withdrawn at suitable time intervals, and the ester assayed for tritium.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]

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

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

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 $C_6H_5CH_2^+$, $C_6H_5CH_2^+{-}{-}FH$, $C_6H_5CH_2F$, $C_6H_5CH_2F{-}{-}H_3O^+$ or $C_6H_5CH_2OH_2^+$ in structure for the following reasons. If it were close to $C_6H_5CH_2^+$ or $C_6H_5CH_2^+{-}{-}FH$, 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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(4) N. B. Chapman and J. T. Levy, *J. Chem. Soc.*, 1677 (1952).

(5) C. W. L. Bevan and R. F. Hudson, *ibid.*, 2187 (1953).

(6) R. Leimu and P. Salomaa, *Acta Chem. Scand.*, **1**, 353 (1974); H. Hart and F. A. Cassis, THIS JOURNAL, **76**, 1634 (1954).

(7) L. P. Hammett and A. J. Deyrup, *ibid.*, **54**, 2721 (1932); L. P. Hammett and M. A. Paul, *ibid.*, **56**, 827 (1934); L. Zucker and L. P. Hammett, *ibid.*, **61**, 2791 (1939); L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 273.

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(9) M. A. Paul and F. A. Long, *Chem. Revs.*, **57**, 1 (1957).

(10) F. A. Long and M. A. Paul, *ibid.*, **57**, 935 (1957).

(11) N. C. Deno and C. Perizzolo, THIS JOURNAL, **79**, 1345 (1957); R. W. Taft, Jr., N. C. Deno and P. S. Skell, *Ann. Rev. Phys. Chem.*, **9**, 303 (1958); N. C. Deno, H. E. Berkheimer, W. L. Evans and H. J. Peterson, THIS JOURNAL, **81**, 2344 (1959).

(12) This small deviation from unity may be due to comparison with H_0 values at 25° in water rather than at 50° in 90% water–10% acetone. Values of H_0 for H_2SO_4 in water at 50° have been found to differ by less than 0.08 from values at 25° over this range.[8] However, the introduction of 10% dioxane at 25° is estimated to give a slope of 1.10 for H_0 in 10% dioxane *vs.* H_0 in water from 0.25 to 4.0 *M* $HClO_4$, interpolating from data for 40% dioxane obtaind by C. A. Bunton, J. B. Ley, A. J. Rhind-Tutt and C. A. Vernon, *J. Chem. Soc.*, 2327 (1957), and ref. 9, p. 31. This is close to the 1.08 factor observed.

not to h_0 but instead to h_R (the acidity function also called j_0 and c_0, defined as $(c_{R^+}/c_{ROH})K_{R^+}$, and measured using equilibria between arylmethanols and arylcarbonium ions), which changes roughly as the square of h_0; if it were close to $C_6H_5CH_2F + H_3O^+$ or $C_6H_5CH_2F\text{--}H_3O^+$ or otherwise involved hydronium ion, the rate should be proportional not to h_0 but to $[H_3O^+]$, which changes more slowly than h_0 with acidity; and it cannot be close to $C_6H_5CH_2OH_2^+$ because this is as stable as the reactants.

Mechanisms excluded by these results include ones with the following rate-determining steps.

$$C_6H_5CH_2F + H_3O^{\oplus} \longrightarrow C_6H_5CH_2^{\oplus} + HF + H_2O \quad (I)$$

$$C_6H_5CH_2F\text{--}H_3O^{\oplus} \longrightarrow C_6H_5CH_2^{\oplus} + HF + H_2O \quad (III)$$

$$(\text{or } C_6H_5CH_2^{\oplus}\text{--}FH + H_2O)$$

$$C_6H_5CH_2^{\oplus} + H_2O \longrightarrow C_6H_5CH_2OH_2^{\oplus} \quad (IV)$$

$$C_6H_5CH_2^{\oplus}\text{--}FH + H_2O \longrightarrow C_6H_5CH_2OH_2^{\oplus} + HF \quad (V)$$

$$C_6H_5CH_2F + H_3O^{\oplus} \longrightarrow C_6H_5CH_2OH_2^{\oplus} + HF \quad (VI)$$

$$C_6H_5CH_2F\text{--}H_3O^{\oplus} \longrightarrow C_6H_5CH_2OH_2^{\oplus} + HF \quad (VII)$$

$$H_2O + C_6H_5CH_2F + H_3O^{\oplus} \longrightarrow C_6H_5CH_2OH_2^{\oplus} + HF + H_2O \quad (VIII)$$

$$H_2O + C_6H_5CH_2F\text{--}H_3O^{\oplus} \longrightarrow C_6H_5CH_2OH_2^{\oplus} + HF + H_2O \quad (II)$$

I, III, IV and V would necessarily have transition states close to the very unstable carbonium ion intermediate and should follow h_R; VI and VII would not have transition states close to $C_6H_5CH_2OH_2^+$ (since it is of low free energy) and should follow H_3O^+ concentration; VIII and II should show a still slower increase of rate with acid concentration because of the slightly decreasing water activity with increasing acidity.

Mechanisms consistent with these results include ones with the following rate-determining steps

$$C_6H_5CH_2F + H_3O^{\oplus} \longrightarrow C_6H_5CH_2FH^{\oplus} + H_2O \quad (IX)$$

$$C_6H_5CH_2F\text{--}H_3O^{\oplus} \longrightarrow C_6H_5CH_2FH^{\oplus} + H_2O \quad (X)$$

$$C_6H_5CH_2FH^{\oplus} \longrightarrow C_6H_5CH_2^{\oplus} + HF \quad (XI)$$

$$(\text{or } C_6H_5CH_2^{\oplus}\text{--}FH)$$

$$C_6H_5CH_2FH^{\oplus} + H_2O \longrightarrow C_6H_5CH_2OH_2^{\oplus} + FH \quad (XII)$$

provided that the transition state in each case comes close to $C_6H_5CH_2FH^+$, *i.e.*, water molecules are only loosely bonded to the organic molecule at the transition state. This is possible for all of these steps because $C_6H_5CH_2FH^+$ is certainly an intermediate of high energy compared to $C_6H_5CH_2F$, $C_6H_5CH_2F\text{--}H_3O^+$ or $C_6H_5CH_2OH_2^+$ and we cannot exclude the possibility that it may be more reactive than $C_6H_5CH_2^+$. At the present time, we tend to favor XI as the actual rate-determining step. The reaction of phenylcarbonium ion with water and the ionization of hydrogen fluoride then occur in subsequent fast steps.

Triphenylmethyl (trityl) fluoride may also react by mechanism XI in its acid-catalyzed hydrolysis, as suggested in the previous paper.[1] It is known to give triphenylcarbonium ion as an intermediate. It exhibited specific hydrogen-ion catalysis in dilute water solution. Reactions showing specific hydrogen-ion catalysis are usually h_0 dependent in strong acid media. On the other hand, reactions showing general acid catalysis usually increase in rate more slowly with acidity in strong acid media, because water is then involved as a base in the rate-determining step. For the acid-catalyzed hydrolysis of methyl fluoride, we expect that the rate will be found to increase much more slowly than h_0, because $CH_3^{\oplus}$, lacking any stabilization by resonance, is not a probable reaction intermediate, hence a nucleophilic attack by water should be required in the rate-determining step, with the water strongly bonded at the transition state.[13]

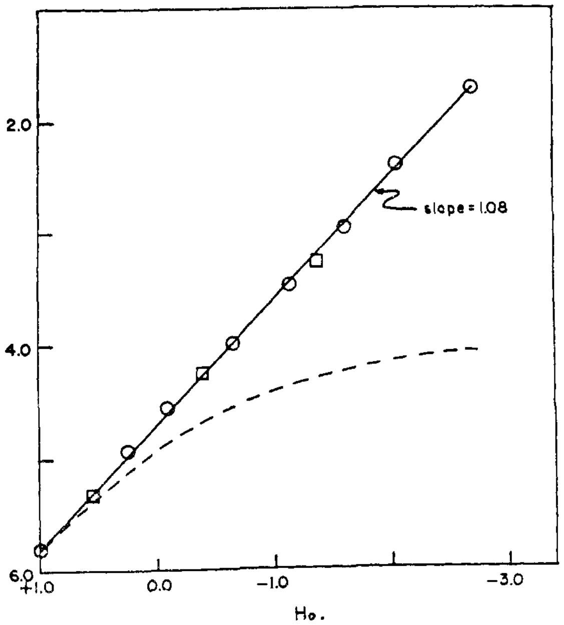

Fig. 1.—Log k_a for hydrolysis of benzyl fluoride *vs.* H_0 (for points and solid line) or $-\log\ [H_3O^+]$ (for dashed line): ○, in $HClO_4$; □, in H_2SO_4.

TABLE I

SOLVOLYSIS OF BENZYL FLUORIDE IN 90% WATER–10% ACETONE AT 50.0°

Acid, *M*	$k \times 10^{6,a}$ sec.$^{-1}$	$k_a \times 10^{6,b}$ sec.$^{-1}$	$\log\left(\frac{k_a}{[H_3O^+]}\right)$	$H_0{}^c$	$\log\left(\frac{k_a}{h_0}\right)$
None	0.34	..	...	...	...
$HClO_4$, 0.10	1.9	1.6	−4.8	1.0	−4.8
$HClO_4$, 0.50	12.2	11.9	−4.62	0.26	−4.66
$HClO_4$, 1.00	28.7	28.4	−4.55	− .12	−4.66
$HClO_4$, 2.00	102.5	102	−4.29	− .66	−4.65
$HClO_4$, 3.00	351	351	−3.93	−1.13	−4.58
$HClO_4$, 4.00	1160	1160	−3.54	−1.59	−4.53
$HClO_4$, 5.00	4200	4200	−3.08	−2.06	−4.44
$HClO_4$, 6.00	20000	20000	−2.5	−2.70	−4.4
H_2SO_4, 0.25	5.6	5.3	−4.7	+0.56	−4.7
H_2SO_4, 1.50	59.8	59.5	−4.40	−0.43	−4.66
H_2SO_4, 3.30	452	452	−3.86	−1.37	−4.72

[a] Total first-order rate constant. [b] Acid-catalyzed part. [c] $H_0 = -\log h_0$ in water at 25°.[7]

The isotope effect (k_H/k_D) is unity within experimental error. Using 0.0088–0.0097 *M* benzyl fluoride and 1.00 *M* perchloric acid at 50°, the average rate constant from five runs in 90% water–10% dioxane was 3.09×10^{-5} sec.$^{-1}$; the average rate constant from two runs in 90% heavy water–10% dioxane where the total exchangeable hydrogen in the solution was 94.1 mole % D was 3.04×10^{-5}

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(13) For detailed consideration of acid-catalyzed reactions sensitive to water activity in strong acid media, *cf.* C. G. Swain and A. S. Rosenberg, paper submitted for publication.

sec.$^{-1}$. This isotope effect is inconsistent with mechanisms VI, VII, VIII and II but possible for the other mechanisms considered, including IX-XII.[14]

Comparable data on benzyl chloride are shown in Table II. Benzyl chloride is about 300 times more reactive than benzyl fluoride toward hydrolysis in the absence of acid, but addition of perchloric acid up to 4 *M* decreases its rate. Sodium perchlorate produces a salt effect in the same direction. But, whereas the rate of hydrolysis decreases continuously as the sodium perchlorate concentration increases up to 6 *M* and log *k* is a linear function of the ionic strength, the rate of hydrolysis passes through a minimum in 4 *M* perchloric acid, the rate in 6 *M* perchloric acid being slightly greater than 1 *M*. This effect is not observed on the rate of hydrolysis of methyl bromide in acid solutions (Table III) and is, perhaps, due to some contribution from a mechanism like IX-XII.

TABLE II

SOLVOLYSIS OF BENZYL CHLORIDE IN 90% WATER-10% ACETONE AT 49.8°

$HClO_4$, *M*	$NaClO_4$, *M*	$k \times 10^5$, sec.$^{-1}$	$HClO_4$, *M*	$NaClO_4$, *M*	$k \times 10^5$, sec.$^{-1}$
0.000	0.00	10.7	6.00	0.00	7.75
.099	.00	10.3	0.00	0.50	10.1
.496	.00	9.47	.00	1.00	9.45
1.00	.00	7.32	.00	2.00	8.00
2.00	.00	6.42	.00	4.00	6.19
4.00	.00	5.72	.00	6.00	4.48

TABLE III

SOLVOLYSIS OF METHYL BROMIDE IN 95% WATER-5% ACETONE AT 50°

$HClO_4$, *M*	0.00	0.47	0.99	1.98	6.04
$k \times 10^6$, sec.$^{-1}$	9.17	7.91	6.54	4.47	0.67

The effect of temperature on the solvolysis of benzyl fluoride is shown in Table IV. The data give linear plots of log (k/T) *vs.* $1/T$, where *T* is °K. For the uncatalyzed reaction, $\Delta H^* = 19.1$ kcal. mole^{-1} and $\Delta S^* = -29.1$ cal. deg.$^{-1}$ mole^{-1} at 50°. For the acid-catalyzed reaction, $\Delta H^* = 21.2$ kcal mole^{-1} and $\Delta S^* = -14.1$ cal. deg.$^{-1}$ mole^{-1} at 50°.

TABLE IV

SOLVOLYSIS OF BENZYL FLUORIDE IN 90% WATER-10% ACETONE AT DIFFERENT TEMPERATURES

$HClO_4$, *M*	Temp., °C.	$k \times 10^6$, sec.$^{-1}$	$HClO_4$, *M*	Temp., °C.	$k \times 10^6$, sec.$^{-1}$
0.00	50.0	0.34	3.00	25.1	19.9
.00	75.0	3.5	3.00	50.0	351
.00	100.5	21.9	3.00	75.0	3930

Experimental

Materials.—Benzyl fluoride was prepared from benzyl chloride according to the procedure of Ingold and Ingold.[15] The alcoholic solution of trimethylamine used in this preparation was prepared from Eastman trimethylamine hydrochloride according to the procedure of Adams and Brown.[16] Benzyl fluoride has a marked tendency to polymerize violently when distilled in Pyrex glassware. This tendency was greatly reduced by adding a few drops of pyridine to the ether extract of benzyl fluoride as recommended by Bernstein, Roth and Miller,[17] and drying the solution for a few days over calcium hydride. As a further precaution all of the Pyrex glassware used in the distillation of the product was carefully fire-polished to remove all scratches, since the polymerization reaction appeared to be initiated at faults on the surface of the glass. After removal of the ether, the benzyl fluoride was distilled under reduced pressure and the fraction distilling at 41–42° at 17–18 mm. was collected. The product was stored in a fire-polished, glass-stoppered bottle in a desiccator over calcium hydride. The benzyl fluoride appeared to be stable under these conditions for several weeks.

Benzyl chloride was redistilled Mallinckrodt reagent grade, b.p. 75.0–75.5° (21 mm.).

Methyl bromide was Dow industrial grade (99.5% pure). Stock solutions of methyl bromide in dry acetone were prepared by passing methyl bromide vapor through a drying tube filled with calcium chloride, condensing the vapor on a cold finger cooled by a Dry Ice–acetone mixture, and collecting the condensate in the dry acetone.

Acetone was Mallinckrodt reagent grade used without further purification in making up water–acetone solvent mixtures. For stock solutions of the alkyl halides, it was dried over Drierite for several weeks and distilled just before use.

Dioxane was commercial grade purified to eliminate acetals and peroxides.[18]

Heavy water was Stuart Oxygen Co. 99.5% deuterium oxide, O^{18} enriched (> 1.4%).

Sodium perchlorate was G. F. Smith Chemical Co. anhydrous reagent. Perchloric acid and other inorganic chemicals were reagent grade.

Product.—Benzyl alcohol was isolated from a run in 6 *M* perchloric acid. It yielded a 3,5-dinitrobenzoate in 70.6% yield after purification, based on the weight of benzyl fluoride solvolyzed, which produced no depression in the m.p. of an authentic sample of benzyl 3,5-dinitrobenzoate. The details of the isolation follow. One liter of a 90% water–10% acetone solution, 0.0098 *M* in benzyl fluoride and 6 *M* in perchloric acid, was heated at 50° for 10 min. Analysis of an aliquot for fluoride ion then indicated a 97% yield of fluoride ion. The rest of the reaction mixture was cooled rapidly in an ice-bath and neutralized by adding solid sodium carbonate. The solution was finally saturated with sodium carbonate and extracted with five 200-ml. portions of ether. After drying the ether extract over magnesium sulfate the ether was distilled, leaving a light yellow liquid residue weighing 1.25 g. This was dissolved in 5 ml. of dry pyridine, and 2.3 g. of freshly prepared 3,5-dinitrobenzoyl chloride added. After the initially vigorous reaction had subsided, the mixture was poured into 20 ml. of water. The resulting precipitate was filtered off and dried overnight. The crude product, m.p. 101–103°, weighed 2.61 g. Recrystallization once from alcohol and once from ligroin yielded 2.09 g., m.p. 114.0–114.6°, reported[19] 114–115°.

Analysis for Fluoride Ion.—The method of determining fluoride ion produced by the solvolysis of benzyl fluoride was essentially that of Ballczo.[20] To 50 ml. of a solution containing from 0.1 to 6.0 mg. of fluoride ion was added 1.00 ml. of 0.05% sodium alizarin sulfonate indicator solution. The *p*H was adjusted with 2% aqueous sodium hydroxide and 1:200 aqueous perchloric acid until the solution was just acid to the indicator. Buffer solution (1.00 ml. of a 0.5 *M* chloroacetic acid, 0.5 *M* sodium chloroacetate solution) and 4.00 ml. of 0.001% methylene blue hydrochloride indicator solution were added and the sample titrated with 0.05 *N* thorium nitrate solution. Near the end-point the green color of the solution gradually faded to a neutral gray. On further addition of thorium nitrate the solution acquired a purple-gray coloration. The end-point was taken when the solution first became purple-gray. It was found that the volume of thorium nitrate used was not directly proportional to the concentration of fluoride ion over the

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[14] K. B. Wiberg, *Chem. Revs.*, **55**, 713 (1955); C. G. Swain, A. J. DiMilo and J. P. Cordner, This Journal, **80**, 5983 (1958); C. G. Swain and R. F. W. Bader, *Tetrahedron*, in press; C. G. Swain, A. D. Ketley and R. F. W. Bader, This Journal, **81**, 2353 (1959).

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[17] J. Bernstein, J. S. Roth and W. T. Miller, Jr., This Journal, **70**, 2310 (1948).

[18] L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., Boston, Mass., 3rd ed., 1955, p. 285, method a.

[19] O. T. Benfey, J. R. Stanmyer, Jr., B. Milligan and E. W. Westhead, Jr., *J. Org. Chem.*, **20**, 1777 (1955).

[20] H. Ballczo, *Osterr. Chem.-Ztg.*, **50**, 146 (1949); *C. A.*, **43**, 8960 (1949).

range of concentrations encountered in the kinetic runs. However, after calibration against standard solutions prepared from Merck reagent potassium fluoride which had been dried overnight at 120°, this method permitted the determination of fluoride ion with an average error of 0.7%.

The presence of large amounts of sodium perchlorate or sodium sulfate interferred seriously with the determination of fluoride ion by the above method. To separate fluoride ion from solutions containing either of these salts a modification of the method developed by Willard and Winter was used.[21] The method involves steam distilling fluoride as fluosilicic acid from a concentrated solution of perchloric acid. Aliquots containing sodium fluoride and sodium perchlorate were rinsed into a 125-ml. distilling flask of the type described by Willard and Diehl[22] with the minimum amount of distilled water. Several glass beads and 10 ml. of 60% perchloric acid were added to the solution, which was distilled until the temperature of the boiling liquid reached 145° as measured by a thermometer inserted in a well extending nearly to the bottom of the distilling flask. Steam was then passed through the solution slowly while the temperature was held between 145° and 150° by adjusting a small flame beneath the flask until 50–60 ml. of distillate had been collected. The fluoride in the distillate was titrated with standard thorium nitrate as described above, with an over-all average error of 1.3% on samples containing 0.2–2.4 mg. of fluoride ion and up to 12.6 g. of sodium perchlorate. Increasing the volume of distillate collected did not improve the separation appreciably, while raising the temperature at which the distillation was carried out had a detrimental effect. Apparently at higher temperatures a sufficient quantity of perchloric acid was carried over into the distillate to affect seriously the determination of fluoride with thorium nitrate.

The presence of larger amounts of sodium perchlorate in the aliquots retarded the distillation of fluosilicic acid, producing large negative errors in the separation and determination of fluoride by the above procedure. However, by adding 10 ml. of 71% perchloric acid to the aliquots containing fluoride and sodium perchlorate and steam distilling the fluosilicic acid at temperatures between 155° and 160°, fluoride was separated from amounts of sodium perchlorate ranging from 12.6 to 19.3 g. and determined with accuracy comparable to that attained when smaller amounts of sodium perchlorate were present.

Fluoride was separated successfully from sodium sulfate by adding 10 ml. of concentrated sulfuric acid to the solution containing sodium fluoride and sodium sulfate and steam distilling the fluosilicic acid at temperatures between 160° and 165°.

Kinetic Procedure.—With benzyl fluoride, fresh stock solutions were prepared each day by weighing a sample into a volumetric flask and making up to volume with dry acetone. An aliquot of this solution was added to the other premixed components in a glass-stoppered Pyrex flask at 50° to initiate reaction. The final solution was 10% acetone based on volumes at 25° before mixing. Initial concentrations of benzyl fluoride were 0.003–0.011 *M*. Aliquots were withdrawn from time to time and immediately extracted with 20 ml. of ice-cold chloroform to quench the reaction. The chloroform layer was drawn off and extracted with a small volume of 0.5 *M* aqueous sodium hydroxide. The sodium hydroxide layer was added to the aqueous layer from the first extraction and the combined solutions made basic to phenolphthalein indicator with 50% aqueous sodium hydroxide. The basic solution was then evaporated nearly to dryness and the residue rinsed into a 125-ml. steam-distillation flask with a minimum amount of distilled water. Fluoride was then distilled and determined by titration with standard thorium nitrate solution as described previously. The reactions at 75° and 100° in the absence of added acid were carried out in sealed Pyrex test-tubes.

For comparison of light and heavy water, dioxane was used instead of acetone to avoid exchange of D_2O with acetone. Dioxane (7.50 ml.), 6.35 ml. of 11.82 *M* perchloric acid and 61.15 ml. of H_2O or D_2O were measured into a 125-ml. erlenmeyer flask. After thermostat temperature had been reached, 3.00 ml. of 0.2613 *M* benzyl fluoride in dry dioxane was added, producing a solution 10% in dioxane (by volume before mixing), and 1.00 *M* in perchloric acid in which 94.1 mole % of the total exchangeable hydrogen was deuterium.

In all cases the reactions followed a first-order rate law accurately through 80–90% reaction. The % reaction was based on the titer at infinite time (10 or more half-lives) as 100%. This final titer was generally within 3.5% of the theoretical based on the weight of benzyl fluoride used. However, in the runs in 6 *M* perchloric acid, the final titer was only 92.5% of that calculated and in 3.3 *M* sulfuric it was only 95.5% of that calculated.

All rate constants reported with benzyl fluoride or chloride are averages of at least two and usually three or more separate kinetic runs. The average deviation was always less than 6% and averaged less than 2%.

With benzyl chloride kinetic runs were made in the same way as those for benzyl fluoride. Kinetic runs for methyl bromide were carried out in sealed Pyrex test-tubes. Initial concentrations were 0.0039–0.0057 *M* for benzyl chloride and 0.0099–0.011 *M* for methyl bromide. Aliquots were extracted with chloroform or carbon tetrachloride and the aqueous layer analyzed for chloride or bromide ion by titration with standard mercuric nitrate solution using diphenyl carbazide as indicator.[23] The accuracy of this method of determining chloride or bromide was not affected by the presence of large amounts of sodium perchlorate.

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[21] H. H. Willard and O. B. Winter, *Ind. Eng. Chem., Anal. Ed.*, **5**, 7 (1933).

[22] H. H. Willard and H. Diehl, "Advanced Quantitative Analysis," D. Van Nostrand Company, Inc., New York, N. Y., 1943, p. 273.

[23] I. Roberts, *Ind. Eng. Chem., Anal. Ed.*, **8**, 365 (1936).