TABLE IV

KINETIC DATA ON THE SOLVOLYSIS OF TRITYL CHLORIDE

Solvent[a]	Temp., °C.	$k \times 10^3$, sec.$^{-1}$	Solvent[a]	Temp., °C.	$k \times 10^3$, sec.$^{-1}$
MeOH, 100	−68.4	3.00	EtOH, 90	−60.3	4.85
MeOH, 100	−67.7	2.92	EtOH, 90	−60.0	4.72
MeOH, 100	−58.0	13.1	EtOH, 90	−52.4	17.8
MeOH, 100	−57.6	13.1	EtOH, 90	−51.8	17.0
MeOH, 100	−56.8	18.7	Me_2CO, 95	−32.5	1.01
EtOH, 100	−50.2	1.33	Me_2CO, 95	−32.3	0.987
EtOH, 100	−50.1	1.38	Me_2CO, 95	−18.0	4.28
EtOH, 100	−40.6	4.75	Me_2CO, 95	−17.6	4.28
EtOH, 100	−40.6	5.02	Me_2CO, 95	− 7.8	12.6
EtOH, 100	−40.3	5.45	Me_2CO, 95	− 7.6	10.2
EtOH, 100	−33.7	12.6	Me_2CO, 95	− 7.5	11.0
EtOH, 100	−33.4	13.8	Me_2CO, 90	−39.6	4.02
EtOH, 100	−33.4	13.9	Me_2CO, 90	−39.0	3.63
EtOH, 95	−59.8	2.23	Me_2CO, 90	−37.8	4.27
EtOH, 95	−59.6	2.20	Me_2CO, 90	−32.3	7.65
EtOH, 95	−50.5	8.88	Me_2CO, 90	−32.3	7.80
EtOH, 95	−50.2	8.75	Me_2CO, 90	−20.6	41.3
EtOH, 95	−40.3	38.5	Me_2CO, 90	+25.0	1833.
EtOH, 95	−40.2	39.8	Me_2CO, 80	+25.0	21700.
EtOH, 90	−70.2	0.94	AcOH, 100	+25.0	240.

[a] Same notation as in Table I.

the upper flask in less than 1 sec., quenching the reaction in the cold acetone. The excess base was then titrated with *p*-toluenesulfonic acid in isopropyl alcohol using the yellow to colorless end-point of brom phenol blue. The titration had to be done slowly near the end-point because of a slow response of the indicator at this temperature. Two different concentrations of sodium acetate (1.5×10^{-3} and 2.9×10^{-3} *M*) were used to show that the rate was independent of acetate ion.

Data and Calculations.—Table IV gives the kinetic measurements. Heats of activation (ΔH^*) were obtained from plots of log k/T *vs.* $1/T$, and extrapolations to 25° made using the equation log $(k_2T_1/k_1T_2) = \Delta H^*(T_2 - T_1)/2.303\ RT_1T_2$ are given in Table I.

The rate of solvolysis of trityl chloride in the standard solvent (80% ethanol–20% water) was expected to be out of the range of either the cooling technique or the flow system. Therefore advantage was taken of the ability of eq. 1 to correlate very well the rates for a single compound in a single type solvent pair. The rates for the three other ethanol–water mixtures determined the straight line for extrapolation to 80% ethanol.

The trityl chloride parameters c_1 and c_2 were obtained from the least squares equations

$$c_1\Sigma d_1^2 + c_2\Sigma d_1d_2 = \Sigma d_1 \log (k/k^0)_{\text{obsd}}$$

$$c_1\Sigma d_1d_2 + c_2\Sigma d_2^2 = \Sigma d_2 \log (k/k^0)_{\text{obsd}}$$

using the d_1 and d_2 solvent parameters previously determined with other compounds and listed in Table I. On Figs. 1 and 2, for 90% acetone only the value determined by the flow method at 25° is plotted. However the figure (0.165 higher) obtained by extrapolation from low temperatures was used as additional datum, and the points for 80% ethanol were omitted (since they must fit), in calculating m, c_1, c_2 and Φ for eq. 1 and 2.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND THE LABORATORY FOR NUCLEAR SCIENCE, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE 39, MASS.]

II. Rates of Solvolysis of Triphenylmethyl Acetate and Fluoride[1–3]

BY C. GARDNER SWAIN, TERENCE E. C. KNEE AND ALEXANDER MACLACHLAN

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Rates of solvolysis of triphenylmethyl (trityl) acetate in nine solvents at 25° are reported. The rate in acetic acid was measured by using trityl acetate labeled with tritium in the acetate group. The log $(k/k^0) = mY$ equation gives only a fair correlation of the data, but the log $(k/k^0) = c_1d_1 + c_2d_2$ equation gives a good correlation. In its solvolytic behavior, trityl acetate is similar to trityl fluoride previously studied. The hydrolysis of trityl fluoride shows specific hydronium-ion catalysis in water solution. It is accelerated by sodium perchlorate but retarded by sodium chloride.

Table I summarizes the solvolytic data for triphenylmethyl (trityl) acetate in nine solvents. Like trityl fluoride[4] this compound reacts about a million times slower than trityl chloride in the standard solvent (80% ethanol–20% water). Its relative rate in acetic acid (measured by exchange of solvent with trityl acetate labeled with tritium in the acetate group) is also similar to that of trityl fluoride. This rate was not changed by addition of 0.012 *M* sodium acetate. The rates of solvolysis of *t*-butyl chloride and trityl chloride in acetic acid are very abnormally slow by comparison.[2]

TABLE I

RATES OF SOLVOLYSIS OF TRITYL ACETATE AT 25°

Solvent[a]	$k_1 \times 10^5$, sec.$^{-1}$	log (k/k^0)	Y[b]	d_1[c]	d_2[c]
MeOH, 96.7	56	+0.03	−0.72	−0.11	−0.05
MeOH, 69.5	420	+ .90	+1.02	− .06	+1.32
EtOH 100	4.73	−1.05	−2.03	− .53	−1.03
EtOH, 80	52.7	0.00	0.00	0.00	0.00
EtOH, 60	190	+ .56	+1.12	− .22	+1.34
EtOH, 40	912	1.24	+2.20	− .26	+2.13
Me_2CO, 80	1.45	−1.56	−0.67	− .45	−0.68
Me_2CO, 50	72	+0.14	+1.40	− .25	+0.97
AcOH, 100	789	+1.18	−1.68	−4.82	+3.12

[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] "Ionizing power," from ref. 5. [c] Solvent constants from ref. 6.

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(1) Supported in part by the research programs of the Office of Naval Research, the National Science Foundation, and the Atomic Energy Commission and by a National Institutes of Health Research Fellowship to A.M.

(2) *Cf.* C. G. Swain and A. MacLachlan, THIS JOURNAL, **82**, 6095 (1960).

(3) For complete experimental data on trityl acetate, *cf.* T. E. C. Knee, Ph.D. Thesis in Organic Chemistry, M.I.T., September, 1956; for trityl fluoride, A. MacLachlan, Ph.D. Thesis in Organic Chemistry, M.I.T., August, 1957.

(4) C. G. Swain and R. B. Mosely, THIS JOURNAL, **77**, 3727 (1955).

(5) E. Grunwald and S. Winstein, *ibid.*, **70**, 846 (1948); A. H. Fainberg and S. Winstein, *ibid.*, **78**, 2770 (1956).

(6) C. G. Swain, R. B. Mosely and D. E. Bown, *ibid.*, **77**, 3731 (1955).

The c_1 (nucleophilic) and c_2 (electrophilic) parameters for trityl acetate in the four-parameter equation[6] were determined by the method of least squares using the d_1 and d_2 solvent parameters previously reported,[6] and found to be 0.37 and 1.12.

Table II compares these parameters with those for several other compounds. An objective measure of the goodness of the fit, Φ,[7] is also listed. These are all "good" (50–80%) or "excellent" (80–100%) fits. In contrast, the fits by the mY equation[5] are only 47% for benzhydryl chloride, 48% for trityl chloride, 24% for trityl acetate and 17% for trityl fluoride.

Table II

Values of Parameters for Compounds

Compound[a]	c_1	c_2	c_1/c_2	Φ
t-BuCl	1.00	1.00	1.00	85
Ph_3CCl	1.40	1.08	1.29	85
Ph_3COAc	0.25	0.71	0.35	57
Ph_3CF	.37	1.12	.33	79
Ph_2COAr	.18	0.59	.31	74
Ph_2CHCl	1.24	1.25	.99	84
Ph_2CHF	0.37	1.12	.33	80

[a] Bu, Ph, Ac, Ar = C_4H_9, C_6H_5, $COCH_3$, p-$C_6H_4NO_2$.

Comparison of Solvolytic Reactivities of Trityl Acetate, Fluoride and Chloride.—In its solvolytic behavior, trityl acetate is similar to trityl fluoride previously studied.[4]

One might have expected trityl carboxylic esters, phenolic esters and fluoride to be more sensitive than trityl chloride to variations in electrophilic reactivity (acidity or anion solvating power) of the solvent because oxygen and fluorine are more electronegative and more basic than chlorine and better at forming hydrogen bonds. However, taken at face value, the values of c_1 and c_2 given in Table II, which we believe are rough measures of sensitivity of rate to variations in solvent nucleophilic reactivity or electrophilic reactivity, respectively, suggest that an even more important factor may be the outcome of the competition between ion-pair collapse to regenerate starting material *vs.* reaction of solvent with the ion pair. Although reaction of solvent with carbonium ion may be rate-determining in the solvolysis of trityl fluoride in acetic acid,[2] it is not likely to be rate-determining over as wide a range of solvents as with trityl chloride because of the lower nucleophilic reactivity of fluoride ion. This could account for the lower average c_1/c_2 ratio for trityl fluoride (0.33) than for trityl chloride (1.29).

Acid Catalysis of the Hydrolysis of Trityl Fluoride.—Table III shows that the solvolysis of trityl fluoride in 50% water–50% acetone at 25° is subject to specific hydronium-ion catalysis. This suggests that at sufficiently high acidity a new mechanism appears which involves the conjugate acid of the alkyl fluoride as reactant in the rate-determining step rather than alkyl fluoride itself. Studies of the dependence of rate of hydrolysis on the Hammett acidity function h_f for the related compound benzyl fluoride reported in the following paper[8] are consistent with a mechanism having

$$\mathrm{RFH}^{\oplus} \xrightarrow{\text{slow}} \mathrm{R}^{\oplus} + \mathrm{HF}$$

as its rate-determining step.

Table III

Solvolysis of 0.0040 *M* Trityl Fluoride in 50% Water–50% Acetone at 25°

$NaClO_4$, *M*	Addend, *M*	$k \times 10^4$, sec.$^{-1}$
0.200	....	8.8[a]
.200	....	9.0
.100	....	8.9
.100	HCl, 0.100	34.5[a]
.100	$HClO_4$, .100	46.1[a]
.200	HOAc, .100	9.2[a]
...	....	7.6
...	NaCl, .100	7.4
...	NaCl, .200	6.2
...	NaCl, .300	5.6
.100	NaCl, .100	7.5
.100	NaBr, .100	8.3

[a] Followed by titration of fluoride ion; all other runs followed by titration of acid.

There is no evidence for general acid catalysis by acetic acid in Table III. Higher concentrations of acetic acid than 0.1 *M* were not examined because of the necessity and difficulty of correcting for changes in rate constants with changing dielectric constant beyond that point.

Salt Effects in the Hydrolysis of Trityl Fluoride.—Although 0.1 *M* sodium perchlorate accelerates the hydrolysis of trityl fluoride in 50% water, sodium chloride depresses the rate. The retardation by added sodium chloride cannot be a common ion effect because trityl chloride was found to hydrolyze instantly in 50% acetone even in the presence of 0.5 *M* sodium chloride.

Such specific salt effects have been observed before in first-order solvolyses. Lucas and Hammett[9] found that the hydrolysis of t-butyl nitrate in 40% water–60% dioxane was strongly accelerated by added sodium perchlorate but slightly retarded by sodium hydroxide, with other ions having intermediate effects paralleling their effect on the activity of water. They determined the freezing points of 0.108 *M* solutions in 40% water–60% dioxane to be $-4.80°$ ($NaClO_4$) *vs.* $-4.65°$ without salt, $-3.92°$ (KNO_3), -3.35 (NaCl), -3.08 ($NaOCOCH_3$), -2.70 (NaOH). They concluded that added sodium hydroxide raises the activity of dioxane but lowers the activity of water. Thus sodium hydroxide seems to "dry" the solvent and therefore may decrease a rate of solvolysis in spite of increasing the ionic strength.

The "drying" explanation was criticized[10] when similar effects were observed in the solvolysis of benzhydryl chloride even in single-component solvents (pure methanol or ethanol). Sodium bromide and iodide produced large accelerations, while sodium alkoxides produced little or no net effect. Ingold proposed that rate depression is possible only with a common product anion (which

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[7] C. G. Swain, D. C. Dittmer and L. E. Kaiser, This Journal, **77**, 3740 (1955).

[8] C. Gardner Swain and R. E. T. Spalding, *ibid.*, **82**, 6104 (1960).

[9] G. R. Lucas and L. P. Hammett, *ibid.*, **64**, 1928 (1942).

[10] O. T. Benfey, E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 2488, 2494 (1952).

captures carbonium ion to regenerate reactant) or with an anion which is the conjugate base of the solvent. The latter anion was considered to impair solvation of the partially formed chloride ion in the transition state through its unique ability to remove protons from solvating solvent molecules.[11] However, it is hard to see how 0.1 *M* alkoxide ion could deprotonate a significant fraction of all the solvent molecules including ones clustered around a partial negative charge. Furthermore, the fact that sodium chloride depresses the rate of hydrolysis of trityl fluoride shows that sodium fluoride and sodium hydroxide are not unique in causing rate depressions with alkyl fluorides in aqueous acetone. Therefore the conclusion that only salts with an anion in common with the reactant or the solvent would give a depression seems to have been the result of investigating too small a range of salts.

The explanation of Lucas and Hammett seems adequate to explain the retardation of hydrolysis of trityl fluoride by added sodium chloride, as due to association between sodium chloride and water. Furthermore the similar retardation of the solvolysis of benzhydryl chloride in one-component alcoholic solvents by added sodium alkoxides[10] may be explained in essentially the same way, as due to association between sodium alkoxide and alcohol, *i.e.*, an activity coefficient effect stabilizing reactants (including solvent) relative to transition state.

Experimental

Materials.—Acetic acid was prepared from Mallinckrodt reagent grade (dichromate test) glacial acetic acid by refluxing for 3 days with an amount of J. T. Baker Chemical Co. reagent grade acetic anhydride equivalent to three or four times the amount of water present. The acetic acid was then separated from the anhydride by distilling through a 4-foot glass-helices column. The concentration of anhydride in the acetic acid was shown to be less than 0.1% by the Kilpi anthranilic acid test.[12]

Ethanol was U. S. Industrial Chemicals Co. U. S. P. absolute ethanol, used without further purification for the runs in aqueous ethanol. For runs in absolute ethanol it was dried by addition of excess sodium metal and ethyl formate in excess of the water and less than equivalent to the sodium. After refluxing for 4 hours, distillation gave ethanol containing less than 0.01% water.[13]

Methanol was Fisher Scientific Co. reagent grade used without further purification.

Acetone was obtained by storing Fisher reagent grade acetone over Drierite and distilling just before use.

The scintillation liquid was made up by dissolving 20 g. of Arapahoe Chemicals scintillation grade 2,5-diphenyloxazole and 50 mg. of Matheson, Coleman and Bell 1,6-diphenylhexatriene in one liter of reagent grade toluene which had been dried over sodium wire.

Sodium hydroxide carbonate-free solutions were made from filtered 50% aqueous sodium hydroxide by diluting with carbonate-free (boiled) distilled water. Sodium acetate was dried by fusing reagent grade trihydrate at 140° for 3 hours.

Trityl chloride was Matheson material, which was recrystallized by solution in 100 ml. of benzene with a little acetyl chloride, and precipitation on addition of 200 ml. of petroleum ether and cooling, m.p. 112–113°.

Trityl acetate was prepared by placing silver acetate (8.4 g., 0.05 mole) in a round-bottom flask with 300 ml. of benzene, and distilling about 100 ml. of benzene to dry both the salt and the solvent. Trityl chloride (14 g., 0.05 mole) was then added, and refluxed for 20 hours. The mixture was filtered, the precipitate washed with ether, and the solvents combined. Most of the solvent was then removed, and the trityl acetate precipitated by addition of petroleum ether. The ester was purified by short path distillation at 1 mm. The trityl acetate was liquid in the pot and collected on the "cold finger" as a solid, m.p. 84°.

Trityl acetate labeled with tritium in the methyl group was prepared in the same manner as the unlabeled except for the use of labeled silver acetate. Silver acetate labeled with tritium in the methyl group was prepared by heating acetic acid (5 ml.), tritiated water (5 ml.) and a few drops of hydrochloric acid as catalyst in a combustion tube for 7 days at 180°. The acetic acid was then neutralized, and silver nitrate added to precipitate the silver acetate, which was filtered and dried.

Trityl fluoride was prepared by submerging 20 g. (0.072 mole) of trityl chloride in anhydrous hydrofluoric acid. A copper beaker was found to be most satisfactory. Stainless steel seemed to impart an especially tenacious yellow color to the final product. The solution was allowed to stand for 30 min., and then the excess hydrofluoric acid was boiled off on a hot-plate, care being taken to keep the temperature below 80°. The brown-yellow crystals that remained were taken up in anhydrous cyclohexane to give a yellow solution. Addition of a few grams of freshly dried potassium fluoride dissipated most of the yellow color. The solution was then cooled, and large almost pure-white rhombohedral crystals formed. The mother liquor was decanted and the crystals were washed twice with pentane at 0°. The crystals were dried under vacuum. The yield of this first crop of crystals was 11.6 g. (62%), m.p. 130.2–104.2°. The mother liquor was then heated with Norit and a few grams of potassium carbonate, and when filtered yielded an almost colorless solution. The solution was then evaporated by blowing dry nitrogen through, but soon became bright yellow. Evaporation was stopped, and the solution was boiled with anhydrous potassium carbonate. After a few minutes the solution became almost colorless. After the solution was evaporated to the correct volume, it was decanted off the potassium carbonate and cooled to promote crystallization. Again large white crystals formed with a yield of 6.3 g., m.p. 103.2–103.7° (lit. m.p. 102.4–103.4°,[14] 101.3-102.0°[4]). The total yield was therefore 17.9 g. (95%). Purity was 93% by titration with thorium nitrate of fluoride ion liberated on hydrolysis; or 93.8% by titration of liberated acid.

Kinetic Procedure with Trityl Acetate.—Initial concentrations of trityl acetate ranged from 0.003 to 0.012 *M*. For exchanges in acetic acid, where initial concentrations of trityl acetate were 0.0027 to 0.0038 *M*, variations of initially added sodium acetate from zero to 0.012 *M* had no effect on the rate. The rate constants reported in Table I are averages; the average deviation was always less than 6%. In all cases the zero point was taken as the time of withdrawal of the first aliquot, and the first-order rate constant was calculated from the half-life. Temperature control in all runs was ± 0.1°.

Intermittent Titrations.—The kinetic procedure for runs with trityl acetate in the seven aqueous alcohol or acetone solvents utilized the method of intermittent titration, already described.[2,4] Rate constants in four of these solvents were reported earlier.[6,14] The runs in 100% ethanol were carried out in excess base (0.010 *M* sodium hydroxide) by quenching 5-ml. aliquots in 20 ml. of ethyl ether. Extraction of the ether with water and titration of the remaining base afforded a measure of the extent of reaction.

Tritium Exchange between Trityl Acetate and Acetic Acid.—For the exchange runs in acetic acid a sufficient quantity of labeled triphenylmethyl acetate was dissolved in 25 ml. of acetic acid held at 25° in a thermostat so that the initial 5-ml. aliquot contained sufficient ester to give a counting rate of about 10,000 counts/min. Aliquots were then

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(11) To quote directly[10]: "We have to assume that the distributed proton defect in a solvent containing lyate ions impairs the solvation of the forming halide ion more than it aids that of the developing carbonium ion. The difference in the detailed condition of the molecules composing the solvation shell of the transition state would then be likely so to influence the energy and entropy of activation as to reduce the reaction rate. We have to assume also that hydrogen ions, on the contrary, do not, in dilute solution, disturb the solvation shells of forming halide ions except through their electrostatic effect."

(12) S. Kilpi, *C. A.*, **35**, 2445 (1945).

(13) G. R. Robertson, "Laboratory Practice of Organic Chemistry," The Macmillan Co., New York, N. Y., 1943, pp. 178, 296; 1954, pp. 300–301.

(14) C. G. Swain, C. B. Scott and K. H. Lohmann, THIS JOURNAL, **75**, 136 (1953).

withdrawn at suitable time intervals, and the ester assayed for tritium. Each aliquot was quenched by dilution by adding it to 35 ml. of toluene in a separatory funnel, and the acetic acid extracted by washing the toluene five times with distilled water. The toluene was dried over magnesium sulfate and counted for tritium. A check that the trityl acetate did not hydrolyze during the extraction of acetic acid was made with unlabeled trityl acetate by dissolving a weighed quantity in acetic acid, treating an aliquot as above, evaporating the toluene and then hydrolyzing the ester in 69.5% methanol. The rate observed was the same as previously measured, and the final titer checked with the calculated figure within 3%.

The liquid scintillation counter used was Tracerlab model CE-1. The correct voltage for the pulse height selector (20 volts) was determined to obtain a maximum for the ratio of "sample counting rate" to "background counting rate." This was determined by counting a sample and a blank at a series of voltages. The voltage used on the photomultiplier tubes was invariably 1650 volts. The efficiency was very dependent on the positioning of the cell holder (one sample was found to vary 15% in counting rate for two different settings), and for comparative counting it was found imperative that this not be disturbed in relation to the two phototubes. Each sample was prepared in the special counting bottles and made up to 65 ml. with 15 ml. of scintillation liquid and extra toluene. It was dark adapted and cooled in the counter for 30 minutes before counting. Counting was usually done over periods of 10 minutes. A coincidence factor correction was shown to be unnecessary at the counting rates used, by measuring the activity of a compound with different size samples and showing that it did not vary significantly over the range used (up to 1200 counts sec.$^{-1}$).

The remote possibility that exchange of the tritium with the solvent could occur *via* some other mechanism than solvolysis was considered. The only likely possibility is enolization of the ester. However, the rate of uptake of bromine (0.010 *M*) by the ester (0.015 *M*), a measure of the rate of enolization, was shown to be negligible during the time for complete exchange of the acetate group (only 0.7% reaction of the ester in 190 min.). A check was also made that the reaction was purely first-order in acetic acid by adding 0.012 *M* acetate ion in the form of sodium acetate to one run. This did not affect the rate.

Kinetic Procedure with Trityl Fluoride.—The initial concentration of trityl fluoride was 0.0040 *M* in all runs. Because the rate of hydrolysis of trityl fluoride is extremely sensitive to small changes in the composition of the solvent even in the region of 50% water, it was necessary to exercise extreme care in making up the solvent solutions. Where indicated in Table III, runs were followed by quenching aliquots with benzene, extracting fluoride ion with water and titrating with 0.01 *N* thorium nitrate as in the study of hydrolysis of benzyl fluoride.[5] Other runs were followed by the method of intermittent titration as described in the previous paper,[2] using sodium hydroxide in 50% water–50% acetone as the titrating solution.

[Contribution from the Department of Chemistry, Massachusetts Institute of Technology, Cambridge 39, Mass.]

III. Mechanism of Acid Catalysis of the Hydrolysis of Benzyl Fluoride[1,2]

By C. Gardner Swain and Richard E. T. Spalding

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The rate of solvolysis of benzyl fluoride in 90% water–10% acetone solution containing 0.1–6.0 *M* perchloric acid or 0.25–3.3 *M* sulfuric acid at 50° is closely proportional to the Hammett acidity function h_0. The rate in 1 *M* perchloric acid containing 10% dioxane was unchanged when H_2O was replaced by D_2O. These results exclude a transition state resembling benzyl fluoride or benzyl cation or including hydronium ion or tightly bound water; they are consistent with a transition state structurally close to $C_6H_5CH_2FH^+$.

Acid catalysis has been observed in solvolyses of benzyl fluoride,[3] *t*-butyl, *t*-amyl and cyclohexyl fluorides,[4] and benzoyl fluoride.[5] Alkyl chlorides, bromides and iodides rarely show acid catalysis, although a few examples have been observed.[6] Rate-determining steps proposed were direct reaction with hydronium ion to give a carbonium ion (mechanism I)[4–6] or reaction of a hydrogen-bonded halide-hydronium ion complex with solvent (II).[3]

$$RF + H_3O^{\oplus} \longrightarrow R^{\oplus} + HF + H_2O \qquad (I)$$

$$H_2O + RF\text{--}H_3O^{\oplus} \longrightarrow ROH_2^{\oplus} + HF + H_2O \qquad (II)$$

Figure 1 and Table I show that the rate of solvolysis of benzyl fluoride in 90% water–10% acetone containing 0.1-6 *M* perchloric acid or 0.25–3.3 *M* sulfuric acid at 50° is not proportional to hydronium ion concentration, but is very nearly proportional to the Hammett acidity function h_0.[7–11] The slope of a plot of the logarithm of the rate *vs.* H_0 ($= -\log h_0$) is 1.08.[12] The good first-order kinetics contradict a mass effect by HF on the rate.

The transition state must be close to $C_6H_5CH_2FH^+$ in structure (with water only loosely bound) to explain this dependence on acidity, *i.e.*, it must differ from benzyl fluoride in much the same way that a Hammett indicator acid (anilinium ion) differs from the indicator base (aniline). It cannot be close to $C_6H_5CH_2^+$, $C_6H_5CH_2^+\text{--}FH$, $C_6H_5CH_2F$, $C_6H_5CH_2F\text{--}H_3O^+$ or $C_6H_5CH_2OH_2^+$ in structure for the following reasons. If it were close to $C_6H_5CH_2^+$ or $C_6H_5CH_2^+\text{--}FH$, the rate should be proportional

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[1] For related work on triphenylmethyl fluoride, *cf.* C. G. Swain, T. E. C. Knee and A. MacLachlan, This Journal, **82**, 6101 (1960).

[2] For complete experimental details *cf.* R. E. T. Spalding, Ph.D. Thesis in Organic Chemistry, M.I.T., August, 1954.

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