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

Rates of Solvolysis of Triphenylmethyl, *t*-Butyl and *n*-Butyl Halides[1]

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Rates of solvolysis of triphenylmethyl (trityl) fluoride in nine solvents are reported. Comparison of trityl fluoride, *t*-butyl chloride and *n*-butyl bromide makes it appear that *t*-butyl chloride is intermediate between the other two in its dependence of rate on type of solvent. It proves to be impossible quantitatively to correlate the behavior of all three compounds on the basis of a duality of mechanism, using simple two-parameter linear free energy relationships. However, the data are consistent with the assumption that there is a fairly smooth gradation in the character of the transition states over the series trityl, *t*-butyl, *n*-butyl, methyl, *p*-nitrobenzoyl with no fundamental change in type at any point.

In the last twenty years many attempts have been made to classify nucleophilic displacement reactions into mechanistic categories. The concept of a duality of mechanism involving "unimolecular" (S_N1) and "bimolecular" (S_N2) mechanisms has been popular.[2] There can be no argument about the experimental distinction between first- and second-order reactions, but there is serious doubt whether the currently accepted distinction between S_N1 and S_N2 "mechanisms" is sharp enough to be maintained. For example, when isopropyl bromide reacts with solvent molecules in alcohol solution by first-order kinetics, do part of the molecules react by an S_N1 mechanism and part by an S_N2 mechanism, or do they all react by the same mechanism? If they all react by the same mechanism, the current duality concept is false and misleading. However, one might then be able to use the terms in a useful new sense: a reaction might be described as going by an intermediate or hybrid mechanism having a certain fraction of "S_N1 character" (referring to the magnitude of the partial charge on carbon in the transition state) in the same way that the C–Br bond in the reactant, isopropyl bromide, is described as having a certain fraction of "ionic character."[3]

To help decide whether there are two fundamentally different types of transition state or whether the character of the transition state grades smoothly over the whole range from triphenylmethyl (trityl) to methyl or *p*-nitrobenzoyl halides or from acidic to basic reagents, we previously examined kinetic orders in an inert solvent[4] and the effect of structure of the halide and the reagents on Hammett's reaction constant (ρ).[5] No discontinuity was apparent. We have now made a study of rates of solvolysis of trityl fluoride in different solvents for comparison with similar data on *t*-butyl chloride and *n*-butyl bromide determined by previous workers, again to see whether there appear to be two classes, or whether there is a smooth gradation in behavior. Trityl fluoride was used instead of trityl chloride simply because the latter compound reacts at rates much too fast for convenient measurement.

On the duality concept we would have expected trityl fluoride to be similar in its rate-solvent dependence to *t*-butyl chloride, and *p*-nitrobenzoyl chloride or fluoride to be similar to *n*-butyl bromide. However, assuming that there is a smooth gradation in the character of the transition state, we predicted that *t*-butyl chloride would prove to be just intermediate in behavior between trityl fluoride and *n*-butyl bromide.

For comparing the solvolytic behavior of two compounds an equation proposed by Grunwald and Winstein is useful.[6] This is

$$\log (k/k^0) = mY \qquad (1)$$

where k is the first-order rate constant in any solvent, k^0 is the corresponding rate constant in a standard solvent (80% ethanol–20% water), m is a parameter characteristic of the alkyl halide or ester, and Y is a parameter characteristic of the solvent. Values of Y were determined for the different solvents by choosing *t*-butyl chloride as a standard compound for which m was taken as 1.00 at 25°. Rates of hydrolysis, alcoholysis, acetolysis and formolysis of the following compounds were well correlated by equation 1 and Y values based on *t*-butyl chloride in all the solvents studied[6]: *t*-butyl bromide, α-methylallyl chloride, neopentyl bromide, α-methylneopentyl *p*-bromobenzenesulfonate and *trans*-2-bromocyclohexyl *p*-bromobenzenesulfonate. Highly branched *t*-alkyl halides also fit.[7]

n-Butyl bromide shows a different behavior. We have found that if one chooses it as a standard, instead of *t*-butyl chloride, one can obtain a new set of Y values which will successfully correlate the available data on rates of solvolysis of ethyl bromide, ethyl *p*-toluenesulfonate, benzyl chloride and benzyl *p*-toluenesulfonate. However, these new Y values probably depend more on the nucleophilic reactivity of the solvents than on their electrophilic reactivity.

Equation 1 has been applied[6] to solvent mixtures as well as to pure solvents. Unfortunately its application to mixed solvents is theoretically slightly unsound: if it held rigorously for pure solvents it

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[1] We gratefully acknowledge support of this work by the Office of Naval Research, under ONR Contract N5ori-07838, Project NR-056-198 (now NR-055-198). For complete experimental data see R. B. Mosely, Ph.D. thesis, M.I.T., July, 1952.

[2] E. D. Hughes, *Trans. Faraday Soc.*, **37**, 603 (1941); *J. Chem. Soc.*, 968 (1946); C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, Chap. VII.

[3] It has been suggested that a distinction might be based on the success or lack of it achieved in trying to demonstrate a carbonium ion intermediate. However, lack of success is far from satisfactory evidence for an S_N2 mechanism because it is possible that intermediates of at least some slight stability occur in all displacement reactions although they are hard to demonstrate in even the most favorable cases.

[4] C. G. Swain, THIS JOURNAL, **70**, 1119 (1948); C. G. Swain and R. W. Eddy, *ibid.*, **70**, 2989 (1948).

[5] C. G. Swain and W. P. Langsdorf, Jr., *ibid.*, **73**, 2813 (1951).

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

[7] M. S. Swain, Ph.D. thesis, Radcliffe College, 1948.

should fail for ideal binary solvent mixtures for all compounds for which m is not equal to one. This follows because one electrophilic component of a mixture should be relatively more important than another by a factor which will vary with the selectivity of the substrate, resulting in a different average Y for the mixture with each substrate. The Y for an ideal binary mixture of C and D in terms of the Y's and mole fractions (x) for the pure components should be given by

$$10^{mY} = (k_C x_C + k_D x_D)/k_0 = x_C 10^{mY_C} + x_D 10^{mY_D} \quad (2)$$

and thus should depend on m as well as on Y_C, Y_D, x_C and x_D. Therefore it might seem preferable to measure Y values for only pure solvents, and to use equation 2 to calculate Y for mixtures. However, the binary mixtures used in practice are so non-ideal that 2 does not adequately describe the variation in rate with composition for even a single compound.[8] Consequently the assumption of Grunwald and Winstein that Y for a binary mixture is independent of m but can be determined empirically for each mixture gives a better fit (because of more adjustable parameters and hence more flexibility) than the assumption of ideal behavior embodies in equation 2. The theoretical objection that Y for a mixture may depend on m is still valid; however, m is generally close enough to 1.0 so that the dependence may be neglected.

Grunwald and Winstein found that isopropyl *p*-bromobenzenesulfonate fails to fit equation 1 with Y values based on *t*-butyl chloride for all solvents; from the deviation observed, the per cent. reacting by a different mechanism (S_N2), assumed to be zero for acetic acid–acetic anhydride solvents, was estimated to be 77% in 80% ethanol, 91% in pure methanol and 96% in pure ethanol.[6] In their later paper they scrutinized this compound further and found that the fit to two simultaneous processes was in fact rather rough; accordingly, they abandoned the concept of duality of mechanism for isopropyl *p*-bromobenzenesulfonate, but still maintained that *t*-butyl chloride, α-methylneopentyl *p*-bromobenzenesulfonate and related compounds are essentially in a "limiting" category, where only "solvent ionizing power" (electrophilic reactivity) is important in determining the rate. They made no prediction about the behavior of trityl compounds or *p*-nitrobenzoyl compounds or fluorides. However, since these compounds are different in several respects from the compounds so far studied, they may be of particular importance to help determine whether *t*-butyl chloride is or is not an extreme in its solvolytic behavior.

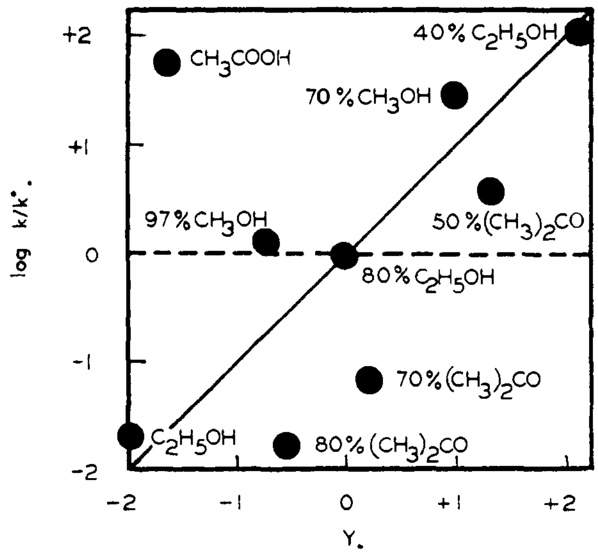

Fig. 1.—Solvolysis of trityl fluoride at 25°.

Results and Discussion

Table I summarizes rates of solvolysis of trityl fluoride in nine solvents. Figure 1 is a plot of equation 1 using Y values based on *t*-butyl chloride. If there had been a good correlation with *t*-butyl chloride, all of the points should have fallen on a single straight line with a slope close to unity (solid line in Fig. 1).

Table I

Solvolysis of Trityl Fluoride at 25°

Solvent[a]	Y[b]	k_1, sec.$^{-1}$[c]	ΔE, kcal.[d]
MeOH, 96.7	−0.72	3.39×10^{-4}	..
MeOH, 69.5	+1.02	8.28×10^{-3}	14.1
EtOH, 100	−1.97	4.88×10^{-6}	19.8
EtOH, 80	0.00	2.61×10^{-4}	15.3
EtOH, 40	+2.15	2.74×10^{-2}	10.2
Me_2CO, 80	−0.68	4.23×10^{-6}	..
Me_2CO, 70	+0.13[e]	1.60×10^{-5}	24.4
Me_2CO, 50	+1.29[e]	9.83×10^{-4}	..
AcOH, 99.3[f]	−1.63	1.5×10^{-2}	..

[a] Number after solvent is % by volume based on volumes before mixing; the residue is water; Me, Et, Ac = CH_3, C_2H_5, CH_3CO. [b] Based on *t*-butyl chloride. [c] Measured at 25° for 96.7% MeOH, 80 and 50% Me_2CO and 99.3% AcOH; calculated for 25° from measurements at 30 and 40° for the other solvents. [d] Arrhenius activation parameters from measurements at 30 and 40°. [e] Value supplied by Marguerite S. Swain. [f] Anhydrous but contained 0.7% acetic anhydride.

An idea of the magnitude of the discrepancy may be gained by noting a few of the deviations. Solvolysis in 70% methanol–30% water is predicted to be one-half as fast as in 50% acetone–50% water, whereas the observed rate is 7 times faster. Similarly, solvolysis in 80% acetone–20% water is predicted to be 30 times faster than in pure ethanol, but it is found experimentally to be slightly slower. Solvolysis in 97% methanol–3% water should be about two-thirds as fast as in 80% acetone–20% water, yet the measured rate is actually 80 times faster. The rate for acetic acid is at least 1,000 times faster than would be predicted from the behavior of the ethanol–water mixtures, whereas the rate for 70% acetone–30% water is about 1/25th as fast. This is a spread of over 2.5×10^4, which is more than the spread between the slowest and fastest reactions. Acetic acid is faster than all the other solvents except 40% ethanol, whereas it should have been slower than all of them except for 100% ethanol.

Closer inspection reveals that the deviations are all in such a direction that *t*-butyl chloride is intermediate in behavior between trityl fluoride and *n*-butyl bromide and approximately midway between

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[8] M. (Inka) Allen, S. M. Thesis, M.I.T., August, 1953.

TABLE II

SOLVOLYSIS OF *t*-BUTYL CHLORIDE AT 25°

Solvent	Y_A[a]	Y_B[b]	Obsd. k (sec.$^{-1}$)	Calcd. k_A (sec.$^{-1}$)[c]	Calcd. k_B (sec.$^{-1}$)[d]	k_A/k
40% C_2H_5OH–60% H_2O	+2.02	....	1.29×10^{-3}	3.9×10^{-7}	....	0.000
50% $(CH_3)_2CO$—50% H_2O	+0.58	....	4.79×10^{-4}	1.4×10^{-8}	....	.000
69.5% CH_3OH–30.5% H_2O	+1.50	+0.47	9.75×10^{-5}	1.2×10^{-7}	2.7×10^{-5}	.001
70% $(CH_3)_2CO$–30% H_2O	−1.21	....	1.00×10^{-5}[e]	2.3×10^{-10}	....	.000
80% C_2H_5OH–20% H_2O	0.00	0.00	9.24×10^{-6}	3.5×10^{-9}	(9.24×10^{-6})	.000
80% $(CH_3)_2CO$–20% H_2O	−1.79	....	1.94×10^{-6}	6.0×10^{-11}	....	.000
96.7% CH_3OH–3.3% H_2O	+0.11	−0.24	1.75×10^{-6}	4.8×10^{-9}	5.4×10^{-6}	.003
CH_3COOH	+1.76	....	2.13×10^{-7}	(2.13×10^{-7})	(None)	100
C_2H_5OH	−1.73	−0.73	9.70×10^{-8}	6.9×10^{-11}	1.7×10^{-6}	0.001

[a] Based on trityl fluoride at 25°. [b] Based on *n*-butyl bromide at 25° calcd. using $E = 22$ kcal.[9] [c] Calculated from Y_A using $m_A = 1$ (reaction in CH_3COOH assumed to be all S_N1). [d] Calculated from Y_B using $m_B = 1$ (using 80% C_2H_5OH as a standard). [e] Estimated value.

them. Rather than call trityl fluoride abnormal, it might seem better to call it merely limiting and treat *t*-butyl chloride as an intermediate or borderline compound in the way that Grunwald and Winstein handled isopropyl *p*-bromobenzenesulfonate. The results of this approach are given below.

First let us suppose that there are two discrete types of transition state, A (S_N1) and B (S_N2), and that the observed first-order rate constant (k_1) represents the sum of rate constants for the two processes; furthermore let us assume that we can express the solvent dependence for molecules reacting *via* transition state A with a Y_A scale based on trityl fluoride, and the solvent dependence for molecules reacting *via* transition state B with a Y_B scale based on *n*-butyl bromide.

$$k_1 + k_A + k_B$$
$$\log (k_A/k^0_A) = m_A Y_A$$
$$\log (k_B/k^0_B) = m_B Y_B$$

In Table II are given the Y_A and Y_B values for different solvents, the observed and calculated rates for *t*-butyl chloride, and the calculated fraction reacting by transition state A(S_N1). Even assuming this fraction to be 100% for reaction in acetic acid, it is necessary to conclude that less than 1% of the solvolysis of *t*-butyl chloride occurs by this route in all the other solvents, including 40 and 80% ethanol, and more than 99% by transition state B (S_N2).

In these calculations the observed and calculated rates were adjusted to agree for the standard solvent, 80% ethanol–20% water, and m_A and m_B were taken as unity; different values of m_A and m_B do not change the results appreciably. The conclusion that most of the reaction of *t*-butyl chloride is S_N2 even in the chiefly aqueous water–alcohol and water–acetone mixtures does not conform with conclusions previously reached on the basis of the hypothesis of a duality of mechanism.[2]

The assumption that trityl fluoride, *t*-butyl chloride and *n*-butyl bromide each solvolyze by both S_N1 and S_N2 mechanisms with each mechanism fitting a different equation of the form 1 leads to results even more absurd than those reached under the previous assumption. Calculations on this new basis show that if a significant fraction (5% or more) of the solvolysis of *t*-butyl chloride in 80% ethanol occurs by S_N1, then over 98% of the solvolysis of trityl fluoride in acetic acid must occur by the S_N2 path, even though this medium is perhaps the best of the nine solvents studied for promoting S_N1 reactions and even though the compound solvolyzing is a trityl halide. To avoid this unreasonable conclusion, it is necessary to assume that less than 5% of the solvolysis of *t*-butyl chloride in 80% ethanol is S_N1. Then calculations from the data for *t*-butyl chloride in ethanol and 80% ethanol show that over 94% of the solvolysis of *n*-butyl bromide in absolute ethanol occurs by the S_N1 route, in spite of the fact that *n*-butyl bromide has been generally accepted as a compound which reacts entirely by S_N2. It is clear that the assumption of a duality of mechanisms with each mechanism fitting an equation of the form 1 does not lead to any correlation even though m_A, Y_A, m_B and Y_B are unrestricted and independently adjustable parameters.

Figure 2 shows that *p*-nitrobenzoyl chloride and fluoride also fail to fit equation 1, but here the deviation for carboxylic acid solvents is in the opposite direction.[10]

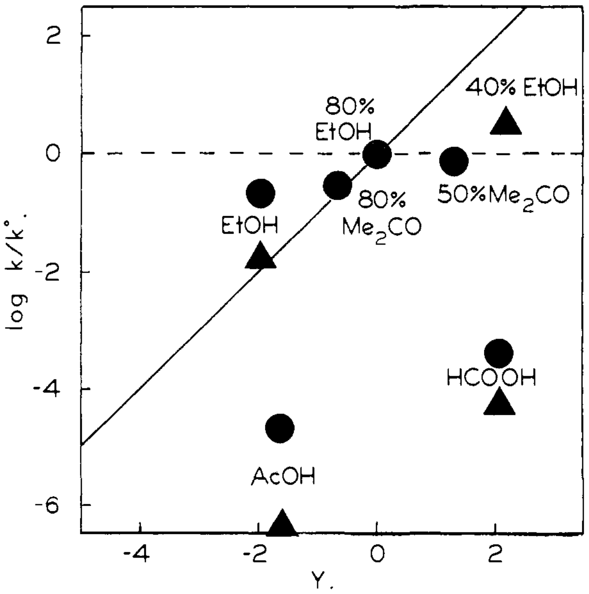

Fig. 2.—Solvolysis of *p*-nitrobenzoyl chloride (●) and fluoride (▲) at 25°.

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[9] M. L. Bird, E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 255 (1943).

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

Thus there does not appear to be any obvious tendency for the data that we have considered to fall into two classes with respect to behavior in solvolysis. Instead there seems to be a fairly smooth gradation, in the character of the transition states over the series trityl, *t*-butyl-, *n*-butyl- and *p*-nitrobenzoyl halides. On this basis it was anticipated that carboxylic acids, which are slower-reacting solvents than the corresponding alcohols toward *n*-butyl bromide and slightly faster than the alcohols toward *t*-butyl chloride, would be enormously faster toward trityl fluoride; and likewise that acetone–water mixtures would be abnormally poor toward trityl fluoride.

This in no way diminishes the utility of the Grunwald–Winstein equation 1 when applied to any closely related group of compounds. Out of the whole range of possible compounds one can pick any compound as a standard to determine a set of Y values for different solvents using equation 1. The resulting Y values will then be useful to correlate and predict the reactivity of compounds closely similar in structure to the standard. They begin to be poor when the structure is varied as much as from a *t*-butyl to an isopropyl, benzhydryl or trityl halide or from an *n*-butyl- to a *p*-nitrobenzoyl, methyl or isopropyl halide; but for smaller changes, as from *n*-butyl bromide to ethyl chloride, bromide or *p*-toluenesulfonate, the correlation should be excellent. Only when one wants to bridge a spread in solvolytic behavior many times this great, as from *t*-butyl chloride to *n*-butyl bromide, are different equations needed for a significantly better fit to the data.

In a previous paper[5] we showed that the difference in positive charge between transition state and ground state on the carbon atom undergoing displacement may vary smoothly from positive values for trityl halides to negative values for acyl halides.[11] Expressed in a different way, this represents a gradual variation in the looseness (*vs.* tightness) of the transition states, *i.e.*, in the degree of ionic (*vs.* covalent) character in the bonds that are breaking or forming. In most reactions of tertiary halides these bonds are relatively loose, while in most reactions of *p*-nitrobenzoyl halides they are relatively tight. We regard *t*-butyl, *n*-butyl and methyl halides as intermediate cases.

This conclusion that there is a fairly smooth gradation in solvolytic behavior is an encouraging one from the point of view of trying to correlate rates of solvolysis. It means that it may not be necessary, when trying to correlate rates in dilute solution to a first approximation, to consider detailed differences of mechanism such as internal and external return, tight and loose ion pair intermediates, etc. Instead of using two or more equations to represent reaction by two or more mechanisms, it might be possible to correlate rates of solvolysis for a wide range of compounds (including both *t*-butyl and *n*-butyl halides) on the basis of a *single* equation and *single* set of parameters. The following paper demonstrates that this can in fact be done using a single equation based on the idea that both nucleophilic solvation and electrophilic solvation must be considered in all cases. The third paper demonstrates that it can be done with even fewer adjustable parameters, *i.e.*, only one for the compound and one for the solvent, provided that second-order differences are employed. Both treatments are consistent with a very gradual change in reactivity over the whole range from tertiary to primary halides and from acidic to basic solvents.

Experimental

Reagents.—Trityl fluoride was prepared by the reaction of trityl chloride with anhydrous hydrogen fluoride. This method was worked out by Dr. Robert Ehrenfeld in this Laboratory. Trityl chloride (37 g. which had been recrystallized from benzene in the presence of acetyl chloride to prevent hydrolysis) was placed in a nickel crucible and gaseous hydrogen fluoride was led in by a copper tube through a hole in the cover. The hydrogen fluoride quickly dissolved all the solid to give a yellow-brown solution. After 20 minutes the excess hydrogen fluoride was evaporated, 20 ml. of benzene was added, the solution reevaporated and cooled, and the resulting white, crystalline solid recrystallized from anhydrous ether (7.5 ml. per g.) at Dry Ice temperatures, yielding 23 g. (62%), m.p. 101.3–102.0°. The purity as judged from acid liberated on solvolysis varied from 97–85% in different preparations. Repeated recrystallizations did not give higher purities. Kinetic analysis showed that no trityl chloride was present, hence it was assumed that the impurity was triphenylcarbinol. Since triphenylcarbinol does not react with hydrogen fluoride under the conditions of the synthesis,[12] the per cent. triphenylcarbinol was never less than that in the trityl chloride used.

Absolute ethanol was prepared from U.S.I. "absolute" ethanol by the ethyl formate method.[13] This lowered the water content from 0.15% to less than 0.01% by the paraffin oil test.[11] For the 80 and 40% ethanol solution, the commercial product was used without further purification. The absolute methanol used for the methanol-water runs was Mallinckrodt reagent grade. The acetone was Mallinckrodt reagent grade dried over Drierite before use; it did not turn anhydrous copper sulfate blue in 2 hours. Acetic acid was prepared from Mallinckrodt reagent (dichromate test) glacial acetic acid by refluxing for at least 2 hours with acetic anhydride equivalent to three or four times the amount of water present and then distilling. The concentration of acetic anhydride in acetic acid was determined by the anthranilic acid method using brom phenol blue indicator.[14] The acetic acid containing 0.071 *M* (0.69%) acetic anhydride froze at 16.22°. The acetic anhydride was J. T. Baker reagent grade. Anhydrous sodium acetate was prepared by fusing Mallinckrodt reagent sodium acetate trihydrate and drying for 3 hours at 140°.

Reaction Products.—The analytical method used made it certain that hydrofluoric acid was quantitatively formed in all runs with the exception of those in acetic acid. To prove that trityl acetate was the principal product in the runs in acetic acid, the crude product was isolated by quickly removing the solvent under reduced pressure 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. The melting point was 71–90° in contrast to 87–88° for pure trityl acetate.[15] The low melting point is believed due to the 14% triphenylcarbinol known to have been present (from base titration) in the original trityl fluoride used. The crude product proved difficult to free from triphenylcarbinol by recrystallization, indicating the possibility of

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(11) *E.g.*, for alcoholysis of benzoyl halides, where the reaction constant (ρ) in the Hammett equation is positive. The factors determining the sign and magnitude of this reaction constant were discussed in reference 5.

(12) C. G. Swain, R. M. Esteve, Jr., and R. H. Jones, This Journal, **71**, 965 (1949).

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

(14) S. Kilpi, *C. A.*, **35**, 2445 (1941).

(15) Observed for an authentic sample prepared in this Laboratory by C. B. Scott and also reported by M. Gomberg and G. T. Davis, *Ber.*, **36**, 3924 (1903).

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

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

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

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

CAMBRIDGE 39, MASSACHUSETTS

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

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

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

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

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

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

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

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

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

or

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

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

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

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

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

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

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

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

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

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

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