRITYL FLUORIDE IN 40% ETHANOL - 60% WATER AT 30.05°

Time, sec.	0.0456 M. NaOH, ml.	HF liberated, % of 8.13×10^{-4} M.
0.0	0.000	0
7.2	.400	22
15.0	.600	34
25.2	1.050	59
30.0	1.200	67
42.0	1.400	79
58.2	1.600	90
300.0	1.782	100

$k_1 = 3.73 \times 10^{-2}$ sec.$^{-1}$

TABLE XX A

RUN 7. SOLVOLYSIS OF 7.48×10^{-4} M. TRITYL FLUORIDE IN 69.5% METHANOL - 30.5% WATER AT 29.90

Time, sec.	0.0456 M. NaOH, ml.	HF liberated, % of 7.48×10^{-4} M.
0.0	0.000	0.0
24.0	.500	30.5
40.0	.770	46.8
55.2	.820	50.0
64.8	1.025	62.4
79.2	1.105	67.3
109.8	1.195	73.0
134.4	1.305	79.4
148.2	1.350	82.3
162.0	1.400	85.3
184.8	1.460	89.1
600.0	1.640	100.0

$k_1 = 1.15 \times 10^{-2}$ sec.$^{-1}$

TABLE XXI

RUN 8. SOLVOLYSIS OF 8.62×10^{-4} M. TRITYL FLUORIDE IN 69.5% METHANOL - 30.5% WATER AT 30.06°

Time, sec.	0.0456 M. NaOH, ml.	HF liberated, % of 8.62×10^{-4} M.
0.0	0.000	0.0
15.6	.400	21.2
28.8	.600	31.8
43.2	.795	42.1
64.2	1.008	53.3
75.0	1.100	58.3
85.8	1.200	63.5
103.2	1.295	68.6
120.0	1.415	74.9
138.0	1.500	79.4
151.8	1.555	82.4
168.0	1.608	85.1
183.0	1.650	87.3
202.8	1.700	89.9
600.0	1.890	100.0

$$k_1 = 1.10 \times 10^{-2} \text{ sec.}^{-1}$$

TABLE XXII

RUN 9. HYDROLYSIS OF 9.08×10^{-4} M. TRITYL FLUORIDE IN 70% ACETONE - 30% WATER AT 30.04°

Time, sec.	0.0456 M. NaOH, ml.	HF liberated, % of 9.08×10^{-4} M.
0	0.004	0.0
540	.054	2.5
1560	.107	5.2
2640	.156	7.6
4800	.254	12.5
5820	.304	15.1
7560	.404	20.1
9780	.504	25.1
12,420	.622	31.0
16,860	.788	39.3
21,180	.962	48.2
24,600	1.061	53.2
34,740	1.332	66.7
35,340[a]	1.995	100.0

[a] Diluted with sufficient boiled distilled water to make the solution 40% acetone - 60% water. The half-life in this medium is 55 seconds.

$$k_1 = 3.10 \times 10^{-5} \text{ sec.}^{-1}$$

TABLE XXIII

RUN 11. ETHANOLYSIS OF 9.63 x 10^{-4} M. TRITYL FLUORIDE IN ETHANOL AT 30.00°

Time, sec.	0.0566 M. $NaOC_2H_5$, ml.	HF liberated % of 9.63 x 10^{-4} M.
0	0.000	0.0
3480	.050	2.9
7020	.100	5.9
15,780	.220	12.9
24,600	.343	20.2
31,120	.424	25.0
42,120	.559	32.9
77,160	.874	51.4
94,320	.980	57.7
109,560	1.065	62.6
800,000	1.700	100.0

$k_1 = 9.38 \times 10^{-6}$ sec.$^{-1}$

TABLE XXIV

RUN 12. ETHANOLYSIS OF 9.35×10^{-4} M. TRITYL FLUORIDE IN ETHANOL AT 39.72°

Time, sec.	0.0566 M. $NaOC_2H_5$, ml.	HF liberated, % of 9.35×10^{-4} M.
0	0.000	0.0
900	.030	1.8
3180	.120	7.2
5520	.206	12.3
7500	.273	16.4
10,500	.368	22.1
13,500	.452	27.0
16,500	.536	32.1
22,620	.706	42.3
24,600	.760	45.6
27,300	.822	49.2
28,988	.860	51.5
36,000	.960	57.5
39,060	1.045	62.5
280,000	1.669	100.0

$k_1 = 2.52 \times 10^{-5}$ sec.$^{-1}$

TABLE XXV

RUN 13. SOLVOLYSIS OF 1.022 x 10^{-3} M. TRITYL FLUORIDE IN 80% ETHANOL - 20% WATER AT 39.5°

Time, sec.	0.0566 M. $NaOC_2H_5$, ml.	HF liberated, % of 1.022 x 10^{-3} M.
0	0.000	0.0
120	.172	9.5
195	.265	14.5
275	.363	20.1
351	.454	25.1
410	.512	28.3
513	.620	34.3
629	.732	40.5
736	.820	45.4
829	.893	49.4
1129	1.092	60.3
1268	1.162	64.2
1525	1.302	72.0
9000	1.807	100.0

k_1 = 8.50 x 10^{-4} sec. $^{-1}$

TABLE XXVI

RUN 14. SOLVOLYSIS OF 8.44 x 10^{-4} M. TRITYL FLUORIDE IN 40% ETHANOL - 60% WATER AT 39.6°

Time, sec.	0.0456 M. NaOH, ml.	HF liberated, % of 8.44 x 10^{-4} M.
0.0	0.000	0.
3.6	.300	16
7.8	.600	32
12.0	.900	49
16.2	1.200	65
21.0	1.300	70
24.0	1.400	76
25.8	1.500	81
30.0	1.600	86
420.0	1.852	100

$k_1 = 6.47 \times 10^{-2}$ sec.$^{-1}$

TABLE XXVII

RUN 15. SOLVOLYSIS OF 8.57 x 10^{-4} M. TRITYL FLUORIDE IN 69.5% METHANOL - 30.5% WATER AT 39.6°

Time, sec.	0.0456 M. NaOH, ml.	HF liberated, % of 8.57 x 10^{-4} M.
0.0	0.005	0
5.4	.300	16
16.8	.625	33
30.0	.910	49
49.2	1.240	67
55.2	1.300	70
61.8	1.400	75
73.8	1.500	81
87.0	1.600	86
510.0	1.860	100

$k_1 = 2.14 \times 10^{-2}$ sec.$^{-1}$

TABLE XXVIII

RUN 16. HYDROLYSIS OF 8.48×10^{-4} M. TRITYL FLUORIDE IN 70% ACETONE - 30% WATER AT 39.6°

Time, sec.	0.0456 M. NaOH, ml.	HF liberated, % of 8.48×10^{-4} M.
0	0.050	0.0
1080	.200	8.1
1740	.300	13.4
4320	.640	31.7
5700	.810	40.8
6900	.950	48.4
15,600	1.550	80.7
870,000	1.910	100.0

$k_1 = 1.12 \times 10^{-4}$ sec.$^{-1}$

TABLE XXIX

RUN 18. HYDROLYSIS OF 7.90×10^{-4} M. TRITYL FLUORIDE IN 50% ACETONE - 50% WATER AT 25.0°

Time, sec.	0.0473 M. NaOH, ml.	HF liberated, % of 7.90×10^{-4} M.
0	0.000	0.0
75	.100	6.0
155	.202	12.0
180	.300	18.0
262	.400	24.0
358	.500	30.0
453	.600	36.0
556	.700	42.0
671	.800	48.0
799	.900	54.0
937	1.000	60.0
1087	1.100	66.0
87,000	1.670	100.0

$k_1 = 9.83 \times 10^{-4}$ sec.$^{-1}$

TABLE XXX

RUN 19. SOLVOLYSIS OF 9.12×10^{-4} M. TRITYL FLUORIDE IN 96.7% METHANOL - 3.3% WATER AT 25.0°

Time, sec.	0.0493 M. $NaOCH_3$, ml.	HF liberated, % of 9.12×10^{-4} M.
0	0.000	0.0
210	.100	5.4
390	.200	10.8
645	.300	16.2
1020	.500	27.0
1245	.600	32.4
1494	.700	37.8
1770	.800	43.2
2055	.900	48.6
2376	1.000	54.0
2724	1.100	59.4
3165	1.200	64.8
3570	1.300	70.2
63000	1.848	100.0

$k_1 = 3.54 \times 10^{-4}$ sec.$^{-1}$

TABLE XXXI

RUN 20. ACETOLYSIS OF 0.040 M. TRITYL FLUORIDE IN ACETIC ACID CONTAINING 0.25 M. SODIUM ACETATE AT 25°

Time, sec.	0.0282 N. $Th(NO_3)_4$, ml.	HF liberated, % of 0.040 M.
0	2.8	0
13	3.6	19
43	4.9	49
71	5.6	65
100	6.4	84
128	6.8	94
1800	7.1	100

$k_1 = 1.51 \times 10^{-2}$ sec.$^{-1}$

TABLE XXXII

RUN. 21. ACETOLYSIS OF 0.055 M. TRITYL FLUORIDE IN ACETIC ACID CONTAINING 0.25M. SODIUM ACETATE AT 25°

Time, sec.	0.0282 N. $Th(NO_3)_4$, ml.	HF liberated, % of 0.055 M.
0	3.6	0
25	4.9	31
50	5.9	55
75	6.6	71.5
100	6.6	71.5
120	7.1	83.5
149	7.8	100
1800	7.8	100

$$k_1 = 1.51 \times 10^{-2} \text{ sec.}^{-1}$$

TABLE XXXIII

RUN 23. ACETOLYSIS OF 0.040 M. TRITYL FLUORIDE IN ACETIC ACID CONTAINING 0.125 M. SODIUM ACETATE AT 25°

Time, sec.	0.125 N. $Th(NO_3)_4$, ml.	HF liberated, % of 0.040 M.
0	0.80	0
24	1.10	37.5
46	1.30	62.5
67	1.35	69
90	1.40	75
111	1.45	81.3
133	1.55	94
1800	1.60	100

$$k_1 = 1.78 \times 10^{-2} \text{ sec.}^{-1}$$

TABLE XXXIV

RUN 33. HYDROLYSIS OF 9.9 x 10^{-4} M. TRITYL THIOCYANATE IN 70% ACETONE - 30% WATER AT 25.0°

Time, sec.	0.0506 M. NaOH, ml.	HSCN liberated, % of 9.9 x 10^{-4} M.
0	0.000	0.0
30	.060	3.1
60	.104	5.3
84	.150	7.7
112	.200	10.2
145	.255	13.1
174	.300	15.4
207	.350	17.9
240	.404	20.7
277	.450	23.0
314	.500	25.6
353	.553	28.25
394	.604	30.9
480	,700	35.8
529	.753	38.6
575	.802	41,1
625	.851	43.3
674	.898	46.0
737	.950	48.6
798	1.000	51.2
859	1.050	53.8
915	1.099	56.2
987	1.156	59.1
1052	1.202	61.4
1128	1.250	63.9
1214	1.304	66.7
1302	1.349	69.0
1400	1.400	71.6
1509	1.450	74.1
1620	1.500	76.8
1753	1.550	79.3
1894	1.600	81.9
7800	1.955	100.0

$k_1 = 9.03 \times 10^{-4}$ sec.$^{-1}$

TABLE XXXV

RUN 34. HYDROLYSIS OF 9.5×10^{-4} M. TRITYL THIOCYANATE IN 70% ACETONE - 30% WATER AT 25.0°

Time, sec.	0.0506 M. NaOH, ml.	HSCN liberated, % of 9.5×10^{-4} M.
0	0.000	0.0
34	.100	5.3
71	.150	8.1
107	.200	10.7
149	.250	13.4
180	.300	16.0
223	.360	19.2
260	.420	22.4
290	.450	24.0
330	.508	27.1
258	.580	31.0
415	.606	32.4
448	.650	34.8
494	.700	37.4
536	.750	40.1
592	.810	43.4
635	.850	45.5
727	.950	50.8
795	1.000	53.5
859	1.050	56.2
949	1.130	60.4
997	1.155	61.8
1130	1.250	67.0
1335	1.350	72.3
1435	1.410	75.3
1545	1.460	78.1
1650	1.500	80.2
1770	1.550	83.0
1935	1.600	85.6
106,800	1.870	100.0

$k_1 = 9.62 \times 10^{-4}$ sec. $^{-1}$

TABLE XXXVI

RUN 35. HYDROLYSIS OF 9.5×10^{-4} M. TRITYL THIOCYANATE IN 80% ACETONE - 20% WATER AT 25.0°

Time, sec.	0.0506 M. NaOH, ml.	HSCN liberated, % of 9.5×10^{-4} M.
0	0.100	0.00
90	.200	5.3
145	.250	8.0
195	.300	10.6
245	.350	13.3
293	.400	15.9
355	.450	18.8
412	.500	21.25
485	.550	23.9
575	.600	26.6
637	.650	29.3
703	.700	32.0
787	.760	35.1
855	.800	37.2
935	.850	39.9
1010	.900	42.5
1090	.950	45.2
1190	1.000	47.8
1290	1.050	50.4
1380	1.100	53.1
1495	1.150	55.8
1610	1.200	58.5
1720	1.250	61.2
1850	1.300	63.8
2010	1.350	66.4
2130	1.400	69.2
2280	1.450	71.8
2490	1.500	74.3
113,100	1.980	100.0

$k_1 = 5.53 \times 10^{-4}$ sec.$^{-1}$

TABLE XXXVII

RUN 36. SOLVOLYSIS OF 6.3×10^{-4} M. TRITYL THIOCYANATE IN 69.5% METHANOL - 30.5% WATER AT 25.0°

Time, sec.	0.0506 M. NaOH, ml.	HSCN liberated, % of 6.3×10^{-4} M.
0	0.000	0.0
15	.100	8.0
25	.200	16.0
53	.300	24.0
100	.400	32.0
145	.490	39.2
175	.545	43.6
202	.590	47.2
232	.640	51.2
254	.673	53.9
280	.710	56.8
308	.750	60.1
333	.780	62.5
359	.813	65.0
383	.840	67.3
415	.875	69.6
445	.905	72.3
495	.950	76.1
535	.983	78.6
594	1.023	82.0
660	1.060	84.9
710	1.090	87.3
800	1.124	90.0
3000	1.250	100.0

$k_1 = 2.56 \times 10^{-3}$ sec.$^{-1}$

TABLE XXXVIII

RUN 37. SOLVOLYSIS OF 1.96 x 10^{-4} M. TRITYL THIOCYANATE IN 40% ETHANOL - 60% WATER AT 25.0°

Time, sec.	0.0506 M. NaOH, ml.	HSCN liberated, % of 1.96 x 10^{-4} M.
0	0.000	0.0
15	.028	7.2
35	.043	11.1
60	.084	21.6
84	.116	29.9
99	.136	35.0
145	.185	37.7
173	.203	52.3
227	.240	61.8
273	.260	69.6
325	.280	72.2
400	.302	77.8
510	.324	83.5
600	.340	87.7
775	.358	92.4
7800	.388	100.0

$k_1 = 3.85 \times 10^{-3}$ sec.$^{-1}$

TABLE XXXIX

RUN 38. SOLVOLYSIS OF 7.2×10^{-4} M. TRITYL ACETATE IN 69.5% METHANOL - 30.5% WATER AT 25.0°

Time, sec.	0.0506 M. NaOH, ml.	CH_3COOH liberated, % of 7.2×10^{-4} M.
0	0.200	0.0
43	.400	17.2
60	.450	21.5
77	.500	25.8
103	.600	34.5
122	.650	38.7
140	.700	43.1
161	.750	47.3
183	.800	51.7
205	.850	56.0
235	.905	60.8
256	.950	64.6
289	1.000	68.9
324	1.050	73.3
367	1.100	77.4
415	1.150	81.7
470	1.200	86.1
546	1.250	90.6
650	1.300	94.7
6000	1.362	100.0

$k_1 = 4.20 \times 10^{-3}$ sec.$^{-1}$

TABLE XL

RUN 39. SOLVOLYSIS OF 7.05×10^{-4} M. TRITYL ACETATE IN 96.7% METHANOL - 3.3% WATER AT 25.0°

Time, sec.	0.0618 M. NaOH, ml.	CH_3COOH liberated, % of 7.05×10^{-4} M.
0	0.295	0.0
187	.385	8.2
312	.440	13.2
452	.500	18.8
562	.550	23.2
697	.600	27.7
827	.650	32.2
952	.700	36.8
1087	.750	41.3
1257	.800	45.8
1412	.850	50.4
1587	.900	55.0
1807	.950	59.5
2007	1.000	64.0
2267	1.050	68.6
2512	1.100	73.2
2872	1.150	77.8
3232	1.200	82.2
60,000	1.435	100.0

$$k_1 = 5.63 \times 10^{-4} \text{ sec.}^{-1}$$

TABLE XLI

RUN 40. HYDROLYSIS OF 7.5×10^{-4} M. TRITYL ACETATE IN 80% ACETONE - 20% WATER AT 25.0°

Time, sec.	0.0618 M. NaOH, ml.	CH_3COOH liberated, % of 7.5×10^{-4} M.
0	0.200	0.0
1380	.230	2.5
5700	.290	7.4
8700	.330	10.7
18,600	.475	22.6
28,200	.600	32.8
40,680	.730	43.4
82,800	1.050	69.7
900,000	1.420	100.0

$$k_1 = 1.45 \times 10^{-5} \text{ sec.}^{-1}$$

TABLE XLII

RUN 45. SOLVOLYSIS OF 3.72×10^{-4} M. TRITYL THIOCYANATE IN 96.7% METHANOL - 3.3% WATER AT 25.0°

Time, sec.	0.0506 M. NaOH, ml.	HSCN liberated, % of 3.72×10^{-4} M.
0	0.229	0.0
225	.302	10.0
480	.400	23.0
870	.500	37.0
1380	.600	50.5
1620	.650	57.2
2370	.750	70.7
2820	.800	77.5
6180	.934	93.8
37,800	.965	100.0

$k_1 = 5.20 \times 10^{-4}$ sec.$^{-1}$

TABLE XLIII

RUN 92. ACETOLYSIS OF 9.58×10^{-3} M. BENZHYDRYL CHLORIDE IN ACETIC ACID CONTAINING 8.3×10^{-2} M. POTASSIUM ACID PHTHALATE AT 25.0°

Time, sec.	0.175M. $HClO_4$ in HOAc, ml.	HCl liberated, % of 9.58×10^{-3} M.
0	0.720	0.0
4320	.693	4.9
15,100	.650	12.8
41,800	.572	27.0
87,200	.460	47.4
183,500	.323	72.5
283,000	.250	85.8
1,214,000	.172	100.0

$k_1 = 6.88 \times 10^{-6}$ sec.$^{-1}$

TABLE XLIV

RUN 93. ACETOLYSIS OF 9.50×10^{-3} M. BENZHYDRYL CHLORIDE IN ACETIC ACID CONTAINING 0.025 M. POTASSIUM ACID PHTHALATE AT 25.0°

Time, sec.	0.175 M. $HClO_4$ in HOAc, ml.	HCl liberated, % of 9.50×10^{-3} M.
0	1.506	0.0
22,800	1.413	17.1
66,400	1.289	40.0
107,300	1.196	57.2
152,000	1.128	69.7
259,000	1.033	87.2
1,026,000	0.963	100.0

$k_1 = 8.02 \times 10^{-6}$ sec.$^{-1}$

TABLE XLV

RUN 130. FORMOLYSIS OF 1.16 x 10^{-2} M. t-BUTYL CHLORIDE IN 83.3% FORMIC ACID - 16.7% ACETONE AT 25.0 CONTAINING 2.78 x 10^{-2} M. SODIUM FORMATE AT 25.0°

Time, sec.	0.112M. KSCN, ml.	HCl liberated, % of 1.16 x 10^{-2} M.
0	1.75	0.0
607	1.57	17.4
1202	1.43	30.0
1800	1.31	42.5
2400	1.21	52.2
3300	1.10	62.8
4247	0.98	74.5
25,200	.715	100.0

k_1 = 2.96 x 10^{-4} sec.$^{-1}$

TABLE XLVI

RUN 131. FOLMOLYSIS OF 1.74×10^{-2} M. t-BUTYL CHLORIDE IN 83.3% FORMIC ACID - 16.7% ACETONE CONTAINING 2.78×10^{-2} M. SODIUM FORMATE AT 25.0°

Time, sec.	0.112 M. KSCN, ml.	HCl liberated, % of 1.74×10^{-2} M.
0	1.73	0.0
600	1.49	15.5
1194	1.19	34.8
1800	1.12	39.4
2405	1.02	45.8
3325	0.78	61.3
4200	.65	69.7
25,200	.13	100.0

$k_1 = 2.89 \times 10^{-4}$ sec.$^{-1}$

TABLE XLVII

RUN 135. FORMOLYSIS OF 1.40 x 10^{-2} M. BENZHYDRYL CHLORIDE IN 83.3% FORMIC ACID - 16.7% ACETONE CONTAINING 2.78 x 10^{-2} M. SODIUM FORMATE AT 0.0°

Time, sec.	0.112 M. KSCN, ml.	HCl liberated, % of 1.40 x 10^{-2} M.
0	1.74	0.0
20	1.26	38.4
37	0.96	62.4
53	.82	73.6
66	.74	80.0
80	.68	84.8
95	.63	88.8
109	.60	91.2
3600	.49	100.0

$k_1 = 2.38 \times 10^{-2}$ sec.$^{-1}$

TABLE XLVIII

RUN 136. FORMOLYSIS OF 1.22 x 10^{-2} M. BENZHYDRYL CHLORIDE IN 83.3% FORMIC ACID - 16.7% ACETONE CONTAINING 2.78 x 10^{-2} M. SODIUM FORMATE AT 0.0°

Time, sec.	0.112 M. KSCN, ml.	HCl liberated, % of 1.22 x 10^{-2} M.
0.0	1.74	0.0
13.5	1.43	28.7
28.0	1.17	52.8
41.5	1.02	66.7
57.8	0.91	75.8
72.0	.85	82.4
86.5	.79	88.0
101.0	.72	94.4
3600.0	.655	100.0

$k_1 = 2.31 \times 10^{-2}$ sec.$^{-1}$

TABLE XLIX

RUN 137. FORMOLYSIS OF 1.18×10^{-2} M. BENZHYDRYL CHLORIDE IN 83.3% HCOOH - 16.7% ACETONE CONTAINING 4.14×10^{-2} M. SODIUM FORMATE AT 0.0°

Time, sec.	0.112 M. KSCN, ml.	HCl liberated, % of 1.18×10^{-2} M.
0	1.85	0.0
22	1.38	44.8
36	1.17	64.8
49	1.09	72.4
65	1.00	81.0
79	0.96	84.8
95	.94	86.7
109	.88	92.4
3600	.80	100.0

$k_1 = 2.27 \times 10^{-2}$ sec.$^{-1}$

TABLE L

RUN 140. FORMOLYSIS OF 1.26 x 10^{-2} M. BENZHYDRYL CHLORIDE IN 83.3% FORMIC ACID - 16.7% ACETONE CONTAINING 4.17 x 10^{-2} M. SODIUM FORMATE AT 5.0°

Time, sec.	0.112 M. KSCN, ml.	HCl liberated, % of 1.26 x 10^{-2} M.
0	1.85	0.0
24	1.11	65.8
38	0.90	84.5
53	.80	93.3
69	.765	96.5
3600	.725	100.0

$k_1 = 4.84 \times 10^{-2}$ sec.$^{-1}$

TABLE LI

RUN 141. FORMOLYSIS OF 1.21×10^{-2} M. BENZHYDRYL CHLORIDE IN 83.3% FORMIC ACID - 16.7% ACETONE CONTAINING 4.17×10^{-2} M. SODIUM FORMATE AT 5.0°

Time, sec.	0.112 M. KSCN, ml.	HCl liberated, % of 1.21×10^{-2} M.
0.0	1.82	0.0
20.2	1.13	63.9
40.4	0.89	86.2
59.4	.84	90.8
82.8	.77	97.3
2400.0	.74	100.0

$k_1 = 4.84 \times 10^{-2}$ sec.$^{-1}$

TABLE LII

RUN 142. FORMOLYSIS OF 1.76×10^{-2} M. BENZHYDRYL CHLORIDE IN 83.3% FORMIC ACID - 16.7% ACETONE CONTAINING 4.17×10^{-2} M. SODIUM FORMATE AT 5.0°

Time, sec.	0.112 M. KSCN, ml.	HCl liberated, % of 1.76×10^{-2} M.
0.0	1.82	0.0
22.5	0.77	67.0
43.4	.45	87.4
63.5	.36	93.2
85.5	.28	98.2
2400.0	.25	100.0

$k_1 = 4.68 \times 10^{-2}$ sec.$^{-1}$

TABLE LIII

RUN 150. SOLVOLYSIS OF 3.36×10^{-3} M. BENZHYDRYL FLUORIDE IN 50% ETHANOL - 50% WATER CONTAINING 6.73×10^{-3} M. SODIUM HYDROXIDE AT 75.3°

Time, sec.	0.01494 M. HCl, ml.	HCl liberated, % of 3.36×10^{-2} M.
0	4.50	0.0
675	3.63	38.7
960	3.34	51.7
1200	3.18	58.8
1455	2.90	71.2
1755	2.76	77.5
2110	2.67	81.5
2460	2.60	84.6
16,380	2.25	100.0

$$k_1 = 8.40 \times 10^{-4} \text{ sec.}^{-1}$$

TABLE LIV

RUN 151. SOLVOLYSIS OF 2.87×10^{-3} M. BENZHYDRYL FLUORIDE IN 80% ETHANOL - 20% WATER CONTAINING 6.76×10^{-3} M. SODIUM HYDROXIDE AT 100.0°

Time, sec.	0.01494 M. HCl, ml.	HF liberated, % of 2.87×10^{-3} M.
0	4.52	0.0
840	4.42	5.2
4440	3.55	50.5
7560	3.18	69.8
10,980	2.87	85.9
12,780	2.83	88.0
39,600	2.60	100.0

$k_1 = 1.77 \times 10^{-4}$ sec.$^{-1}$

TABLE LV

RUN 152. SOLVOLYSIS OF 2.51×10^{-3} M. BENZHYDRYL FLUORIDE IN 50% ETHANOL - 50% WATER CONTAINING 3.49×10^{-3} M. SODIUM HYDROXIDE AT 75.3°

0	2.33	0.0
300	2.07	15.5
600	1.74	35.1
900	1.53	47.6
1200	1.33	59.5
1500	1.18	68.5
1810	1.08	74.4
2100	1.05	76.2
3000	0.80	91.0
13,500	.65	100.0

$k_1 = 8.25 \times 10^{-4}$ sec.$^{-1}$

TABLE LVI

RUN 153. SOLVOLYSIS OF 2.96×10^{-3} M. BENZHYDRYL FLUORIDE IN 80% ETHANOL - 20% WATER CONTAINING 6.62×10^{-3} M. SODIUM HYDROXIDE AT 100.0°

Time, sec.	0.01494 M. HCl, ml.	HF liberated, % of 2.96×10^{-3} M.
0	4.43	0.0
900	4.35	4.0
1800	4.035	20.0
3000	3.79	32.4
4800	3.43	50.5
6300	3.14	65.1
7980	2.88	78.3
9420	2.88	78.3
11,520	2.72	85.4
66,000	2.45	100.0

$$k_1 = 1.77 \times 10^{-4} \text{ sec.}^{-1}$$

TABLE LVII

RUN 157. SOLVOLYSIS OF 2.95×10^{-3} M. BENZHYDRYL FLUORIDE IN 80% ETHANOL - 20% WATER CONTAINING 6.58×10^{-3} M. SODIUM HYDROXIDE AT 75.3°

Time, sec.	0.01494 M. HCl, ml.	HF liberated, % of 2.95×10^{-3} M.
0	4.40	0.0
3900	4.27	6.6
8100	4.04	18.3
11,700	3.93	21.8
21,720	3.56	42.6
30,240	3.50	45.7
38,400	3.14	63.9
46,440	2.99	71.5
86,400[a]	2.43	100.0

[a] at 100

$$k_1 = 2.81 \times 10^{-5} \text{ sec.}^{-1}$$

TABLE LVIII

RUN.158. SOLVOLYSIS OF 3.21×10^{-3} M. BENZHYDRYL FLUORIDE IN 80% ETHANOL - 20% WATER CONTAINING 3.33×10^{-3} M. SODIUM HYDROXIDE AT 75.3°

Time, sec.	0.01494 M. HCl, ml.	HF liberated, % of 3.21×10^{-3} M.
0	2.23	0.0
7620	1.78	20.9
22,200	1.14	50.7
30,780	0.85	64.1
37,800	.66	73.0
41,400	.61	75.3
46,800	.51	80.0
86,400[a]	.08	100.0

[a] at 100

$k_1 = 3.49 \times 10^{-5}$ sec.$^{-1}$

TABLE LIX

RUN 161. SOLVOLYSIS OF 2.46×10^{-3} M. BENZHYDRYL FLUORIDE IN 80% ETHANOL - 20% WATER CONTAINING 3.77×10^{-3} M. SODIUM HYDROXIDE AT 75.3°

Time, sec.	0.01494 M. HCl, ml.	HF liberated, % of 2.46×10^{-3} M.
0	2.52	0.0
6600	2.26	15.6
12,180	2.05	28.6
18,300	1.86	40.1
24,800	1.56	58.4
27,900	1.57	57.8
31,500	1.54	59.6
35,280	1.44	65.6
75,900	1.04	90.0
75,900[a]	0.87	100.0
75,900[a]	.88	100.0

[a] at 100

$k_1 = 3.08 \times 10^{-5}$ sec.$^{-1}$

TABLE LX

RUN 162. SOLVOLYSIS OF 2.69 x 10^{-3} M. BENZHYDRYL FLUORIDE IN 80% ETHANOL - 20% WATER CONTAINING 6.58 x 10^{-3} M. SODIUM HYDROXIDE AT 75.3°

Time, sec.	0.01494 M. HCl, ml.	HF liberated, % of 2.69 x 10^{-3} M.
0	4.40	0.0
6600	4.09	17.2
12,300	3.87	29.4
18,600	3.64	47.8
24,800	3.47	51.7
27,900	3.41	55.0
31,500	3.26	63.3
35,280	3.23	65.0
75,900[a]	2.60	100.0
75,900[a]	2.60	100.0

[a] at 100

k_1 = 3.16 x 10^{-5} sec.$^{-1}$

TABLE LXI

RUN 165. ACETOLYSIS OF 1.10 x 10^{-2} M. BENZHYDRYL FLUORIDE IN ACETIC ACID CONTAINING 7.5 x 10^{-2} M. POTASSIUM ACID PHTHALATE AT 25.0°

Time, sec.	0.0214 N. $Th(NO_3)_4$, ml.	$(C_6H_5)_2CHF$ remaining, % of 1.10 x 10^{-2} M.
0	5.16	0.0
3660	4.43	14.1
10,080	3.60	30.2
21,000	2.54	50.7
27,740	2.05	60.3
36,300	1.68	67.4
39,720	1.60	69.0
43,200	1.00	80.7

k_1 = 1.50 x 10^{-5} sec.$^{-1}$

TABLE LXII

RUN 166. ACETOLYSIS OF 1.01 x 10^{-2} M. BENZHYDRYL FLUORIDE IN ACETIC ACID CONTAINING 5.0 x 10^{-2} M. POTASSIUM ACID PHTHALATE AT 25.0°

Time, sec.	0.0214 N. $Th(NO_3)_4$, ml.	$(C_6H_5)_2CHF$ remaining, % of 1.01 x 10^{-2} M.
0	4.72	0.0
3720	4.30	8.9
11,120	3.60	23.7
16,320	2.85	39.6
20,220	2.70	42.8
27,000	2.15	55.4
35,640	1.64	65.3
41,300	1.02	78.5

$k_1 = 1.46 \times 10^{-5}$ sec.$^{-1}$

TABLE LXIII

RUN 175. FORMOLYSIS OF 7.86 x 10^{-3} M. BENZHYDRYL FLUORIDE IN 83.3% FORMIC ACID - 16.7% ACETONE CONTAINING 1.00 x 10^{-1} M. SODIUM FORMATE AT 0.0°

Time, sec.	0.0214 N. $TH(NO_3)_4$, ml.	$(C_6H_5)_2CHF$ remaining, % of 7.86 x 10^{-3} M.
0.0	3.82	0.0
21.4	3.65	4.8
52.9	2.32	42.0
114.4	1.95	52.4

$k_1 = 6.98 \times 10^{-3}$ sec.$^{-1}$

TABLE LXIV

RUN 176. FORMOLYSIS OF 8.13 x 10^{-3} M. BENZHYDRYL FLUORIDE IN 83.3% FORMIC ACID - 16.7% ACETONE CONTAINING 1.00 x 10^{-1} M. SODIUM FORMATE AT 0.0°

Time, sec.	0.0214 N. $Th(NO_3)_4$, ml.	$(C_6H_5)_2CHF$ remaining, % of 8.13 x 10^{-3} M.
0.0	4.00	0.0
39.6	3.17	21.9
81.6	2.15	48.7
122.4	1.60	63.2
162.0	1.04	78.0

k_1 = 9.24 x 10^{-3} sec.$^{-1}$

TABLE LXV

RUN 177. FORMOLYSIS OF 6.27 x 10^{-3} M. BENZHYDRYL FLUORIDE IN 83.3% FORMIC ACID - 16.7% ACETONE CONTAINING 5.00 x 10^{-2} M. SODIUM FORMATE AT 0.0°

Time, sec.	0.0214 N. $Th(NO_3)_4$, ml.	$(C_6H_5)_2CHF$ remaining, % of 6.27 x 10^{-3} M.
0.0	3.18	0.0
30.5	2.46	24.6
66.0	2.24	32.1
134.6	1.20	67.5

k_1 = 8.18 x 10^{-3} sec.$^{-1}$

TABLE LXVI

RUN 178. FORMOLYSIS OF 6.87 x 10^{-3} M. BENZHYDRYL FLUORIDE IN 83.3% FORMIC ACID - 16.7% ACETONE CONTAINING 1.00 x 10^{-1} M. SODIUM FORMATE AT 0.0°

Time, sec.	0.0214 N. $Th(NO_3)_4$, ml.	$(C_6H_5)_2CHF$ remaining, % of 6.87 x 10^{-3}M.
0.0	3.46	0.0
57.0	2.34	34.6
93.0	1.78	52.0
128.5	1.40	63.7
166.0	1.23	69.0

k_1 = 7.28 x 10^{-3} sec.$^{-1}$

TABLE LXVII

RUN 180. SOLVOLYSIS OF 2.65 x 10^{-3} M. BENZHYDRYL FLUORIDE IN 50% ETHANOL - 50% WATER CONTAINING 3.95 x 10^{-3} M. SODIUM HYDROXIDE AT 50.0°

Time, sec.	0.01494 M. HCl, ml.	HF liberated, % of 2.65 x 10^{-3} M.
0	1.97	0.0
900	1.86	6.2
1800	1.74	13.0
2940	1.55	23.7
4320	1.39	32.7
6060	1.18	44.6
8160	0.98	55.9
10,860	.78	67.2
84,600[a]	.20	100.0

[a] at 100

k_1 = 1.07 x 10^{-4} sec.$^{-1}$

TABLE LXVIII

RUN 181. SOLVOLYSIS OF 2.54 x 10^{-3} M. BENZHYDRYL FLUORIDE IN 50% ETHANOL - 50% WATER CONTAINING 6.31 x 10^{-3} M. SODIUM HYDROXIDE AT 50.0°

Time, sec.	0.01494 M. HCl, ml.	HF liberated, % of 2.54 x 10^{-3} M.
0	4.22	0.0
1260	3.99	13.5
3000	3.72	29.4
5040	3.40	48.2
6540	3.28	55.3
7560	3.20	60.0
9480	3.07	67.6
5400[a]	2.54	100.0
5400[a]	2.50	100.0

[a] at 100

$k_1 = 1.22 \times 10^{-4}$ sec.$^{-1}$

TABLE LXIX

RUN 184. SOLVOLYSIS OF 3.05 x 10^{-3} M. BENZHYDRYL FLUORIDE IN 50% ETHANOL - 50% WATER CONTAINING 5.16 x 10^{-3} M. SODIUM HYDROXIDE AT 49.8°

Time, sec.	0.01494 M. HCl, ml.	HF liberated, % of 3.05 x 10^{-3} M.
0	3.45	0.0
1380	3.24	10.3
4080	2.83	30.4
4920	2.68	37.7
6420	2.52	45.6
9720	2.20	61.3
11,760	2.05	68.7
14,400	1.95	73.6
4800[a]	1.41	10.0

[a] at 100

$k_1 = 1.00 \times 10^{-4}$ sec.$^{-1}$

TABLE LXX

RUN 185. SOLVOLYSIS OF 2.69 x 10^{-3} M. BENZHYDRYL FLUORIDE
IN 50% ETHANOL - 50% WATER CONTAINING
5.29 x 10^{-3} M. SODIUM HYDROXIDE AT 49.8°

Time, sec.	0.01494 M. HCl, ml.	HF liberated, % of 2.69 x 10^{-3} M.
0	3.54	0.0
1500	3.27	15.0
3000	3.06	26.7
4800	2.755	43.7
6000	2.685	47.7
7560	2.46	60.6
10,980	2.25	71.9
7200[a]	1.75	100.0
3600[a]	1.74	100.0

[a] at 100

$k_1 = 1.20 \times 10^{-4} \text{sec.}^{-1}$

TABLE LXXI

RUN 186. FORMOLYSIS OF 4.17 x 10^{-3} M. BENZHYDRYL FLUORIDE
IN 83.3% FORMIC ACID - 16.7% ACETONE CONTAINING
1.00 x 10^{-1} M. SODIUM FORMATE AT 10.0°

Time, sec.	0.0214 N. $Th(NO_3)_4$, ml.	$(C_6H_5)_2CHF$ remaining, % of 4.17 x 10^{-3} M.
0.0	2.40	0.0
14.2	1.75	33.3
28.8	1.34	54.4
43.4	1.03	70.3
59.6	0.75	84.6

$k_1 = 3.04 \times 10^{-2} \text{ sec.}^{-1}$

TABLE LXXII

RUN 187. FORMOLYSIS OF 4.07×10^{-3} M. BENZHYDRYL FLUORIDE IN 83.3% FORMIC ACID - 16.7% ACETONE CONTAINING 1.00×10^{-1} M. SODIUM FORMATE AT 10.0°

Time, sec.	0.0214 N. $Th(NO_3)_4$, ml.	$(C_6H_5)_2CHF$ remaining, % of 4.07×10^{-3} M.
0.0	2.40	0.0
15.8	1.90	26.3
29.7	1.35	55.3
43.6	1.10	68.4
60.2	0.73	87.9

$k_1 = 3.26 \times 10^{-2}$ sec.$^{-1}$

TABLE LXXIII

RUN 188. SOLVOLYSIS OF 3.74×10^{-3} M. TRITYL ACETATE IN 80% ETHANOL - 20% WATER CONTAINING 4.49×10^{-3} M. SODIUM HYDROXIDE AT 25.0°

Time, sec.	0.01494 M. HCl, ml.	CH_3COOH liberated, % of 3.74×10^{-3} M.
0.	3.00	0.0
600	2.30	28.0
960	2.00	40.0
1320	1.74	50.4
1740	1.51	59.6
2400	1.24	70.4
3000	1.03	78.8
3600	0.84	86.4
23,400	.50	100.0

$k_1 = 5.13 \times 10^{-4}$ sec.$^{-1}$

TABLE LXXIV

RUN 189. SOLVOLYSIS OF 3.83×10^{-3} M. TRITYL ACETATE IN 80% ETHANOL - 20% WATER CONTAINING 4.53×10^{-3} M. SODIUM HYDROXIDE AT 25.0°

Time, sec.	0.01494 M. HCl, ml.	CH_3COOH liberated, % of 3.83×10^{-3} M.
0	3.03	0.0
420	2.56	18.3
900	2.10	36.3
1200	1.84	46.4
1560	1.58	56.6
1920	1.39	64.1
2760	1.01	78.8
3660	0.80	87.1
15,600	.47	100.0

$k_1 = 5.42 \times 10^{-4}$ sec.$^{-1}$

TABLE LXXV

RUN 190. SOLVOLYSIS OF 3.80×10^{-3} M. TRITYL ACETATE IN 60% ETHANOL - 40% WATER CONTAINING 4.58×10^{-3} M. SODIUM HYDROXIDE AT 25.0°

Time, sec.	0.01494 M. HCl, ml.	CH_3COOH liberated, % of 3.80×10^{-3} M.
0	3.06	0.0
43	2.86	7.9
69	2.72	13.4
98	2.64	16.5
145	2.48	22.8
183	2.30	29.9
214	2.16	35.4
253	2.08	38.6
303	1.97	42.9
1200[a]	0.52	100.0

[a] at 50

$k_1 = 1.91 \times 10^{-3}$ sec.$^{-1}$

TABLE LXXVI

RUN 192. SOLVOLYSIS OF 2.92×10^{-3} M. BENZHYDRYL CHLORIDE IN 96.7 % METHANOL - 3.3% WATER AT 25.0°

Time, sec.	0.021 M. NaOH, ml.	HCl liberated, % of 2.92×10^{-3} M.
0	0.01	0.0
54	.11	7.3
105	.20	13.8
165	.30	21.0
233	.40	28.3
304	.50	35.6
387	.60	42.8
434	.65	46.4
483	.70	50.1
534	.75	53.7
592	.80	57.4
650	.85	60.9
713	.90	64.5
780	.95	68.2
870	1.00	71.9
43,200	1.39	100.0

$k_1 = 1.46 \times 10^{-3} \text{sec.}^{-1}$

TABLE LXXVII

RUN 193. SOLVOLYSIS OF 2.69×10^{-3} M. BENZHYDRYL CHLORIDE IN 96.7% METHANOL - 3.3% WATER AT 25.0°

Time, sec.	0.21 M. NaOH, ml.	HCl liberated, % of 2.69×10^{-3} M.
0	2.00	0.0
57	2.10	7.8
117	2.20	15.6
179	2.30	23.4
217	2.35	27.3
254	2.40	31.2
297	2.45	35.2
339	2.50	39.1
385	2.55	42.9
432	2.60	46.8
481	2.65	50.8
538	2.70	54.7
595	2.75	58.6
660	2.80	62.5
731	2.85	66.4
814	2.90	70.3
43,200	3.28	100.0

$k_1 = 1.49 \times 10^{-3}$ sec.$^{-1}$

TABLE LXXVIII

RUN 195. SOLVOLYSIS OF 4.03×10^{-4} M. TRITYL p-NITROPHENYL ETHER IN 80% ETHANOL - 20% WATER CONTAINING 2.26×10^{-3} M. SODIUM HYDROXIDE AT 25.0°

Time, sec.	Optical Density,	$NaOC_6H_4NO_2$ liberated, % of 4.03×10^{-4} M.
0	.081	0.0
181	.145	8.4
600	.271	25.0
962	.350	36.2
1200	.403	43.2
1453	.440	48.2
1813	.496	56.1
2165	.540	62.0
158,400	.815	100.0

$k_1 = 4.54 \times 10^{-4}$ sec.$^{-1}$

TABLE LXXIX

RUN 196. SOLVOLYSIS OF 2.83×10^{-4} M. TRITYL p-NITROPHENYL ETHER IN 80% ETHANOL - 20% WATER CONTAINING 2.26×10^{-2} M. SODIUM HYDROXIDE AT 25.0°

Time, sec.	Optical Density,	$NaOC_6H_4NO_2$ liberated, % of 2.84×10^{-4} M.
0	0.075	0.0
300	.136	11.6
600	.194	22.5
1020	.259	35.2
1384	.316	46.5
1620	.339	50.4
2100	.375	57.4
2702	.438	69.4
16,200	.595	100.0

$k_1 = 4.44 \times 10^{-4}$ sec.$^{-1}$

TABLE LXXX

RUN 198. SOLVOLYSIS OF 4.36×10^{-5} M. TRITYL p-NITROPHENYL ETHER IN 40% ETHANOL - 60% WATER CONTAINING 2.26×10^{-2} M. SODIUM HYDROXIDE AT 25.0°

Time, sec.	Optical Density,	$NaOC_6H_4NO_2$ liberated, % of 4.36×10^{-5} M.
0	0.334	0.0
10	.398	7.8
20	.450	14.5
30	.498	20.4
40	.542	26.2
50	.583	31.2
60	.623	36.3
70	.659	40.8
80	.693	45.2
90	.725	49.3
100	.753	53.0
115	.790	57.6
135	.840	64.3
160	.885	70.0
185	.925	75.0
225	.975	81.7
250	1.000	84.8
300	1.036	89.5
350	1.067	92.7
1860	1.117	100.0

$k_1 = 7.58 \times 10^{-3}$ sec.$^{-1}$

TABLE LXXXI

RUN 199. SOLVOLYSIS OF 3.02×10^{-5} M. TRITYL p-NITROPHENYL ETHER IN 40% ETHANOL - 60% WATER CONTAINING 2.26×10^{-2} M. SODIUM HYDROXIDE AT 25.0°

Time, sec.	Optical Density,	$NaOC_6H_4NO_2$ liberated, % of 3.02×10^{-5} M.
0	0.330	0.0
10	.373	7.9
20	.410	14.6
30	.450	21.9
40	.483	27.8
50	.515	33.8
60	.540	38.4
70	.568	43.4
80	.596	48.3
90	.616	52.0
100	.635	55.6
115	.665	61.3
200	.768	80.1
235	.798	85.8
275	.824	90.4
325	.842	93.7
3600	.875	100.0

$k_1 = 8.26 \times 10^{-3}$ sec.$^{-1}$

TABLE LXXXII

RUN 200. SOLVOLYSIS OF 4.31×10^{-5} M. TRITYL p-NITROPHENYL ETHER IN 69.5% METHANOL - 30.5% WATER CONTAINING 2.26×10^{-2} M. SODIUM HYDROXIDE AT 25.0°

Time, sec.	Optical Density,	$NaOC_6H_4NO_2$ liberated, % of 4.31×10^{-5} M.
0	0.117	0.0
25	.170	6.5
50	.220	12.8
75	.267	18.8
100	.317	25.1
125	.356	29.9
150	.398	35.3
175	.435	39.9
200	.469	44.3
225	.502	48.5
250	.532	52.4
275	.557	55.7
300	.586	59.4
325	.609	62.2
350	.627	64.8
375	.650	67.7
400	.670	70.0
450	.704	74.5
500	.738	78.9
550	.762	82.1
625	.792	85.8
750	.828	90.5
900	.854	93.9
3000	.900	100.0

$k_1 = 3.04 \times 10^{-3} sec.^{-1}$

TABLE LXXXIII

RUN 203. ACETOLYSIS OF 2.16 x 10^{-5} M. TRITYL p-NITROPHENYL ETHER IN ACETIC ACID CONTAINING 5.00 x 10^{-2} M. POTASSIUM ACID PHTHALATE AT 25.0°

Time, sec.	Optical Density,	$HOC_6H_4NO_2$ liberated, % of 2.16 x 10^{-5} M.
0	0.402	0.0
42	.466	16.7
82	.512	28.3
124	.561	40.8
164	.594	49.1
208	.627	57.9
257	.659	65.7
303	.680	71.3
2400	.792	100.0

k_1 = 4.17 x 10^{-3} sec.$^{-1}$

TABLE LXXIV

RUN 206. HYDROLYSIS OF 6.72×10^{-5} M. TRITYL p-NITROPHENYL ETHER IN 50% ACETONE - 50% WATER CONTAINING 1.13×10^{-2} M. SODIUM HYDROXIDE AT 25.0°

Time, sec.	Optical Density,	$NaOC_6H_4NO_2$ liberated, % of 6.72×10^{-5} M.
0	0.000	0.0
50	.056	4.5
100	.106	8.5
150	.160	12.8
200	.211	17.6
250	.267	21.4
300	.306	24.5
350	.352	28.3
400	.395	31.8
450	.437	35.2
500	.477	38.5
575	.536	43.3
650	.587	47.4
775	.668	54.1
850	.708	57.6
925	.750	60.9
1000	.785	63.8
1100	.832	67.8
1225	.882	71.7
1350	.923	75.5
1500	.969	80.0
7800	1.213	100.0

$k_1 = 1.06 \times 10^{-3}$ sec.$^{-1}$

TABLE LXXXV

SUMMARY OF KINETIC RUNS

Run	Compound[a]	Solvent[b]	Added Electrolyte	Conc. of Added Electrolyte, M.x10^3	Temp., °C	k_1 sec.$^{-1}$
4	I	2	-	-	29.93	3.68x10^{-4}
5	"	2	-	-	29.90	3.98x10^{-4}
6	"	5	-	-	30.05	3.73x10^{-2}
7	"	8	-	-	29.90	1.15x10^{-2}
8	"	8	-	-	30.06	1.10x10^{-2}
9	"	10	-	-	30.04	3.10x10^{-5}
11	"	1	-	-	30.00	9.38x10^{-6}
12	"	1	-	-	39.72	2.52x10^{-5}
13	"	2	-	-	39.5	8.50x10^{-4}
14	"	5	-	-	39.6	6.47x10^{-2}
15	"	8	-	-	"	2.14x10^{-2}
16	"	10	-	-	"	1.12x10^{-4}
18	"	11	-	-	25.0	9.83x10^{-4}
19	"	7	-	-	"	3.54x10^{-4}
20	"	12	$NaO_2C_2H_3$	250	"	1.51x10^{-2}
21	"	12	"	250	"	1.51x10^{-2}
23	"	12	"	125	"	1.78x10^{-2}
33	II	10	-	-	"	9.03x10^{-4}
34	"	10	-	-	"	9.62x10^{-4}
35	"	9	-	-	"	5.53x10^{-4}
36	"	8	-	-	"	2.56x10^{-3}
37	"	5	-	-	"	3.85x10^{-3}
45	"	7	-	-	"	5.20x10^{-4}
38	III	8	-	-	"	4.20x10^{-3}
39	"	7	-	-	"	5.63x10^{-4}
40	"	9	-	-	"	1.45x10^{-5}
188	"	2	NaOH	4.49	"	5.13x10^{-4}
189	"	2	"	4.53	"	5.42x10^{-4}
190	"	3	"	4.58	"	1.91x10^{-3}
92	IV	12	$KHO_4C_8H_4$	83.0	"	6.88x10^{-6}
93	"	12	"	25.0	"	8.02x10^{-6}
135	"	13	NaOOCH	27.8	0.0	2.38x10^{-2}
136	"	13	"	27.8	"	2.31x10^{-2}
137	"	13	"	41.4	"	2.27x10^{-2}
140	"	13	"	41.7	5.0	4.84x10^{-2}
141	"	13	"	"	"	4.84x10^{-2}
142	"	13	"	"	"	4.68x10^{-2}
192	"	7	-	-	25.0	1.46x10^{-3}
193	"	7	-	-	"	1.49x10^{-3}

TABLE LXXXV (Cont.)

Run	Compound[a]	Solvent[b]	Added Electrolyte	Conc. of Added Electrolyte, M.x10^3	Temp., °C	k_1, sec.$^{-1}$
130	V	13	NaO_2CH	27.8	25.0	2.96x10^{-4}
131	"	13	"	27.8	25.0	2.89x10^{-4}
150	VI	4	NaOH	6.73	75.3	8.40x10^{-4}
151	"	2	"	6.76	100.0	1.77x10^{-4}
152	"	4	"	3.49	75.3	8.25x10^{-4}
153	"	2	"	6.62	100.0	1.77x10^{-4}
157	"	2	"	6.58	75.3	2.81x10^{-5}
158	"	2	"	3.33	75.3	3.49x10^{-5}
161	"	2	"	3.77	75.3	3.08x10^{-5}
162	"	2	"	6.58	75.3	3.16x10^{-5}
165	"	12	$KHO_2C_8H_4$	75	25.0	1.50x10^{-5}
166	"	12	"	50	25.0	1.46x10^{-5}
175	"	13	NaO_2CH	100	0.0	6.98x10^{-3}
176	"	13	"	100	0.0	9.24x10^{-3}
177	"	13	"	50	0.0	8.18x10^{-3}
178	"	13	"	100	0.0	7.28x10^{-3}
180	"	4	NaOH	3.94	50.0	1.07x10^{-4}
181	"	4	"	6.31	50.0	1.22x10^{-4}
184	"	4	"	5.16	50.0	1.00x10^{-4}
185	"	4	"	5.29	49.8	1.20x10^{-4}
186	"	13	NaO_2CH	100	10.0	3.04x10^{-2}
187	"	13	"	100	10.0	3.26x10^{-2}
195	VII	2	NaOH	2.26	25.0	4.54x10^{-4}
196	"	2	"	22.6	25.0	4.44x10^{-4}
198	"	5	"	22.6	25.0	7.58x10^{-3}
199	"	5	"	22.6	25.0	8.26x10^{-3}
200	"	8	"	22.6	25.0	3.04x10^{-3}
203	"	12	$KHO_4C_8H_4$	50.0	25.0	4.17x10^{-3}
206	"	11	NaOH	25.0	25.0	1.06x10^{-3}
46	VIII	1	-	-	-57.5	1.02x10^{-4}
47	"	1	-	-	-63	3.73x10^{-5}
48	"	1	-	-	-59	6.08x10^{-5}
49	"	7	-	-	-61.0	2.98x10^{-3}
50	"	7	-	-	-61.3	1.92x10^{-3}
51	"	7	-	-	-62.8	1.93x10^{-3}
54	"	7	-	-	-61.8	1.25x10^{-3}
55	"	7	-	-	-62.7	2.02x10^{-3}
56	"	6	-	-	-63.1	6.0 x10^{-4}
57	"	6	-	-	-63.3	7.6x10^{-4}

TABLE LXXXV (Cont).

[a] I = Trityl fluoride;
II = Trityl thiocyanate;
III = Trityl acetate;
IV = Benzhydryl chloride;
V = t-Butyl chloride;
VI = Benzhydryl fluoride;
VII = Trityl p-Nitrophenyl ether;
VIII = Trityl chloride.

[b] 1 = Ethanol
2 = 80% Ethanol - 20% water;
3 = 60% Ethanol - 40% water;
4 = 50% Ethanol - 50% water;
5 = 40% Ethanol - 60% water;
6 = Methanol
7 = 96.7% Methanol - 3.3% water;
8 = 69.5% Methanol - 30.5% water;
9 = 80% Acetone - 20% water;
10 = 70% Acetone - 30% water;
11 = 50% Acetone - 50% water;
12 = Acetic acid;
13 = 83.3% Formic acid - 16.7% water.

4. Reaction Products

In all the runs except those involving trityl fluoride in acetic acid, the analytical method made it certain that reactions proceeded to completion. To prove that trityl acetate was indeed the principal product in these acetic acid runs, the crude product was isolated by quickly removing the solvent after ten times the half life (with no exposure to temperatures above 25°), and extracting the organic material from the sodium acetate and sodium fluoride with ether. After removal of the ether, the remaining material had m.p. 74 - 78°, in contrast to 87 - 88° for pure trityl acetate.[49] The low m.p. is believed to be due to the 14% triphenylcarbinol known to be present (by base titration) in the original trityl fluoride (cf. Table LXXXVI). This crude product proved very difficult to free from triphenylcarbinol by recrystallization. However, its identity was shown by a kinetic analysis. In 50% acetone - 50% water the first-order rate constant for hydrolysis was 7.1 x 10^{-4} sec.$^{-1}$ at 25.0 (TableLXXXVII), compared to 7.2x10^{-4} sec.$^{-1}$ for authentic trityl acetate (Table II). The end-point 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

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(49) M. Gomberg and G. T. Davis, Ber., 36, 3924 (1903).

TABLE LXXXVI

MELTING POINTS OF MIXTURES OF TRITYL ACETATE AND TRIPHENYLCARBINOL

% $(C_6H_5)_3COH$	m.p., °C.
0	87 - 88
5	78.0 - 79.0
10	75.6 - 77.0
20	93.2 - 99.0
30	100.2 - 122.2
40	122 - 126
50	124.6 - 134.2
60	133.8 - 147.4
70	145.0 - 153.0
80	150.4 - 157.0
90	157.4 - 160.8
100	163.4 - 164.2

TABLE LXXXVII

HYDROLYSIS OF PRODUCT OF ACETOLYSIS OF TRITYL FLUORIDE IN 50% ACETONE - 50% WATER AT 25.0°

Time, sec.	0.0506 M. NaOH, ml.	CH_3COOH liberated, % of 7.5×10^{-4} M.
0	0.000	0.0
55	.100	6.8
98	.150	10.1
148	.200	13.5
208	.250	16.8
274	.300	20.2
330	.350	23.6
395	.400	27.0
463	.450	30.3
537	.500	33.8
623	.550	37.1
690	.600	40.4
770	.653	44.0
860	.704	47.4
937	.750	50.7
1053	.800	54.0
1136	.850	57.2
1280	.900	60.8
1410	.950	64.1
1550	1.000	67.3
1680	1.050	71.0
1865	1.100	74.3
2055	1.150	77.5
2280	1.200	81.0
10,200	1.482	100.0

$k_1 = 7.1 \times 10^{-4}$ sec.$^{-1}$

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.

5. Calculations

Rate constants were calculated by use of the fact that the first-order rate constant is equal to 0.693 divided by the half life. Half lives were determined by plotting the % unreacted against time on semi-logarithmic paper, and taking the distance along the abscissa from the origin to point where the best straight line crossed 50%. The best straight line was drawn by sight except in runs 175, 176, 177, 178, 186, and 187, where the method of least squares was used.

Summary.- It has been found possible to correlate the rates of solvolysis of twenty organic compounds in eighteen solvents by means of equation 6. This equation assigns

$$\log k/k_0 = sn + s'e \qquad (6)$$

changes in relative rates to four factors: mucleophilicity of the solvent (n), electrophilicity of the solvent (e), susceptibility of the compound to nucleophilic attack (s), and susceptibility of the compound to electrophilic attack (s').

No support has been found for the hypothesis that two essentially different transition states are involved in solvolyses of organic compounds. Neither is any support apparent in this work for the hypothesis that all compounds which have at least as great a tendency as t-butyl chloride to ionize into a carbonium ion react by way of identical transition-states.

The data are more consistent with the hypothesis that all solvolyses occur by way of one type of transition-state, in which both a mucleophilic and an electrophilic solvent molecule are involved. Only quantitative variations in this transition state are necessary to account for the experimental facts.

Appendix A

KINETIC MEASUREMENTS ON TRITYL CHLORIDE

It would be desirable to obtain kinetic data on trityl chloride at 25° for comparison with the other trityl compounds listed in Table III. Since at 25° trityl chloride reacts too rapidly to measure by conventional methods, some preliminary runs were done at -60° by the intermittent titration method. Unfortunately, the more highly aqueous mixtures and the carboxylic acids froze at temperatures at which the reactions were still too fast to measure, so this work was abandoned. The data obtained are in Tables XCII - CI . Temperature control was ± 2° in the ethanol runs and ± 0.2° in the methanol runs.

Another approach to the problem is the use of a flow technique to measure these reactions at 25°. In this method two streams of liquid, one containing acetone and trityl chloride, and the other containing acetone, water, brom thymol blue indicator, and a known amount of sodium hydroxide less than equivalent to the trityl chloride, were forced from water-jacketed burets into a mixer and thence down a pyrex capillary tube. When sufficient hydrochloric acid had been liberated by the hydrolysis to neutralize the sodium hydroxide, the indicator changed color. This could be observed as a more or less sharp line in the capillary.

By measuring the time necessary for a given amount of liquid to pass down the capillary and knowing the cross-sectional area of the capillary, the velocity down the capillary could be calculated. Then by measuring the distance from the point of mixing to the point at which the indicator changed color, and knowing the amount of sodium hydroxide and trityl chloride initially present, the time necessary for a given % of reaction to occur could be calculated. A series of such measurements and calculations could be combined to give a kinetic run.

The plots of such runs always exhibited marked curvature (Fig. 17). Since no explanation for this curvature could be found which would allow use of the method to obtain the data desired, the method was abandoned.

It was shown that adequate mixing was obtained by adding triphenylcarbinol and hydrochloric acid in place of trityl chloride to the acetone solution. The acid color of the indicator was observed in the liquid just leaving the mixer, indicating that mixing was completed inside the mixer.

Substitution of dioxane for acetone did not change the shape of the curve.

Experimental

The mixer was constructed from teflon rod. A cross-shaped piece was first made. Then a hole of the same diameter as that in the capillary was drilled down one axis. A larger hole, to just fit around the capillary, was next drilled a short distance into the same axis. Next, a hole was drilled a short way into each end of the other axis and threaded. In each of these two holes, two small holes were drilled into the small hole down the other axis. Small, hollow, threaded plugs were constructed of teflon and attached by gum rubber tubing to the water-jacketed burets.

The solutions were forced down the capillary by nitrogen pressure. The exhaust end was evacuated with two aspirators to prevent accumulation of pressure during a run.

The procedure was to apply nitrogen pressure on the liquids in the water-jacketed burets and apply vacuum to the exhaust end of the capillary, preventing the liquids from reaching the mixer by means of a common screw-clamp on the two pieces of gum rubber tubing connecting the burets to the mixer. At zero time the screw-clamp was removed and a stop-watch started. The point at which the indicator changed color was marked, and the time necessary to empty a known volume of liquid observed.

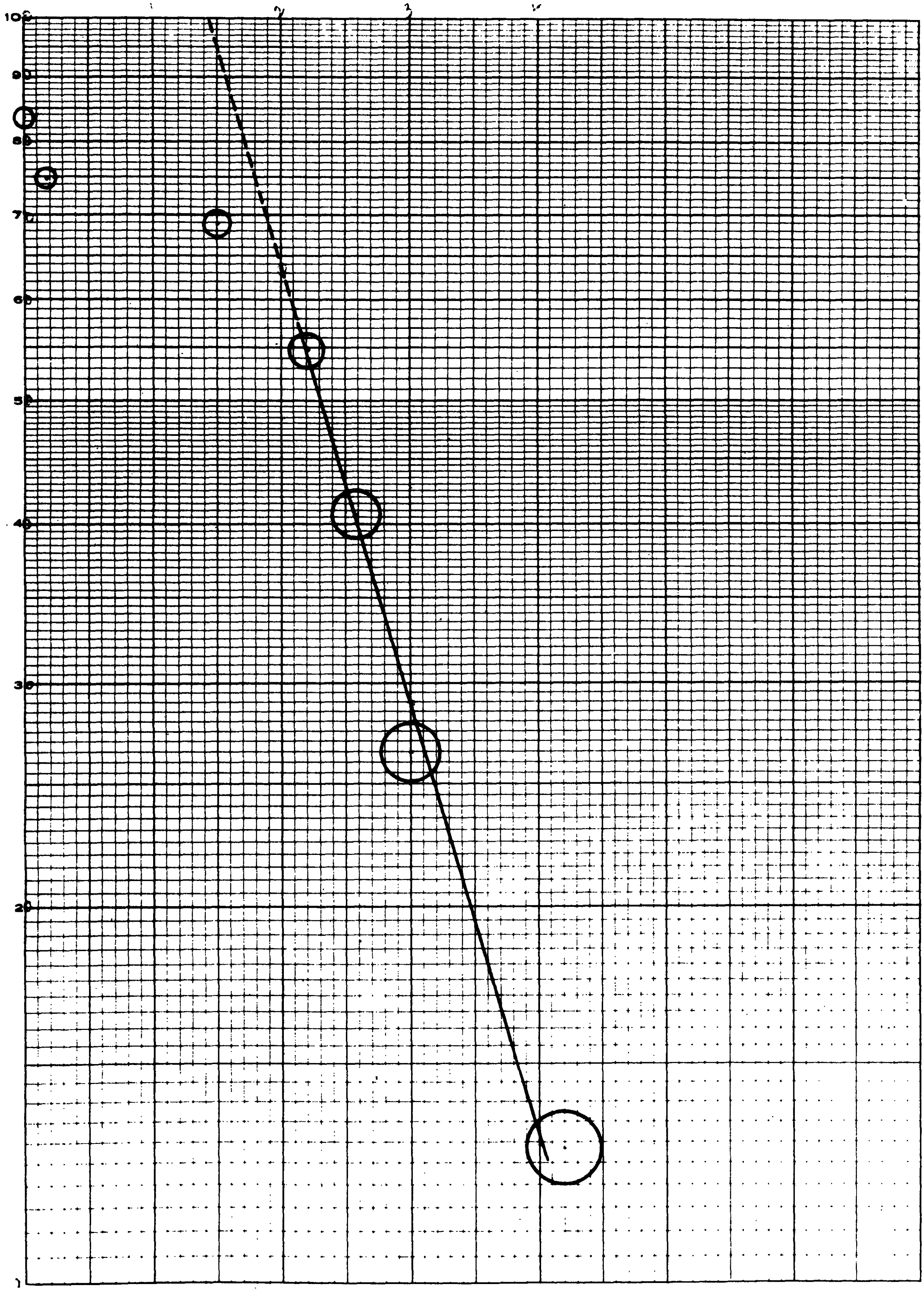

Fig. 17 - Plot of 100-% reacted vs. distance down the flow tube.

TABLE LXXXVIII

RUN 88. HYDROLYSIS OF 2.00 x 10^{-3} M. TRITYL CHLORIDE IN 90% ACETONE - 10% WATER AT 25.0°

Distance from mixer, cm.	0.0932 M. NaOH, ml.	HCl liberated, % of 2.00 x 10^{-3} M.
11.0	0.430	10
14.2	.858	20
17.0	1.288	30
19.5	1.718	40
22.0	2.148	50
24.3	2.578	60
30.5	3.004	70
34-36	3.436	80

Velocity 528 cm./sec.

Reynolds No. 11,000

TABLE LXXXIX

RUN 89. HYDROLYSIS OF 2.00 x 10^{-3} M. TRITYL CHLORIDE IN 90% ACETONE - 10% WATER IN THE PRESENCE OF 2.00 x 10^{-3} POTASSIUM NITRATE AT 25.0°

Distance from mixer, cm.	0.0932 M. NaOH, ml.	HCl liberated, % of 2.00 x 10^{-3} M.
20.6	0.858	20
26.4	1.288	30
30.6	2.148	50
37.0	3.004	70
41.5	3.436	80

Velocity 528 cm./sec.

Reynolds No. 11,000

TABLE XC

RUN 90. HYDROLYSIS OF 2.00 x 10^{-3} M. TRITYL CHLORIDE IN 90% ACETONE - 10% WATER IN THE PRESENCE OF 2.00 x 10^{-3} M. LITHIUM PERCHLORATE AT 25.0°

Distance from mixer, cm.	0.0932 M. NaOH, ml.	HCl liberated, % of 2.00 x 10^{-3} M.
22.7	0.858	20
24.6	1.288	30
28.2	2.148	50
32.4	3.004	70
36.0	3.436	80

Velocity 528 cm./sec.

Reynolds No. 11,000

TABLE XCI

RUN 124. HYDROLYSIS OF 8.33×10^{-4} M. TRITYL CHLORIDE IN 70.7% DIOXANE - 29.3% WATER AT 25.0°

Distance from mixer, cm.	0.1783 M. NaOH, ml.	HCl liberated, % of 8.33×10^{-4} M.
0.0	0.066	16.7
0.2	.009	25.2
1.5	.122	31.1
2.2	.178	45.2
2.6	.234	59.4
3.0	.290	73.5
4.2	.346	87.2

Velocity 449 cm./sec.

TABLE XCII

RUN 46. ETHANOLYSIS OF $6.4x10^{-4}$ M. TRITYL CHLORIDE IN ETHANOL AT -57.5°

Time, sec.	0.0434M. $NaOC_2H_5$, ml.	HCl liberated, % of $6.4x10^{-4}$ M.
0	0.27	0.0
240	.30	2.0
540	.35	5.4
840	.40	8.8
1200	.45	12.2
2040	.55	18.9
2700	.60	22.3
3120	.65	25.7
4020	.77	33.8
4440	.80	35.8
4980	.85	39.2
5100[a]	1.75	100.0

$k_1 = 1.02x10^{-4}$ sec.$^{-1}$

[a] At 25°

TABLE XCIII

RUN 47. ETHANOLYSIS OF $4.9x10^{-4}$ M. TRITYL CHLORIDE IN ETHANOL AT -63°

Time, sec.	0.0434M. $NaOC_2H_5$, ml.	HCl liberated, % of $4.9x10^{-4}$ M.
0	0.08	0.0
2040	.15	6.2
3300	.20	10.7
4020	.24	14.3
5280	.30	19.6
6780	.35	24.1
9540	.45	33.0
12060	.52	39.3
14160	.57	43.7
16440	.61	47.3
19080	.655	51.3
22020	.695	54.9
26580	.760	60.7
26700[a]	1.200	100.0

$k_1 = 3.73x10^{-5}$ sec.$^{-1}$

[a] At 25°

TABLE XCIV

RUN 48. ETHANOLYSIS OF 5.0×10^{-4} M. TRITYL CHLORIDE IN ETHANOL AT -59°

Time, sec.	0.0434M. $NaOC_2H_5$, ml.	HCl liberated, % of 5.0×10^{-4} M.
0	0.258	0.0
1080	.329	6.2
2460	.402	12.5
3360	.458	17.4
4420	.508	21.7
6300	.558	26.0
7140	.608	30.4
9000	.658	34.7
10500	.708	39.1
12420	.758	43.4
13680	.808	47.7
15060	.858	52.1
16200	.908	56.4
17820	.958	60.8
19500	1.008	65.1
19620[a]	1.152	100.0

$k_1 = 6.08\times10^{-5}$ sec.$^{-1}$

[a] At 25°

TABLE XCV

RUN 49. SOLVOLYSIS OF 6.0×10^{-4} M. TRITYL CHLORIDE IN 96.7% METHANOL - 3.3% WATER AT -61.0°

Time sec.	0.0434M. $NaOC_2H_5$, ml.	HCl liberated, % of 6.0×10^{-4} M.
0	0.390	0.0
18	.450	4.3
45	.607	15.6
52	.653	18.9
75	.700	22.3
90	.750	25.9
106	.798	29.4
128	.850	33.1
148	.904	37.0
165	.950	40.3
185	1.006	44.3
207	1.054	47.8
229	1.100	51.1
254	1.150	54.7
2520	1.780	100.0

$k_1 = 2.98\times10^{-3}$ sec.$^{-1}$

TABLE XCVI

RUN 50. SOLVOLYSIS OF 5.9×10^{-4} M. TRITYL CHLORIDE IN 96.7% METHANOL - 3.3% WATER AT -61.3°

Time, sec.	0.0434M. $NaOC_2H_5$, ml.	HCl liberated, % of 5.9×10^{-4} M.
0	0.250	0.0
46	.360	9.9
69	.400	13.5
95	.450	18.0
124	.506	23.1
153	.550	27.0
186	.600	31.5
226	.650	36.0
265	.700	40.0
310	.750	45.0
353	.800	49.5
397	.850	54.1
446	.900	58.6
497	.950	63.1
545	1.000	67.6
606	1.150	72.1
3000	1.360	100.0

$k_1 = 1.92\times10^{-3}$ sec.$^{-1}$

TABLE XCVII

RUN 51. SOLVOLYSIS OF 5.9×10^{-4} M. TRITYL CHLORIDE IN 96.7% METHANOL - 3.3% WATER AT -62.8°

Time, sec.	0.0434M. $NaOC_2H_5$, ml.	HCl liberated, % of 5.9×10^{-4} M.
0	0.030	0.0
60	.302	20.6
97	.353	24.5
125	.400	28.0
153	.450	31.8
183	.503	35.8
218	.553	39.6
254	.600	43.2
293	.652	47.1
335	.700	50.8
377	.750	54.6
422	.800	58.3
470	.850	62.1
523	.901	66.0
579	.950	69.7
636	1.000	73.5
697	1.050	77.3
769	1.103	81.3
824	1.150	84.8
907	1.200	88.6
6300	1.350	100.0

$k_1 = 1.93 \times 10^{-3}$ sec.$^{-1}$

TABLE XCVIII

RUN 54. SOLVOLYSIS OF 2.7×10^{-4} M. TRITYL CHLORIDE IN 96.7% METHANOL - 3.3% WATER AT -61.8°

Time, sec.	0.0434M. $NaOC_2H_5$, ml.	HCl liberated, % of 2.7×10^{-4} M.
0	0.150	0.0
70	.200	10.7
125	.229	16.9
188	.260	23.6
253	.290	30.0
323	.320	36.4
390	.350	42.8
570	.400	53.5
703	.430	60.0
847	.460	66.4
1030	.490	72.8
1150[a]	.617	100

$k_1 = 1.25\times10^{-3}$ sec.$^{-1}$

[a] At 25°

TABLE XCIX

RUN 55. SOLVOLYSIS OF 4.9×10^{-4} M. TRITYL CHLORIDE IN 96.7% METHANOL - 3.3% WATER AT -62.7°

Time, sec.	0.0434M. $NaOC_2H_5$, ml.	HCl liberated, % of 4.9×10^{-4} M.
0	0.160	0.0
21	.200	3.5
45	.250	7.9
75	.300	12.3
103	.350	16.7
133	.400	21.1
353	.800	56.1
503	.880	63.2
558	.920	66.7
648	.970	71.1
778	1.050	78.1
875	1.100	82.5
998	1.150	86.8
1153	1.200	91.2
1275[a]	1.300	100

$k_1 = 2.02\times10^{-3}$ sec.$^{-1}$

[a] At 25°

TABLE C

RUN 56. METHANOLYSIS OF 6.2×10^{-4} M. TRITYL CHLORIDE IN METHANOL AT -63.1°

Time, sec.	0.0434M. $NaOC_2H_5$, ml.	HCl liberated, % of 6.2×10^{-4} M.
0	0.100	0.0
37	.150	3.5
85	.200	7.0
238	.250	10.5
197	.300	13.9
261	.350	17.4
322	.400	20.9
394	.450	24.4
467	.500	27.9
545	.550	31.4
629	.600	34.8
717	.650	38.3
810	.700	41.8
909	.750	45.3
1022	.800	48.8
1132	.850	52.3
1247	.900	55.7
1372	.950	59.2
1497	1.000	62.7
1647	1.050	66.2
1802	1.100	69.7
2037	1.150	73.2
2227	1.203	76.9
2467	1.250	80.1
3500[a]	1.535	100

$$k_1 = 6.0 \times 10^{-5} \text{ sec.}^{-1}$$

[a] At 25°

TABLE CI

RUN 57. METHANOLYSIS OF 2.6×10^{-4} M. TRITYL CHLORIDE IN METHANOL AT -63.3°

Time, sec.	0.0434M. NaOEt, ml.	HCl liberated % of 2.6×10^{-4} M.
0	0.102	0.0
128	.152	9.6
210	.182	15.4
320	.213	21.3
415	.242	26.9
530	.272	32.7
645	.302	38.5
770	.332	44.2
930	.362	50.0
1085	.394	56.2
1265	.422	61.5
1495	.453	67.5
1745	.482	73.1
2050	.512	78.8
1470	.543	84.8
2970	.572	90.4
5040	.622	100

$$k_1 = 7.6\times10^{-4} \text{ sec.}^{-1}$$

Appendix B

SOLVOLYSIS OF t-BUTYL CHLORIDE

As noted above (p. 8) several attempts have been made[15-18] to correlate both the rates and the products of the solvolysis of t-butyl chloride in ethanol - water and methanol - water mixtures. These attempted correlations have all assumed that the rate is proportional to the mole fraction of t-butyl chloride. It has been pointed out[20] that use of such an assumption for n-butyl bromide does not permit satisfactory correlation of rates and products in similar ethanol - water and methanol - water mixtures. Such a correlation may be made[19] for n-butyl bromide if the rate is taken to be proportional to the molarity of t-butyl chloride and the vapor pressures of alcohol and water.

The most nearly successful correlation for t-butyl chloride is that of Winstein.[17] This was based on a one-step termolecular mechanism for solvolyses. Using such a mechanism the measured rate was expressed as

$$\text{Rate} = k_m c_{RCl} = (k_{ww} p_w^2 + k_c p_w p_a + k_{aa} p_a^2) a_{RCl} \qquad (16)$$

$$k_m = (k_{ww} p_w^2 + k_c p_w p_a + k_{aa} p_a^2) f_{RCl}$$

where k_m is the measured first-order rate constant, c_{RCl} the concentration of t-butyl chloride, k_{ww} is the rate constant for an assumed third-order reaction involving two water molecules and a t-butyl chloride molecule, k_c is the rate constant for an assumed reaction involving one water molecule, one alcohol molecule, and one t-butyl chloride molecule, k_{aa} is the rate constant for an assumed reaction of two alcohol molecules and one t-butyl chloride molecule, p_w and p_a are the vapor pressures of water and alcohol respectively, a_{RCl} is the activity of t-butyl chloride, and f_{RCl} is the activity coefficient of t-butyl chloride (determined from the vapor pressure). The first term of equation 16 was assumed to produce alcohol and the third term ether. The middle term could produce either alcohol or ether, since both a water and an alcohol molecule are involved. The ratio of alcohol to ether formed from this term was adjusted so that the total proportions of ether and alcohol were in agreement with those observed. This essentially introduces a second disposable parameter.

The above procedure is not the only possible one. The middle term of equation 16 can be divided on a more rational basis. The most reasonable mechanism involving two solvent molecules assigns a nucleophilic role to one and an electrophilic role to the other. Then k_c may be divided into one term involving a nucleophilic water molecule and an electrophilic alcohol molecule, (k_{wa}).and another term involving nucleophilic alcohol molecule and an electrophilic water molecule (k_{aw}). Now k_{wa} and k_{aw} may be evaluated by considering that the relative nucleophilicity of an alcohol or water molecule should be nearly independent of what electrophilic agent is present, so long as that electrophilic agent is constant. This condition is expressed in equation 18.

If the rate is assumed to be proportional to the mole fraction of t-butyl chloride and the vapor pressures of ethanol and water, both rates and products may be correlated with some success (Tables CII and CIII).

Equation 17 and 18 may be solved for k_{aw} and k_{wa} in terms

$$k_c = k_{wa} + k_{aw} \qquad (17)$$

$$\frac{k_{aw}}{k_{ww}} = \frac{k_{aa}}{k_{wa}} \qquad (18)$$

of k_{aa}, k_{ww}, and k_c. These three rate constants may be evaluated from the kinetic data in acetone - water, dioxane -

$$k_{aw} = \frac{k_c + \sqrt{k_c^2 - 4\,k_{aa}k_{ww}}}{2} \qquad (19)$$

$$k_{wa} = k_c - k_{aw}$$

water, ethanol - water, and methanol - water mixtures.

If the nucleophilic species involved in the transition state is the one which ultimately becomes bonded to the central carbon, then the proportions of alcohol and ether in the product may be calculated from k_{aw}, k_{aa}, k_{ww}, and k_{wa}. In methanol - water mixtures (using the same k_{ww})

TABLE CII

RATE CONSTANTS FOR SOLVOLYSIS OF t-BUTYL CHLORIDE IN ETHANOL - WATER MIXTURES AT 25.0°

Water, mole%	p_w, mm.	p_a, mm.	$10^3 \times k_m$, hr.$^{-1}$(calcd.)	$10^3 \times k_m$, hr.$^{-1}$ (obsd.)
0.0	0.0	59.0	0.349	0.349
26.2	11.5	45.5	6.54	6.16
44.8	16.6	38.4	38.3	32.9
68.4	19.2	31.4	453.	453.
76.4	19.9	28.6	1420.	1320.
82.9	20.5	25.4	4690.	4660.

$k_{aa} = 9.18 \times 10^{-11}$ mm.$^{-2}$ hr.$^{-1}$
$k_{ww} = 1.52 \times 10^{-8}$ mm.$^{-2}$ hr.$^{-1}$
$k_{wa} = 5.15 \times 10^{-10}$ mm.$^{-2}$ hr.$^{-1}$
$k_{aw} = 2.70 \times 10^{-9}$ mm.$^{-2}$ hr.$^{-1}$

TABLE CIII

PRODUCT COMPOSITION FROM SOLVOLYSIS OF t-BUTYL CHLORIDE IN ETHANOL - WATER MIXTURES AT 25.0° USING THE DATA OF TABLE CII

Water, mole %	Ether, % (Calcd.)	Ether, % (Obsd.)
26.4	42	53
44.7	29	33
68.3	23	18

k_{aw} and k_{wa} are found to be complex conjugates according to equation 19. In order to avoid this difficulty, the calculated rate in pure methanol would have to be reduced to less than one-fourth its observed value.

If the rate is assumed to be proportional to the mole fractions of ethanol and water (instead of the vapor pressures), fair correlations of both rates and products may be made (Tables CIV and CV). A somewhat better correlation of rates and poorer correlation of products may be made in methanol - water mixtures (Tables CVI and CVII).

TABLE CIV

RATE CONSTANTS FOR SOLVOLYSIS OF t-BUTYL CHLORIDE IN ETHANOL - WATER MIXTURES AT 25°

Water, mole%	$10^3 \times k_m$, hr.$^{-1}$ (calcd.)	$10^3 \times k_m$, hr.$^{-1}$ (obsd.).
0.0	0.409	0.349
26.2	3.99	6.16
44.8	25.7	32.9
68.4	435.	453.
76.4	1560.	1320.
82.9	5520.	4660.

$k_{ww} = 1.25\times10^{-5}$ hr.$^{-1}$
$k_{aa} = 3.75\times10^{-7}$ hr.$^{-1}$
$k_{wa} = 7.8\times10^{-7}$ hr.$^{-1}$
$k_{aw} = 6.00\times10^{-6}$ hr.$^{-1}$

TABLE CV

PRODUCT COMPOSITION FROM SOLVOLYSIS OF t-BUTYL CHLORIDE IN ETHANOL - WATER MIXTURES AT 25° USING THE DATA OF TABLE CIV

Water, mole %	Ether, % (Calcd.)	Ether, % (obsd.)
26.4	58	53
44.7	37	33
68.3	18	18

TABLE CVI

RATE CONSTANTS FOR SOLVOLYSIS OF t-BUTYL CHLORIDE IN METHANOL - WATER MIXTURES AT 25.0°

Water, mole %	$10^3 \times k_m$, $hr.^{-1}$ (calcd.)	$10^3 \times k_m$, $hr.^{-1}$ (obsd.)
0.0	2.40	2.92
7.0	7.24	6.24
17.5	17.1	15.4
23.0	27.7	25.4
28.2	43.0	40.7
34.6	76.6	75.4
38.3	116.	110.
43.2	186.	188.
49.7	370.	347.

$k_{ww} = 12.5 \times 10^{-6}$ $hr.^{-1}$
$k_{aa} = 3.00 \times 10^{-6}$ $hr.^{-1}$
$k_{wa} = 6.12 \times 10^{-6}$ $hr.^{-1}$
$k_{aw} = 6.12 \times 10^{-6}$ $hr.^{-1}$

TABLE CVII

PRODUCT COMPOSITION FROM SOLVOLYSIS OF t-BUTYL CHLORIDE IN METHANOL - WATER MIXTURES AT 25.0° USING THE DATA IN TABLE CVI

Water, mole %	Ether, % (calcd.)	Ether, % (obsd.)
16.4	71	83
28.4	56	68
49.0	33	40

TABLE CVIII

RATE CONSTANTS FOR SOLVOLYSIS OF t-BUTYL CHLORIDE IN 83.2 MOLE % WATER - 16.8 MOLE % DIOXANE AT 25.0°

Source of k_{ww}	$10^3 \times k_m$, $hr.^{-1}$ (calcd.)	$10^3 \times k_m$, $hr.^{-1}$ (obsd.)
Table CII	570	644
Table CIV	836	644

TABLE CIX

RATE CONSTANTS FOR SOLVOLYSIS OF t-BUTYL CHLORIDE IN 50.3 MOLE % WATER - 49.7 MOLE % ACETONE AT 25.0°

Source of k_{ww}	$10^3 \times k_m$, $hr.^{-1}$ (calcd.)	$10^3 \times k_m$, $hr.^{-1}$ (obsd.)
Table CII	7.96	6.90
Table CIV	5.23	6.90

The assumption that the rate is proportional to the molarity of water fails because the rates in dioxane - water and acetone - water mixtures are not compatible with such a treatment. The k_{ww} calculated from 83.2 mole % water - 16.8 mole % dioxane is 8.33×10^{-3} $M.^{-2}$ $hr.^{-1}$ The k_{ww} calculated from 50.3 mole % water - 49.7 mole % acetone is 33.3×10^{-3} $M.^{-2}$ $hr.^{-1}$

If the rate is assumed to be proportional to the molarity of t-butyl chloride (as was done for n-butyl bromide[19]) and the mole fractions of alcohol and water, then a good fit may be obtained for both rates and products in both methanol - water and ethanol - water mixtures (Tables CX - CXIII). Rates in the dioxane - water and acetone - water mixtures are also correlated fairly well (Table CXIV). The justification for using molarities of t-butyl chloride and mole fractions of water and alcohol is not apparent. It is therefore questionable whether any significance is to be attached to these results.

TABLE CX

RATE CONSTANTS FOR SOLVOLYSIS OF t-BUTYL CHLORIDE IN ETHANOL - WATER MIXTURES AT 25.0°

Water, mole %	$10^3 \times k_m$, hr.$^{-1}$ (calcd.)	$10^3 \times k_m$, hr.$^{-1}$ (obsd.)
0.0	0,349	0.349
26.2	5.63	6.16
44.8	31.7	32.9
68.4	393.	453.
76.4	1320,	1320.
82.9	4220.	4660.

$k_{ww} = 4.00 \times 10^{-4}$ hr.$^{-1}$
$k_{aa} = 5.46 \times 10^{-6}$ hr.$^{-1}$
$k_{wa} = 1.4 \times 10^{-5}$ hr.$^{-1}$
$k_{aw} = 1.96 \times 10^{-4}$ hr.$^{-1}$

TABLE CXI

PRODUCT COMPOSITIONS FROM SOLVOLYSIS OF t-BUTYL CHLORIDE IN ETHANOL - WATER MIXTURES AT 25.0° USING THE DATA OF TABLE CX

Water, mole %	Ether, % (calcd.)	Ether, % (obsd.)
26.2	57.4	53
44.8	37.3	33
68.4	18.4	18

TABLE CXII

RATE CONSTANTS FOR SOLVOLYSIS OF t-BUTYL CHLORIDE IN METHANOL - WATER MIXTURES AT 25.0°

Water, mole %	$10^3 \times k_m$, $hr.^{-1}$ (calcd.)	$10^3 \times k_m$, $hr.^{-1}$ (obsd.)
0.0	2.51	2.92
7.0	7.62	6.24
17.5	17.9	15.4
23.0	28.1	25.4
28.2	42.9	40.7
34.6	74.1	75.4
38.3	110.	110.
43.2	172.	188.
49.7	326.	347.

$k_{aa} = 7.8 \times 10^{-5}\ hr.^{-1}$

$k_{ww} = 4.00 \times 10^{-4}\ hr.^{-1}$

$k_{aw} = 2.79 \times 10^{-4}\ hr.^{-1}$

$k_{wa} = 1.12 \times 10^{-4}\ hr.^{-1}$

TABLE CXIII

PRODUCT COMPOSITIONS FROM SOLVOLYSIS OF t-BUTYL CHLORIDE IN METHANOL - WATER MIXTURES AT 25.0° USING THE DATA OF TABLE CXII

Water, mole %	Ether, % (calcd.)	Ether, % (obsd.)
16.4	80.6	83
28.4	66.9	68
49.0	42.2	40

TABLE CXIV

RATE CONSTANTS FOR SOLVOLYSIS OF t-BUTYL CHLORIDE IN ACETONE - WATER AND DIOXANE - WATER MIXTURES AT 25.0°

Solvent System	Water, mole %	$10^3 \times k_m$, $hr.^{-1}$ (calcd.)	$10^3 \times k_m$, $hr.^{-1}$ (obsd.)
dioxane-water	83.2	784	644
acetone-water	50.3	7.45	6.90

$k_{ww} = 4.00 \times 10^{-4}\ hr.^{-1}$

A similar treatment of the solvolyses of n-butyl bromide in ethanol - water and methanol - water mixtures gives somewhat less satisfactory results (Tables CXV - CXVIII).

TABLE CXV

RATE CONSTANTS FOR SOLVOLYSIS OF n-BUTYL BROMIDE IN METHANOL - WATER MIXTURES AT 59.4°

Water, mole %	$k_{m'-1}$ (calcd.)	$k_{m'-1}$ (obsd.)
0.0	3.8	3.8
14.1	7.0	7.3
26.3	11.6	11.6
30.8	12.2	13.9
48.3	23.7	24.2
60.1	36.9	36.4

$k_{aa} = 0.0805$ hr.$^{-1}$
$k_{ww} = 0.0702$ hr.$^{-1}$
$k_{aw} = 0.0945$ hr.$^{-1}$
$k_{wa} = 0.0615$

TABLE CXVI

PRODUCT COMPOSITIONS FROM SOLVOLYSIS OF n-BUTYL BROMIDE IN METHANOL - WATER MIXTURES AT 59.4°

Water, mole %	Ether, % (calcd.)	Ether, % (obsd.)
14.1	88.8	88
26.3	78.6	74
30.8	74.6	72
48.3	58.4	61
60.1	46.4	51

TABLE CXVII

RATE CONSTANTS FOR SOLVOLYSIS OF n-BUTYL BROMIDE IN ETHANOL - WATER MIXTURES AT 75.1°

Water, mole %	$k_{m}'^{-1}$ (ca.cd.)	$k_{m}'^{-1}$ (obsd.)
0.0	8.0	7.8
25.8	22.6	24.8
56.2	56.8	56.7
73.7	116.4	110.8

$k_{aa} = 0.145$ hr.$^{-1}$
$k_{ww} = 0.200$ hr.$^{-1}$
$k_{aw} = 0.180$ hr.$^{-1}$
$k_{wa} = 0.164$ hr.$^{-1}$

TABLE CXVIII

PRODUCT COMPOSITIONS FROM SOLVOLYSIS OF n-BUTYL BROMIDE IN ETHANOL - WATER MIXTURES AT 75.1°

Water, mole %	Ether, % (Calcd.)	Ether, % (obsd.)
25.8	71.9	63
56.2	41.0	50
73.7	24.2	35

If the rate is taken as proportional to the molarity of t-butyl chloride, then it is not satisfactory to assume that it is proportional to either molarities or vapor pressures of alcohol and water. In both cases, assumed rate constants which fit the rates give very bad fits of the product compositions.

Significance. The experimental error in k_m may be as great as 25% of the value, and the experimental error in the composition of the product is three % absolute, i.e., 53 ± 3%. Thus the correlations obtained above are neither so good nor so poor as to remove all doubts regarding their significance. Probably all that can be safely concluded is that the arguments previously advanced on the grounds that no correlation was possible are on much less sure ground than formerly supposed. It had been argued that since product composition was not connected with the rate of the reaction, the product must be determined in a step subsequent to the rate-determining one. There is other evidence to support this hypothesis[6], but it appears that the argument based on the lack of relation between products and rates in these solvolyses must be viewed with suspicion.

Some support is apparent for the assumption on p. 43 that the nucleophilicities of water and ethanol are much more similar than the electrophilicities. The average value of k^{wa}/k_{aa} in Tables CIV and CX is only 2.32. The corresponding average ratio of k_{wa}/k_{ww} is 22.3

Appendix C

The Program Used for Whirlwind I

A program is a sequence of actions by which the computer (Whirlwind I) handles a problem. This sequence of operations is prepared in coded form by the programmer, converted to another code on punched tape, and fed into the computer. It is necessary only to know the code used by the programmer. An abbreviated table of the coded instructions used in this program is given below. For further information see "Programming for Whirlwind I" by Hrand Saxenian, and "Whirlwind I, Programmer's Manual" by C. W. Adams. Copies may be obtained on loan from C. W. Adams, Barta Bldg., M. I. T.

Whirlwind I uses a binary number system; e.g., 2 is expressed as 10, 3 as 11, 4 as 100, 5 as 101, etc. The computer handles 16 binary digits, but the last one on the left denotes the sign of the number. The convention has been established that all numbers shall be less than unity. Thus the range of numbers handled by the computer is from -1 to -1, with the added condition that the absolute magnitude of the number be either zero or equal to or greater than 2^{-15}. A method of extending this range is indicated below.

The "Accumulator" is a special storage register in which numbers are placed so that arithmetic operations may be performed on them. It is referred to as AC.

The "B-Register" is referred to as BR. It is used in two ways. First, the quotient from a division is left in BR. Second, it may be considered as an extension to the right of the AC; i.e., digits in excess of 15 from a multiplication may be retained in BR; further, after the contents of AC is shifted right (the binary point shifted left), BR contains that part of the original contents of AC which has been shifted <u>out</u> of AC.

TABLE CXIX

SHORT ORDER CODE TO WHIRLWIND I

Order[a]	Function
ca x	Clear AC and BR and place contents of register x in AC.
cs x	Clear AC and BR and place complement of contents of register x in AC.
ad x	Add contents of register x to contents of AC and leave result in AC.
su x	Subtract contents of register x from contents of AC and leave result in AC.
mr x	Multiply contents of accumulator by contents of register x, round off to 15 binary digits, and leave the product in AC.
cm x	Clear AC and BR and place magnitude of contents of register x in AC.
dv x	Divide contents of AC by contents of register x and leave quotient in BR. This order is usually followed by sl 15, which places the quotient in the accumulator.
sl n	Multiply the contents of AC and BR by 2^n. Round off result to 15 binary digits and leave it in AC. Clear BR.
sr* n	Multiply the contents of AC and BR by 2^{-n}. Store the result in AC and BR.
ao x	Add 1×2^{-15} to the contents of register x. Store the result in AC and register x.
ex x	Transfer the contents of AC to register x and transfer contents of register x to AC.
ts x	Transfer contents of AC to register x, discarding previous contents of register x.
td x	Transfer contents of the last 11 rightmost digits of AC to register x, discarding previous contents of the last 11 digits of register x.

TABLE CXIX (Cont.)

Order[a]	Function
sp x	Transfer control to register x, i.e., take the next order from register x.
cp x	If contents of AC is negative, treat as sp x; if positive, disregard this order and proceed to the next order. A zero in the accumulator as the result of an addition or subtraction is a negative number for the purposes of a cp order.
rs o	Stops computer if the operator has not previously thrown a toggle switch.
qp 100	Punch out on paper tape the contents of the rightmost 6 digits of the accumulator.
qp 1100	Feed out paper tape.
qp 220	Carriage return for automatic typewriter.
ta x	Transfer the address of the register following the last sp order to register x.
cl n	Clear BR. Put contents of leftmost n digits of AC in rightmost n digits of BR. Shift the rest of the AC n digits to the left. Put contents of leftmost n digits of BR in AC.

[a] x = a positive integer

n = a positive integer

Greater accuracy may be obtained by use of an "interpretive subroutine". In the interpretive subroutine used in this program any real number, N, is expressed as a signed 24-binary-digit fraction, x, and a signed 6-binary-digit integer, y, provided N is either zero or between 2^{63} and 2^{-63}. The numbers x and y are chosen in such a way that $N = x2^{y}$ within 0.000006%. This is equivalent to about 7 significant decimal digits. An additional advantage of this interpretive routine is that ordinarily no scale factoring is necessary to prevent occurrence of numbers that are too large or too small to be handled by the computer. This interpretive subroutine is known as the 24, 6, 0 subroutine, the floating-point subroutine, or Whirlwind I Library Subroutine Number PA 2.2. Not all orders in the program need to be interpreted by the subroutine. The order "sp ax" signifies that all orders following it are to be interpreted by the subroutine. The next "sp ax" order cancels the previous one, indicating that the orders following it are not to be interpreted by the subroutine.

All addresses in this program are octal numbers. A p before a number indicates that it is a positive decimal number and that the factor 2^{-15} is to be understood. An n indicates that it is a negative decimal number with the factor 2^{-15} understood. Numbers preceded by a plus or minus sign are decimal numbers. Numbers written as a signed number followed by a / and another signed number are to be used in the interpretive routine. A decimal number $N = a \times 10^b$ is represented as a/b, where a and b are both decimal numbers, and $1.0 > a \geqq 0.1$, and b is a positive or negative integer.

The program used in Whirlwind I is given below. Instructions 40-307 are on a "parameter tape," P1189-11. All other instructions are on T1189-15 and P1189-13. The tapes are read in this order: the 24,6,0 conversion program, P1189-11, T1189-15, P1189-13, T957-5 (the interpretive subroutine and the interpretive print subroutine).

The program starts in 324. The only automatic way to stop is by the rs 0 in 704. This register is entered only after each print out.

```
40/ + .1/ -1       40-60 starting n values, not including
41/ + .0/ -9             80% ethanol.
42/ + .0/ -9
43/+ .0/ -9
44/ + .0/ -9
45/ - .1/ -0
46/ - .15/ -0
47/ - .1/ -0
50/ + .45/ -0
51/ + .3/ -0
52/ + .3/ -0
53/ + .9/ -1
54/ - .2/ -1
55/ - .11/ -1
56/ - .227/ -1
57/ - .72/ -0
60/ - .7/ -0
61/ - .56/ -0      61-101 starting e values, not including
62/ - .2/ -0             80% ethanol.
63/ + .28/ -0
64/ + .39/ -0
65/ + .55/ -0
66/- .1/ -0
67/ + .1/ -0
70/ + .42/ -0
71/ -.134/ -1
72/ - .75/ -0
73/ - .55/ -0
74/ + .15/ -0
75/ + .1/ -1
76/ + .9/ -0
77/ + .207/ -1
100/ + .16/ -1
101/ + .156/ -1
102/ + .0/ -9      102-125 to contain s values
103/ + .0/ -9
104/ + .0/ -9
105/ + .0/ -9
106/ + .0/ -9
107/ + .0/ -9
110/ + .0/ -9
111/ + .0/ -9
112/ + .0/ -9
113/ + .0/ -9
114/ + .0/ -9
115/ + .0/ -9
116/ + .0/ -9
117/ + .0/ -9
120/ + .0/ -9
```

```
121/   .0/ -9
122/   .0/ -9
123/   .0/ -9
124/   .0/ -9
125/   .0/ -9
126/   .0/ -9     126-151 to contain s' values
127/   .0/ -9
130/   .0/ -9
131/   .0/ -9
132/   .0/ -9
133/   .0/ -9
134/   .0/ -9
135/   .0/ -9
136/   .0/ -9
137/   .0/ -9
140/   .0/ -9
141/   .0/ -9
142/   .0/ -9
143/   .0/ -9
144/   .0/ -9
145/   .0/ -9
146/   .0/ -9
147/   .0/ -9
150/   .0/ -9
151/   .0 / -9
152/   .0/ -9     to contain Zn or Zs
153/   .0/ -9      "     "    n^2  "  s^2
154/   .0/ -9      "     "    ne   "  ss'
155/   .0/ -9      "     "    e^2  "  s'^2
156/   .0/ -9      "     "    Ze   "  Zs'
157/   .0/ -9     temporary storage
160/   .0/ -9        "        "
161/   .1/  2     No longer used
162-307           Second half of double length numbers.
310/ pl           n,e or s,s' code.
311/ ca 126       Used for resetting.
312/ pl             "   "      "
313/ p 32           "   "      "
314/ n 49         Used to count iterations.
315/ p 49         Used for resetting.
316/ p 19           "   "       "
317/ p 16           "   "       "
320/ p 106          "   ".      "
321/ n 19         Counter for end of an iteration.
322/ p 0             "     "   "  "  a row.
323/ n 105           "     "   "  "  a row.
324/ cs 317      reset counter for end of a row
325/ ts 322
```

```
326/ ca 672    Is the n,e code as large as the column code
                    for the log (k/ko)?
327/ su 310    If it is, go to 350; if not go on
330/ cp 350
331/ ao 322    Have all n's and e's been tried?
332/ cp 334    If yes, go to 412 and solve equations.
333/ sp 412    If no, go on
334/ ao 366    Reset 366, 367, 372, 373, 404, 357, 362,
                and 363 for the next n and e.
335/ ao 367
336/ ao 372
337/ ao 373
340/ ao 404
341/ ao 357
342/ ao 362
343/ ao 363
344/ ca 310    Reset 310 with code for next n and e
345/ ad 312
346/ ts 310
347/ sp 326    Go back and try the next n and e
350/ ad 661    Is this n and e code larger than the column
                 code for log (k/ko)? I no go on.
351/ cp 331
352/ ca o      Put log (k/ko) in mra.
353/ ts 4ax
354/ ca 767
355/ ts 2ax
356/ spax      Go into interpretive subroutine
357/ mr 40     Multiply log (k/ko) by n, add to previous
                 product, and store in 152
360/ ad 152
361/ ts 152
362/ ca 40     Square n and store with previous n^2 in 153.
363/ mr 40
364/ ad 153
365/ ts 153
366/ ca 40     Multiply n by e and store with previous ne in 154
367/ mr 61
370/ ad 154
371/ ts 154
372/ ca 61     Square e and store with previous e^2 in 155
373/ mr 61
374/ ad 155
375/ ts 155
376/ spax      Go out of interpretive subroutine
377/ ca o      Put log (k/ko) in the mra
400/ ts 4ax
401/ ca 767
402/ ts 2ax
```

403/ spax	Go into the interpretive subroutine
404/ mr 61	Multiply log (k/k_0) by e and store with previous products in 156.
405/ ad 156	
406/ ts 156	
407/ spax	Go out of interpretive subroutine.
410/ ao 322	Has this row been finished?
411/ cp 652	If yes, go on and solve equations.
412/ spax	Go into interpretive subroutine
413/ ca 154	Compute $\frac{(\sum ne)^2}{\sum e^2} - \sum n^2$ and store in 157
414/ dv 155	
415/ mr 154	
416/ su 153	
417/ ts 157	
420/ ca 154	Compute $\dfrac{\frac{\sum ne}{\sum e^2} \times \sum Ze - \sum Zn}{\frac{(\sum ne)^2}{\sum e^2} - \sum n^2} = s$
421/ dv 155	
422/ mr 156	
423/ su 152	
424/ dv 157	
425/ ts 102	Transfer s to proper place.
426/ sp 431	
427/ ad 102	No longer used.
430/ ts 102	" " "
431/ mr 153	431-435 Compute $\frac{\sum Zn - s\sum n^2}{\sum ne} = s'$
432/ ts 157	
433/ ca 152	
434/ su 157	
435/ dv 154	
436/ ts 126	Store s' in proper place.
437/ sp 442	
440/ ad 126	No longer used.
441/ ts 126	" " "
442/ ca 160	442-447 Reset 152-156 to zero.
443/ ts 152	
444/ ts 153	
445/ ts 154	
446/ ts 155	
447/ ts 156	
450/ spax	Go out of interpretive subroutine.
451/ ao 425	451-456 Reset 425, 427, 430, 436, 440, 441, for the next s and s'

```
452/ ao 427
453/ ao 430
454/ ao 436
455/ ao 440
456/ ao 441
457/ cs 320    457-460 Reset 323
460/ ts 323
461/ ao 321    Is this iteration complete?
462/ cp 615    If no, go to 615 and start next row.
463/ cs 317    463-464 Reset 321.
464/ ts 321
465/ ao 314    Have 50 iterations been done since last punchout?
466/ cp 472    If no, go to 472.
467/ cs 315    Reset 314.
470/ ts 314
471/ sp 745    Go to punchout routine
472/ ca 721    472-474 Reset 354 and 401 to the first log (k/ko).
473/ ts 354
474/ ts 401
475/ ao 723    475-476 Display number of iterations completed
476/ ts 27         in lights on the panel
477/ ca 516    477-501 Reset 633 and 646 to the first
500/ ts 633        log (k/ko) code.
501/ ts 646
502/ ca 316    502-504 Interchange contents of 316 and 317.
503/ ex 317
504/ ts 316
505/ ca 623    505-512 Reset 650, 326, 625, 635, 623, for the
506/ td 650         next iteration.
507/ ex 326
510/ td 625
511/ td 635
512/ td 623
513/ ca 634    513-515 Interchange contents of 634 and 637.
514/ ex 647
515/ ts 634
516/ ca 1141   516-522 Put first row code in 673 and first
517/ sr* 12         column code in 672.
520/ ts 672
521/ sl 17
522/ ts 673
523/ ca 671    523-525 Interchange contents of 671 and 667.
524/ ex 667
525/ ts 671
526/ td 425    526-530 Reset 425, 427, 430
527/ td 427
530/ td 430
531/ ca 311    531-536 Reset 311, 670, 436, 440, 441 for
532/ ex 670        next iteration
533/ ts 311
```

```
534/ td 436
535/ td 440
536/ td 441
537/ ca 312        537-541 Interchange contents of 312 and 313.
540/ ex 313
541/ ts 312
542/ ao 323
543/ ao 660
544/ sp 600
545/ cs 661        545-574 A proposed normalization procedure
546/ ts 660            which did not work for unknown reasons.
547/ spax              It is no longer used.
550/ ca 102
551/ dv 111
552/ ts 102
553/ spax
554/ ao 550
555/ ao 552
556/ ao 662
557/ cp 547
560/ ca 551
561/ ex 725
562/ ts 551
563/ cs 663
564/ ts 662
565/ ao 726
566/ cp 547
567/ ca 724
570/ td 550
571/ td 552
572/ cs 661
573/ ts 726
574/ sp 600
575/ n 3            Counter
576/ p 3            Used for resetting
577/ sp 324         Stored constant, not an instruction.
600/ ca 312         600-601 Reset 310 to first n, e or s, s' code.
601/ ts 310
602/ ca 667         602-606 Reset 357, 362, 363, 366 so the
603/ td 357             first s or n may be used.
604/ td 362
605/ td 363
606/ td 366
607/ ca 670          607-613 Reset 367, 372, 373, 404 so the
610/ td 367             first s' or e may be used.
611/ td 372
612/ td 373
613/ td 404
```

```
614/ sp 324
615/ ca 721
616/ ts 354     615-617 Reset 354 and 401 so the first log
617/ ts 401              (k/ko) may be used.
620/ ca 516     620-622 Reset 633 and 646 so the first log (k/ko)
621/ ts 633               code may be used.
622/ ts 646
623/ ca 673     623 - 625 Put code for next row (or column)
624/ ad 313               in 673 (or 672).
625/ ts 673
626/ ao 323     626-627 Have all log (k/ko) codes been tried?
627/ cp 633               If no, go to 633.
630/ ca 665     Reset 651 so that 600 will be entered.
631/ ts 651
632/ sp 412
633/ ca 1141    633-635 Is log (k/ko) row (or column) code
634/ sl 5                as large as the desired row (or column)
635/ su 673              code?
636/ cp 644     If yes, go to 644.
637/ ao 354     637-642 Put next log (k/ko) in 354 and 401, and
640/ ao 401              put next log (k/ko) code in 633 and 646.
641/ ao 633
642/ ao 646
643/ sp 626
644/ ad 661      644-645 Is log (k/ko) row (or column) code
645/ cp 637              larger than desired? If yes, go to 637.
646/ ca 1141
647/ sr* 12
650/ ts 672
651/ sp 600
652/ ca 666      652-653 Reset 651 so that 655 will be entered.
653/ ts 651
654/ sp 637
655/ ca 665      655-656 Reset 651 so that 600 will be entered.
656/ ts 651
657/ sp 334
660/ p 0
661/ p 1
662/ n 19        Counter in normalization routine.
663/ p 19        Used in resetting.
664/ ca 160      Stored constant, not an instruction.
665/ sp 600        "        "       "   "      "
666/ sp 655        "        "       "   "      "
667/ ca 40         "        "       "   "      "
670/ ca 61         "        "       "   "      "
671/ ca 102        "        "       "   "      "
672/ p 1           "        "       "   "      "
673/ p 32          "        "       "   "      "
674/ p 0         Temporary storage
675/ spax        Go into interpretive subroutine.
676/ ca 40       Put contents of 40 in AC.
```

```
677/ sp 1336      Go to print routine
700/ spax         Go out of interpretive subroutine.
701/ ao 676       Prepare to print the next number.
702/ su 664       Has contents of 161 been printed.
703/ cp 710       If no, go to 710.
704/ rs 0         Conditional stop.
705/ ca 722       705-706 Reset 676
706/ ts 676
707/ sp 472
710/ ao 717       710-711 Have 5 numbers been printed on this
711/ cp 675          line? If no, go to 675.
712/ ca 713       712-713 Return carriage of automatic typewriter.
713/ qp 220
714/ cs 720       714-715 Reset 717.
715/ ts 717
716/ sp 675
717/ n 4          Counter for carriage return.
720/ p 4          Used for resetting.
721/ ca 767       Stored constant, not an instruction.
722/ ca 40          "        "       "  "       "
723/ p 0            "        "       "  "       "
724/ ca 102         "        "       "  "       "
725/ dv 135         "        "       "  "       "
726/ n 1            "        "
727/ ca 225         "        "       not an instruction.
730/ ta 744       Transfer address to 744.
731/ ts 34
732/ cl 13        732-734 Print rightmost 5 digits of constants
733/ cl 25            of 34.
734/ qp 100
735/ ca 34        735-740 Print digits 6-10 of 34, counting
736/ cl 6             from the right.
737/ cl 25
740/ qp 100
741/ ca 34        741-743 Print leftmost 6 digits of 34.
742/ cl 26
743/ qp 100
744/ sp 0         Go to address set up by 730.
745/ cs 313       745-752 Feed out blank tape for beginning.
746/ ts 10
747/ ca 0
750/ qp 1100
751/ ao 10
752/ cp 747
753/ ca 722       753-755 Punch address of first number to be
754/td 760            punched and set up 760.
755/ sp 730
```

```
756/ ca 563     756-757 Punch out special character for
757/ qp 100        beginning
760/ ca 0       Put first number in AC.
761/ sp 730     Punch out.
762/ ao 760     Put address of next number in 760.
763/ su 727     Have all desired numbers been punched?
764/ cp 756     If no, go to 756.
765/ ca 577     765, 766, 1313, If yes, punch address at
766/ sp 1313      which computer should start.
767/  -.1520     767-1140 0.1 log (k/k_o), not including data
770/  -.0550      for 80% ethanol.
771/  -.0070
772/  -.2580
773/  -.1380
774/  -.0730
775/  +.0980
776/  -.2370
777/  +.2600
1000/  +.1600
1001/  +.2110
1002/  +.5910
1003/  -.0850
1004/  +.0740
1005/  -.0260
1006/  -.0780
1007/  -.0290
1010/  -.2090
1011/  -.1420
1012/  +.1110
1013/  -.0740
1014/  -.1130
1015/  -.0700
1016/  -.0190
1017/  +.0270
1020/  -.0360
1021/  -.0210
1022/  +.0460
1023/  -.1140
1024/  -.1800
1025/  -.0710
1026/  +.1020
1027/  -.1460
1030/  -.0520
1031/  +.0150
1032/  -.1980
```

1033/	-.0730
1034/	+.1130
1035/	+.1590
1036/	+.2140
1037/	-.1060
1040/	-.0730
1041/	+.1020
1042/	-.0680
1043/	+.1290
1044/	+.3550
1045/	-.1640
1046/	-.3290
1047/	+.2070
1050/	+.1500
1051/	-.0770
1052/	+.0580
1053/	+.1120
1054/	-.1150
1055/	-.0580
1056/	+.0370
1057/	-.0290
1060/	-.2390
1061/	-.1020
1062/	+.0860
1063/	+.1990
1064/	-.0140
1065/	-.0810
1066/	-.0370
1067/	-.1390
1070/	-.3080
1071/	-.1020
1072/	+.0700
1073/	-.0460
1074/	-.0970
1075/	-.0750
1076/	+.0410
1077/	+.0220
1100/	+.0680
1101/	-.1780
1102/	-.2440
1103/	-.1360
1104/	-.2050
1105/	-.1620
1106/	-.1290
1107/	-.0630
1110/	-.0700
1111/	-.2080
1112/	+.2390
1113/	+.0560
1114/	+.0030
1115/	+.0900
1116/	-.1560

```
1117/ +.0140
1120/ -.1700
1121/ +.2030
1122/ +.0110
1123/ +.1500
1124/ -.1200
1125/ +.0570
1126/ +.1760
1127/ +.1250
1130/ +.0830
1131/ +.0380
1132/ +.0970
1133/ +.0560
1134/ -.0300
1135/ +.0400
1136/ -.0280
1137/ -.0050
1140/ +.0260
1141/ p 1025
1142/ p 2049
1143/ p 7169
1144/ p 9217
1145/ p 10241
1146/ p 11265
1147/ p 12289
1150/ p 14337
1151/ p 17409
1152/ p 4098
1153/ p 14338
1154/ p 17410
1155/ p 1027
1156/ p 4099
1157/ p 6147
1160/ p 1028
1161/ p 6148
1162/ p 14340
1163/ p 1029
1164/ p 4101
1165/ p 6149
1166/ p 14341
1167/ p 1030
1170/ p 2054
1171/ p 3078
1172/ p 6150
1173/ p 7174
1174/ p 8198
1175/ p 16390
1176/ p 1031
1177/ p 2055
```

1141-1312 code for the log (k/k_o) values in 767-1140. The code for each log (k/k_o) is obtained by assigning a number to each column and to each row. A multiple of 1024 is assigned to each column and a multiple of one to each row. For example, the entry in column one and row one has the code 1024 1 = 1025, and the entry in column 6 and row four has the code 6144 + 4 = 6148.

```
1200/ p 3079
1201/ p 9223
1202/ p 10247
1203/ p 11271
1204/ p 1032
1205/ p 2056
1206/ p 3080
1207/ p 4104
1210/ p 5128
1211/ p 6152
1212/ p 7176
1213/ p 8200
1214/ p 10248
1215/ p 12296
1216/ p 13320
1217/ p 14344
1220/ p 15368
1221/ p 16392
1222/ p 17416
1223/ p 1033
1224/ p 4105
1225/ p 13321
1226/ p 16393
1227/ p 1034
1230/ p 4106
1231/ p 6154
1232/ p 14346
1233/ p 1035
1234/ p 4107
1235/ p 13323
1236/ p 16395
1237/ p 1036
1240/ p 6156
1241/ p 14348
1242/ p 15372
1243/ p 1037
1244/ p 4109
1245/ p 6157
1246/ p 14349
1247/ p 1038
1250/ p 4110
1251/ p 12302
1252/ p 13326
1253/ p 16398
1254/ p 1039
1255/ p 6159
1256/ p 10255
1257/ p 14351
1260/ p 1040
```

```
1261/ p 6160
1262/ p 14352
1263/ p 15376
1264/ p 16400
1265/ p 3089
1266/ p 7185
1267/ p 8209
1270/ p 10257
1271/ p 12305
1272/ p 1042
1273/ p 5138
1274/ p 7186
1275/ p 8210
1276/ p 11282
1277/ p 12306
1300/ p 14354
1301/ p 5139
1302/ p 8211
1303/ p 12307
1304/ p 14355
1305/ p 5140
1306/ p 7188
1307/ p 8212
1310/ p 10260
1311/ p 11284
1312/ p 12308
1313/ sp 730
1314/ ca 607    1314-1315 Punch out final character.
1315/ qp 100
1316/ ao 575    1316-1317 Have four punchouts occurred
1317/ cp 472       since the last printout? If no, go to 472.
1320/ cs 576    1320-1322 If yes, reset 575 and go to print
1321/ ts 575       routine (675-716).
1322/ sp 675
```

APPENDIX D

SOME PROVISIONAL CONSTANTS

Table CXX lists values of s and s' for six compounds. Since data are available in only three solvents for these compounds, no check on the reliability of the values is possible. For this reason they must be considered provisional. It is of interest to note that s/s' is smaller for p-methoxybenzylmethylcarbinyl p-toluenesulfonate than for benzylmethylcarbinyl p-toluenesulfonate in agreement with earlier[49] qualitative observations that greater participation of the neighboring aryl group occurs with the substituted compound. Participation of a neighboring group is expected to lower s/s', since some of the nucleophilic driving force is now supplied by the neighboring group. The assertion[13] that no nucleophilic driving force will be required is highly doubtful, since a partial positive charge is created in the neighboring group (when it is initially neutral), and this fractional positive charge may well require nucleophilic solvation.

The influence of α-methyl groups is readily seen by comparing s/s' for isobutyl p-toluenesulfonate and neopentyl p-toluenesulfonate with that of ethyl p-toluene-

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(49) S. Winstein, M. Brown, K. C. Schreiber, and A. H. Schlesinger, J. Am. Chem. Soc., 74, 1140 (1952).

sulfonate (2.48).

The temperature is listed in Table CXX as 25° for the two anylmethylcarbinyl tosylates. Since part of the data is available at this temperature but part of the data is at 50°, a correction was necessary. This was done with the aid of the relation on page 51.

TABLE CXX

PROVISIONAL VALUES OF s AND s'

Compound	s	s'	s/s'	Temp., °C.	ref.
Methyl p-toluenesulfonate	0.575	0,192	3.00	75	36
Isobutyl p-toluenesulfonate	.599	.502	1.19	75	36
Benzylmethylcarbinyl p-toluenesulfonate	.769	.774	0.99	25	49
p-Methoxybenzylmethylcarbinyl p-toluenesulfonate	.686	.822	.84	25	49
Neopentyl p-toluenesulfonate	.441	.676	.65	75	36,52
-Methylallyl chloride	.378	.924	.41	25	20,50,51

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(50) W. G. Young and L. G. Andrews, J. Am. Chem. Soc., <u>66</u>, 421 (1944).

(51) S. Winstein and E. Grunwald, J. Am. Chem. Soc., <u>70</u>, 828 (1948).

(52). S. Winstein, B. Morse, E. Grunwald, K. C. Schreiber, and J. Corse, J. Am. Chem. Soc., <u>74</u>, 1113 (1952).

AUTOBIOGRAPHICAL NOTE

The author was born in Portland, Oregon on October 22, 1928, and received his early education in the public schools of that city. In September 1946 he entered the University of Chicago on a Pepsi Cola Scholarship, and in June 1948 received the Ph.B. degree. After one more year of study in the Department of Chemistry of that institution, he commenced graduate work in organic chemistry at the Massachusetts Institute of Technology in July 1949. He was a research assistant under an O.N.R. contract from that date until September 1951, when he was awarded an Atomic Energy Commission Predoctoral Fellowship, which he held for the rest of his graduate work. He is a member of Sigma Xi.