

[Contribution from the Department of Chemistry,
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Rates of Solvolysis of Triphenylmethyl, *t*-Butyl
and *n*-Butyl Halides¹

(1) We gratefully acknowledge support of this work by the Office of Naval Research, under O.N.R. Contract N5ori-07838, Project NR-056-198. For full experimental data see R. B. Mosely, Ph.D. Thesis, M.I.T., July, 1952.

By C. Gardner Swain and Robert B. Mosely

Rates of solvolysis of triphenylmethyl (trityl) fluoride in nine solvents are reported. Comparison of the solvolytic behavior of *n*-butyl bromide, *t*-butyl chloride and trityl fluoride makes it clear that *t*-butyl chloride is in every way intermediate between the other two. This casts some doubt on the conclusion that it is in a "limiting" class. 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, there seems to be no difficulty in the assumption that there is a single mechanism which changes in its quantitative aspects very gradually over the series *p*-nitrobenzoyl, methyl, *n*-butyl, *t*-butyl, trityl, with no discontinuity or sharp change in type at any point.

There are quantitative differences between the reactions of tertiary and primary halides: the tertiary halides often react faster with hydroxylic solvents, slower with anions, and give stabler intermediates more easily detected by competition experiments. A question which has vexed chemistry for twenty years is whether these differences are due (a) to the coexistence of two fundamentally different mechanisms, the "unimolecular" or S_N1 mechanism for most reactions of tertiary halides, and the "bimolecular" or S_N2 mechanism for most reactions of primary halides or (b) to a very gradual trend in reactivity over this whole range of reactions and compounds, with no dividing line at any point.

The former view (a), due largely to Hughes, Ingold and co-workers,²

(2) E. D. Hughes, Trans. Faraday Soc., 37, 603 (1941); J. Chem. Soc., 968 (1946).

has been the more popular one. In intermediate cases (e.g., *i*-propyl halides in alcohol solution) part of the molecules are considered to solvolyze by the S_N1 mechanism and the rest of the molecules are considered to react with solvent molecules by the S_N2 mechanism. However, it has been suggested³ that

(3) C. G. Swain and R. W. Eddy, J. Am. Chem. Soc., 70, 2989 (1948).

it may be more useful to consider that there is only one mechanism (b).

The discovery of quantitative correlations between structure and reactivity makes it possible to test predictions of these opposing hypotheses. So long as observations were only qualitative it was hard to decide whether or not there was a discontinuity or grouping of reactions into two adequately differentiated mechanistic categories; it should be easier when reactivities are expressed in quantitative terms. One such quantitative correlation, the Hammett equation, which describes the effect of *m*- and *p*-substituents on the rate, was examined in a previous paper⁴ with this in mind. No discontinuity

(4) C. G. Swain and W. P. Langsdorf, Jr., J. Am. Chem. Soc., 73, 2813 (1951).

was apparent.

Recently another quantitative correlation was discovered by Winstein and Grunwald,⁵ which affords another opportunity to test experimentally the

(5) E. Grunwald and S. Winstein, J. Am. Chem. Soc., 70, 846 (1948); S. Winstein, E. Grunwald and H. W. Jones, ibid., 73, 2700 (1951).

different predictions of the two hypotheses. They discovered a very useful equation for correlating the rates of solvolysis of alkyl halides or esters in different solvents

$$\log (k/k^{\circ}) = mY \quad (1)$$

where k is the first-order rate constant in any medium, k° is the first-order 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 defined as unity. Rates of solvolysis of the following compounds were well correlated by equation 1 and Y values based on t -butyl chloride in all the solvents studied:⁵ t -butyl chloride (standard), t -butyl bromide, α -methylallyl chloride, neopentyl bromide, α -methylneopentyl p -bromobenzenesulfonate and trans-2-bromocyclohexyl p -bromobenzenesulfonate.⁶ Highly branched t -alkyl halides were also found to fit. n -Butyl bromide

(6) H. S. Swain, Ph.D. Thesis, Radcliffe College, 1948.

showed a different behavior⁵ which might be expected to be typical of ordinary saturated primary halides. If one were to choose it as a standard, instead of t -butyl chloride, then the new set of Y values might be expected to correlate the rates of solvolysis of n -butyl bromide, n -butyl chloride, ethyl bromide and closely similar compounds, although these latter compounds were not systematically compared.

Grunwald and Winstein found that i -propyl p -bromobenzenesulfonate failed to fit equation 1 with Y values based on t -butyl chloride for all solvents; from the deviation observed, the percent 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.⁵ 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 i -propyl p -bromobenzenesulfonate, but still maintained that t -butyl chloride, α -methylneopentyl p -bromobenzenesulfonate and related compounds were essentially

in a limiting category, where only "solvent ionizing power" (electrophilic reactivity) was important in determining the rate.

If t-butyl chloride is indeed "limiting" then triphenylmethyl fluoride must certainly also be "limiting," since it is even more sensitive to electrophilic reagents and gives an even stabler carbonium ion. Accordingly we examined triphenylmethyl fluoride to see how well it would correlate with t-butyl chloride.

Results and Discussion.- Rates of solvolysis were measured in nine solvents. The results are summarized in Table I and Fig. 1.

Table I
SOLVOLYSIS OF TRITYL FLUORIDE AT 25°

Solvent ^a	γ^b	$\frac{k_1^c}{\text{sec.}^{-1}}$	$\frac{\Delta E^d}{\text{kcal.}}$
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^{-3}	10.2
Me ₂ CO, 80	-0.68	4.23×10^{-6}	—
Me ₂ CO, 70	+0.13 ^e	1.60×10^{-5}	24.4
Me ₂ CO, 50	+1.29 ^e	9.83×10^{-4}	—
AcOH, 99.3	-1.63	1.51×10^{-3}	—

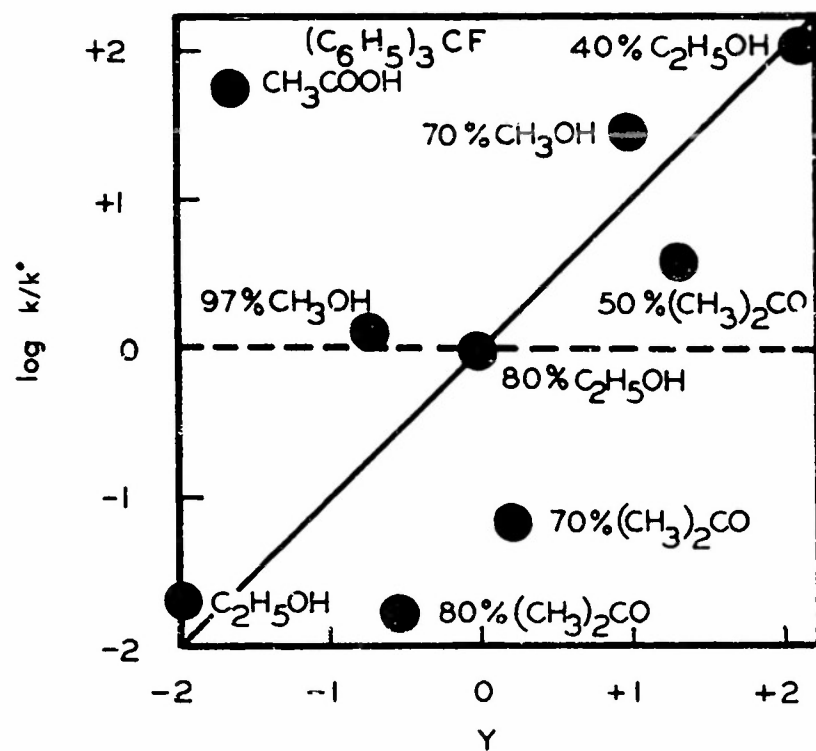
^a Number after solvent is % by volume based on volumes before mixing; the residue is water; Me, Et, Ac = CH₃, C₂H₅, CH₃CO.

^b Based on t-butyl chloride.

^c Measured at 25° for 96.7% MeOH, 80 and 50% Me₂CO 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.



There is considerable scatter of the observed points away from any straight line (see Fig. 1). If the data had correlated well with t-butyl chloride, all of the points should have fallen on a single straight line with slope about unity (solid line on Fig. 1).

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 two times slower than 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 1.5 times slower than 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 25 times slower. 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 them. Rather than call trityl fluoride super-limiting, 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 i-propyl p-bromobenzenesulfonate. The results of this approach are given below.

First let us suppose that there are two discrete mechanisms, A(S_N1) and B (S_N2), and that the observed first-order rate constant (k_1) represents the sum of contributions from the two mechanisms; furthermore let us assume that we can express the solvent dependence of mechanism A with a γ_A

scale based on trityl fluoride, and the solvent dependence of mechanism B with a Y_B scale based on *n*-butyl bromide.

$$k_1 = k_A + k_B$$

$$\log (k_A/k_A^\circ) = m_A Y_B \quad (2)$$

$$\log (k_B/k_B^\circ) = m_B Y_B \quad (3)$$

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 mechanism 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 the S_N1 mechanism in all the other solvents, including 40% and 80% ethanol, and more than 99% by mechanism B (S_N2).

Table II

SOLVOLYSIS OF t-BUTYL CHLORIDE AT 25°

Solvent	$\underline{Y}_A^a$	$\underline{Y}_B^b$	Observed $\underline{k}(\text{sec.}^{-1})$	Calcd. $\underline{k}(\text{sec.}^{-1})^c$	Calcd. $\underline{k}_1(\text{sec.}^{-1})^d$	$\underline{k}_1/\underline{k}$
40% $\text{C}_2\text{H}_5\text{OH}$ -60% H_2O	+2.02	—	1.29×10^{-3}	3.9×10^{-7}	—	0.000
50% $(\text{CH}_3)_2\text{CO}$ -50% H_2O	+0.58	—	4.79×10^{-4}	1.4×10^{-6}	—	0.000
70% CH_3OH -30% H_2O	+1.50	+0.47	9.75×10^{-5}	1.2×10^{-7}	2.7×10^{-5}	0.001
70% $(\text{CH}_3)_2\text{CO}$ -30% H_2O	-1.21	—	$1.00 \times 10^{-5}^e$	2.3×10^{-10}	—	0.000
80% $\text{C}_2\text{H}_5\text{OH}$ -20% H_2O	0.00	0.00	9.24×10^{-6}	3.5×10^{-9}	(9.24×10^{-9})	0.000
80% $(\text{CH}_3)_2\text{CO}$ -20% H_2O	-1.79	—	1.94×10^{-6}	6.0×10^{-11}	—	0.000
97% CH_3OH -3% H_2O	+0.11	-0.24	1.75×10^{-6}	4.8×10^{-9}	5.4×10^{-8}	0.003
CH_3COOH	+1.76	—	2.13×10^{-7}	(2.13×10^{-7})	(none)	100.
$\text{C}_2\text{H}_5\text{OH}$	-1.73	-0.73	9.70×10^{-8}	6.9×10^{-11}	1.7×10^{-6}	0.001

^aBased on trityl fluoride at 25°.

^bBased on n-butyl bromide at 25° calc. using $E = 22 \text{ kcal.}^7$

^cCalculated from $\underline{Y}_A$ using $\underline{m}_A = 1$ (reaction in CH_3COOH assumed to be all $\text{S}_{\text{N}}1$).

^dCalculated from $\underline{Y}_B$ using $\underline{m}_B = 1$ (using 80% $\text{C}_2\text{H}_5\text{OH}$ as a standard).

^eEstimated value.

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

In these calculations the observed and calculated rates were adjusted to agree for the standard solvent, 80% ethanol-20% water, and $\underline{m}_A$ and $\underline{m}_B$ were taken as unity; different values of $\underline{m}_A$ and $\underline{m}_B$ do not change the results appreciably. The conclusion that most of the reaction of t-butyl chloride is $\text{S}_{\text{N}}2$ 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.

The assumption that trityl fluoride, t-butyl chloride, and n-butyl bromide all solvolyze by a mixture of S_N1 and S_N2 mechanisms leads to results even more absurd than those reached under the previous assumption. If data were available for a hypothetical compound solvolyzing entirely by the S_N1 path and for another solvolyzing entirely by the S_N2 path, one might expect that a satisfactory correlation of the solvolysis rates of the three compounds could be obtained with equations (2) and (3) and Y_A and Y_B values based on these hypothetical compounds. However, if one assigns values to the rates of the hypothetical compound solvolyzing exclusively by S_N1 such that a significant fraction (5% or more) of the solvolysis of t-butyl chloride in 80% ethanol occurs by S_N1 , one finds that the predicted rate of solvolysis of trityl fluoride in acetic acid is less than 2% of that observed experimentally. In order to obtain agreement between calculated and observed rates it is necessary to assume that over 98% of the solvolysis of trityl fluoride in acetic acid is by the S_N2 reaction 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 . If one then assigns rates to the hypothetical compound solvolyzing entirely by S_N2 such that agreement between calculated and observed rates is obtained for t-butyl chloride in both ethanol and 80% ethanol, one finds that the predicted rate for n-butyl bromide in absolute ethanol is less than 6% of that experimentally observed. In order to obtain agreement between calculated and observed rates it is necessary to assume 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 it 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 ρ_A , ρ_A' , ρ_B and ρ_B' are independently adjustable parameters.

Fig. 2⁸ shows that *p*-nitrobenzoyl chloride and fluoride also fail

(8) Delos E. Bown, Ph.D. Thesis, M.I.T., April, 1953.

to fit equation 1, but here the deviation for carboxylic acids is in the opposite direction.

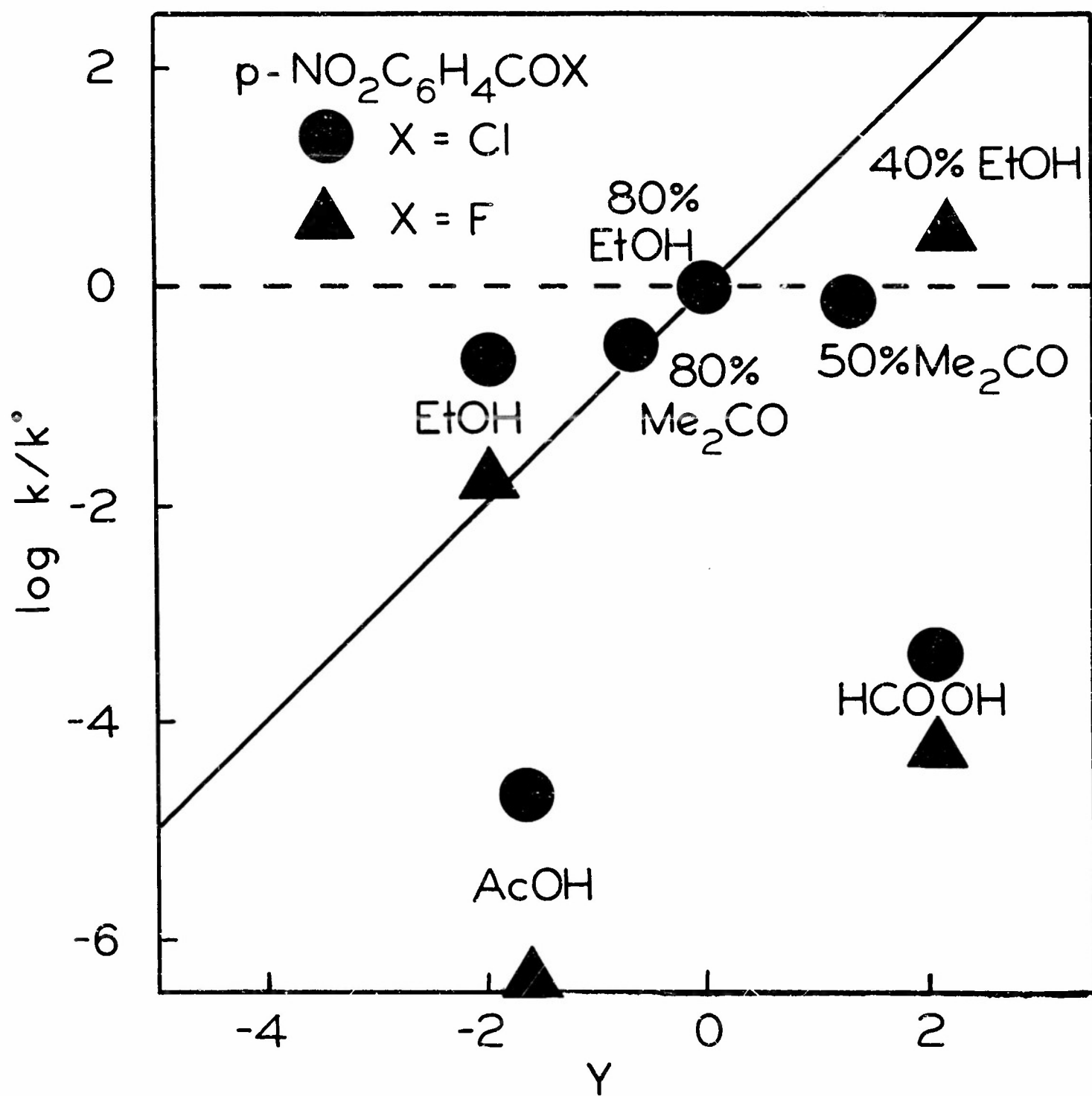
These results are more readily understood if there is no sharp line of demarcation between S_N1 and S_N2 mechanisms, and if instead there is a single mechanism which shades very gradually in type over the series *p*-nitrobenzoyl, methyl, *n*-butyl, *t*-butyl and trityl halides.

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. The experimental verification of these predictions gives us more confidence in a smooth continuous gradation of mechanism over this series of compounds, with no discontinuity or break in the trend at any point.

The difference in positive charge on the carbon atom undergoing displacement between transition state and ground state may vary continuously from negative values for acyl halides⁹ to positive values for trityl halides.

(9) 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 4.

From this point of view *n*-butyl and *t*-butyl halides are not extreme cases of two different mechanisms but are both intermediate cases of a single mechanism.



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 re-evaporated 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. It was established that triphenylcarbinol did not react with hydrogen fluoride under the conditions of the synthesis,¹⁰ hence the percent triphenylcarbinol was never

(10) C. G. Swain, R. M. Esteve, Jr. and R. H. Jones, J. Am. Chem. Soc., 71, 965 (1949).

less than that in the trityl chloride used.

Absolute ethanol was prepared from U.S.I. "absolute" ethanol by the ethyl formate method.¹¹ This lowered the water content from 0.15% to less than

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

0.01% by the paraffin oil test.¹¹ For the 80% and 40% ethanol solutions, 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 after 2 hours' contact. 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 bromophenol blue indicator.¹² The acetic acid

(12) S. Kilpi, Chem. Abstracts, 35, 2445 (1941).

containing 0.071 M (0.69%) acetic anhydride froze at 16.22°. The acetic anhydride was Baker's reagent grade. Anhydrous sodium acetate was prepared by fusing Mallinckrodt reagent sodium acetate trihydrate and drying for 3 hours at 140°. All solvents were prepared volumetrically.

Reaction Products.— The analytical method used made it certain that hydrofluoric acid was quantitatively formed in all runs with the possible 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.¹³ The low melting point is believed due to the 14% triphenyl-

(13) 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).

carbinol 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 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 four-fold 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.¹⁴

(14) C. G. Swain, J. Am. Chem. Soc., 70, 1119 (1948).

Kinetic Measurements.- All of the runs except those in acetic acid were carried out with a cell and technique described previously.^{10,15} Since

(15) P. D. Bartlett and C. G. Swain, ibid., 71, 1406 (1949).

the rate of solvolysis of trityl halides is independent of pH 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. Bromothymol 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.

The 70% methanol was actually 69.5% methanol-30.5% water. The 97% methanol was actually 96.7% methanol-3.3% water. All percentage compositions are by volume before mixing.

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 sodium alizarinsulfonate as indicator. No further fluoride ion was extractable by subsequent washing of the benzene layer with water. In the acetic acid runs two different color changes were observed, a sharper change from yellow to orange and a gradual change to purple. Since the first change was easier to observe and yielded the same final calculated rates as the second, this endpoint alone was used in most of the runs. This titration was not very satisfactory but several runs were averaged and the results are believed accurate to $\pm 25\%$.

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