singlet shifted by addition of CF_3COOH (OH), τ 5.2 [triplet, $CH_2CH(OCH_3)_2$], 6.58 (singlet, 2-OCH_3), 7.77 [doublet, -C-CH_2-$CH(OCH_3)_2$].

Anal. Calcd for $C_7H_{10}F_6O_3$: C, 32.82; H, 3.94; F, 44.50. Found: C, 32.97; H, 4.17; F, 44.72.

5-Dimethoxymethyl-2,2,4,4-tetrakis(trifluoromethyl)-1,3-dioxone (XXII).—Acrolein dimethyl acetal (30.6 g, 0.3 mole) and HFA (100.0 g, 0.6 mole) were heated in a bomb at 150° for 8 hr. The liquid product (86.0 g) was fractionated to give 24.4 g of a low boiler, 11.9 g (9.1%) of XXII, and 11.1 g of a polymeric residue. Compound XXII was purified by gas chromatography using a 6-ft biwall column packed with cyclohexanedimethanol succinate on Chromosorb P at 125° (retention time 3.5 min) to remove trace impurities: $n^{25}D$ 1.3362. There was no hydrogen uptake in microhydrogenation, thus ruling out structures with unsaturation. The infrared spectrum contained no OH, C=C, or C=O bands.

The proton nmr was in agreement with the proposed structure, showing a doublet at τ 4.25 (relative area 1) [H-C(C)-(O-)$_2$], a doublet at 5.75 (relative area 2) (O-CH_2-C), a multiplet at 6.20 (relative area 1) (H-C(-C)$_3$), and two singlets at 6.33 and 6.44 (relative area 3 each) (-O-CH_3).

The mass spectrum shows a parent ion at *m/e* 434 as well as the following fragments which are in agreement with the proposed structure: *m/e* 403 (parent ion − $[CH_3O]^+$), 365 (parent ion − $[CF_3]^+$), 268 (parent ion − $[(CF_3)_2CO]^+$), 238 ($[(CH_3O)_2CH-CH-C(CF_3)_2]^+$), 180 ($[C(CF_3)_2O-CH_2]^+$), 75 ($[(CH_3)_2CH]^+$).

Anal. Calcd for $C_{11}H_{10}F_{12}O_4$: C, 30.43; H, 2.32; F, 52.51; mol wt, 434. Found: C, 30.74; H, 2.52; F, 52.32; mol wt (freezing point in benzene), 424.

The Hydrolysis of Acetyl Fluoride

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The hydrolysis of acetyl fluoride can be followed kinetically in water by using a pH-Stat. For the spontaneous hydrolysis the activation energy is 12.5 kcal mole^{-1}, and activation entropy is −27 eu. Hydrogen and hydroxide ions catalyze hydrolysis. Uni-univalent salts of the strong acids retard hydrolysis, but sulfates assist it; magnesium and copper ions have little effect. Sodium fluoride is a general base catalyst, and sodium formate and pyridine catalyze hydrolysis by generating the more reactive acetyl derivatives. Sodium acetate generates the less reactive acetic anhydride and retards hydrolysis slightly. The hydrolysis is very similar mechanistically to those of the carboxylic anhydrides, but acetyl fluoride is more reactive than acetic anhydride in the acid, basic, and spontaneous hydrolyses.

In the course of recent work we have found that acetyl fluoride is an intermediate in the hydrolysis of acetic anhydride catalyzed by fluoride ion. We, therefore, measured the rate of its hydrolysis in water, because the only studies on this reaction had been made using aqueous acetone as solvent,[1] and our investigation has been extended to cover the kinetic effects of added reagents in order to elucidate the mechanistic details of the hydrolysis of acetyl fluoride.

Experimental Section

Materials.—Acetyl fluoride was prepared from acetyl chloride and zinc fluoride, and purified by repeated redistillation from sodium fluoride, and was stored in a polyethylene bottle under refrigeration.[1] Pyridine was dried over KOH and fractionally distilled and 2,6-lutidine, purified by forming the urea complex,[2] was generously supplied by Dr. R. H. DeWolfe. Inorganic salts were commercial samples, dried before use.

Kinetics.—The hydrolysis was followed by use of a pH-Stat.[3,4] A Sargent model S-30240 was used, and either disodium hydrogen or trisodium phosphate was used as titrant, as recommended by others.[3] When the titrant was sodium hydroxide the rate constants were erratic, and slightly high, because hydroxide ion reacts rapidly with acetyl fluoride.

For temperatures <15° a jacketed cell was used with magnetic stirring, and the temperature was maintained to 0.1° by circulating water from a constant temperature bath. Temperatures >15° were controlled by a thermistor-regulated constant-temperature block on the pH-Stat. For reactions at pH >7 carbon dioxide was excluded by passing a slow stream of nitrogen over the surface of the solution. Control experiments at pH <7 showed that the reaction rate was unaffected by this nitrogen stream, although bubbling it through the solution tended to remove some acetyl fluoride. The pH-Stat was calibrated at the temperature of the kinetic run using phosphate and phthalate buffers. The pH of the reaction solution was remeasured after each experiment, and the kinetic results were not used if the pH variation was >0.02. The calibration of the pH-Stat varied by <0.02 during-1 day.

Reaction was started by adding *ca.* 1/200 ml of a 50% solution of acetyl fluoride in dry dioxane from a hypodermic syringe. The initial concentration of acetyl fluoride was in the range 0.01 to 0.04 *M*. The first-order rate constants, k_ψ, were independent of the concentrations of acetyl fluoride and of the phosphate titrants. For the faster runs the speed of response of the pH-Stat is no longer very much greater than the reaction rate, it is then necessary to use low concentrations of acetyl fluoride, and so decrease the speed of the moving plunger in the buret of the pH-Stat. By this expedient we could follow reactions with half-lives down to *ca.* 1 min.

The values of k_ψ were calculated using the integrated first-order rate equation or Guggenheim's modification of it.[5]

Results

The values of k_ψ in the absence of added reagents are given in Table I, and are plotted *vs.* pH in Figure 1. The hydrolysis is catalyzed by hydrogen and hydroxide ions, and there is an appreciable spontaneous hydrolysis, and k_ψ follows the equation

$$k_\psi = k_H[\overset{+}{H}] + k_W + k_{OH}[\overset{-}{O}H]$$

At 0.4° $10^3\ k_W = 2.95\ sec^{-1}$, and calculating the approximate concentrations of hydrogen and hydroxide ions at 0.4° from the relations

$$pH = -\log [\overset{+}{H}],\ \text{and}\ 14.93 - pH = \log [\overset{-}{O}H]$$

we estimate $k_H = 0.66$ l. mole^{-1} sec^{-1}, and $k_{OH} = 5.7 \times 10^4$ l. mole^{-1} sec^{-1} (from a least-squares plot of k_ψ *vs.* $[\overset{-}{O}H]$).

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[1] C. G. Swain and C. B. Scott, *J. Am. Chem. Soc.*, **75**, 246 (1953).

[2] A. R. Butler and V. Gold, *J. Chem. Soc.*, 4362 (1961).

[3] M. L. Bender and M. S. Feng, *J. Am. Chem. Soc.*, **82**, 6318 (1960); L. Eberson, *Acta. Chem. Scand.*, **18**, 534 (1964).

[4] J. F. Kirsch and W. P. Jencks, *J. Am. Chem. Soc.*, **86**, 837 (1964).

[5] E. A. Guggenheim, *Phil. Mag.*, **2**, 538 (1926).

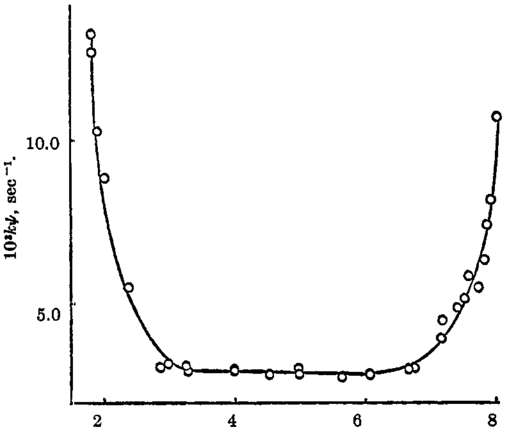


Figure 1.—Plot of k_ψ *vs.* pH for the hydrolysis of acetyl fluoride.

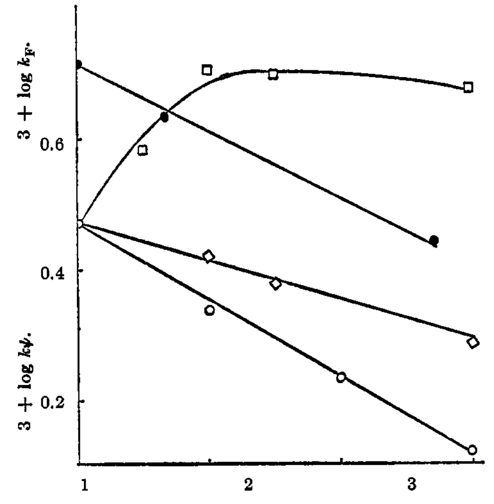


Figure 2.—Effects of salts of strong acids on the spontaneous and fluoride ion catalyzed hydrolyses of acetyl fluoride. ◇, NaCl; □, Na_2SO_4; ○, $NaClO_4$; ●, $NaClO_4$ on the fluoride ion catalyzed hydrolysis.

For the spontaneous hydrolysis the activation energy is 12.5 kcal mole^{-1}, and the entropy of activation is −27 eu, (calculated for 25°).

The values of k_ψ in the presence of electrolytes are given in Table II and III, and log k_ψ is plotted *vs.* ionic strength in Figure 2 for salts of the strong acids. For sodium chloride and perchlorate

$$\log k_\psi{}^s = \log k_\psi{}^0 - bI$$

and $b = 0.06$ for sodium chloride, and 0.11 for sodium perchlorate. (The superscripts refer to reactions in the presence and absence of salt.) Sodium sulfate assists hydrolysis, but the rate constants rise sharply to a maximum, and then decrease slightly. The rate constants with added copper sulfate or magnesium chloride are similar to those for the sodium salts, showing that neither magnesium nor copper ions act as electrophilic catalysts. Salts of the weak acids behave quite differently. Sodium fluoride and formate assist hydrolysis, and plots of k_ψ *vs.* salt concentration are linear (Figure 3). Sodium acetate slightly retards hydrolysis (Table III).

The addition of sodium perchlorate decreases the rate of the fluoride-catalyzed hydrolysis just as it retards the spontaneous hydrolysis. The rate constants are given

TABLE I

HYDROLYSIS OF ACETYL FLUORIDE AT pH 1.8–8.0

Temp, °C	pH[a]	10^3k_ψ, sec^{-1}
0.4	1.80	13.2
0.4	1.80	12.7
0.4	1.90	10.3
0.4	2.00	8.90
0.4	2.40	5.50
0.4	2.80	3.01
0.4	3.00	3.12
0.4	3.26	3.06
0.4	3.30	2.82
0.4	4.00	3.02
0.4	4.00	3.04[b]
0.4	4.53	2.90
0.4	5.00	3.13
0.4	5.00	3.04[b]
0.4	5.00	2.93[c]
0.4	5.66	2.75
0.4	6.00	2.96
0.4	6.70	3.06
0.4	6.80	3.10[c]
0.4	7.20	4.15
0.4	7.20	4.62[c]
0.4	7.40	4.95[c]
0.4	7.50	5.20[c]
0.4	7.75	5.60[c]
0.4	7.80	6.35[c]
0.4	7.90	8.20[c]
0.4	8.00	10.8[c]
5.8	5.00	5.39
5.8	6.00	5.32
11.9	3.00	6.95
11.9	4.00	7.32
11.9	4.50	6.85[b]
11.9	5.00	7.26
11.9	6.00	7.40
11.9	6.50	7.46
14.3	3.30	9.00
14.3	5.40	9.27
18.8	3.00	11.5
18.8	4.00	10.9
18.8	6.30	12.0

[a] Titrant 0.1 *N* Na_2HPO_4 unless specified. [b] Titrant 0.01 *N* Na_2HPO_4. [c] Titrant 0.1 *N* Na_3PO_4.

TABLE II

EFFECTS OF SALTS OF THE STRONG ACIDS[a]

Salt	[Salt], *M*	10^3k_ψ, sec^{-1}
...	...	2.95
NaCl	1.00	2.66
	1.50	2.38
	3.00	1.93
$NaClO_4$	1.00	2.15
	2.00	1.70
	3.00	1.32
Na_2SO_4	0.25	3.80
	0.50	5.11
	0.75	4.96
	1.50	4.73
$MgCl_2$	1.00	2.53
	1.00	2.30
$CuSO_4$	0.10	3.10[b]
	0.10	2.59[c]
...	...	4.1[c]

[a] Temperature 0.4°; pH 4.50; titrant 0.1 *N* Na_2HPO_4 unless specified. [b] Titrant 0.01 *N* NaOH, pH 3.00. [c] Titrant 0.01 *N* NaOH, pH 4.2.

Table III

Effects of Salts of Weak Acids

pH[a]	Salt	[Salt], M	10^3k_ψ, sec^{-1}
5.50	CH_3CO_2Na	0.10	2.74
		0.20	2.47
		0.32	2.04
6.00	HCO_2Na	0.025	4.23
		0.050	5.55
		0.10	8.85
		0.10	9.23
4.50	NaF	0.10	4.36
5.50		0.10	4.36
		0.10	4.34
		0.20	5.20
		0.30	6.75
		0.50	8.10
		0.50	8.20
6.00		0.050	3.56
		0.25	5.90
		0.50	8.88
5.50	$NaClO_4$	...	8.15[b]
		0.67	6.73[b]
		2.71	4.24, 4.17[b]

[a] Temperature 0.4°; titrant 0.1 N Na_2HPO_4. [b] 0.50 M NaF.

in Table II, and Figure 2 includes a plot of log k_F *vs.* sodium perchlorate ($k_F = k_\psi - k_\psi^s$, where k_ψ^s is the rate constant for the spontaneous hydrolysis in aqueous sodium perchlorate). The negative salt effect on k_F (the fluoride-catalyzed component of hydrolysis) is similar to that on the spontaneous hydrolysis, with the slope $b = 0.10$.

Pyridine is a very effective catalyst, but 2,6-lutidine has no effect, and added sodium fluoride affects the pyridine-catalyzed hydrolysis (Table IV).

Table IV

Catalysis by Tertiary Bases and Effect of Sodium Fluoride on Pyridine Catalysis[a]

Base	10^5 [base], M	10^3k_ψ, sec^{-1}	10^5 [pyridine], M	[NaF], M	10^3k_ψ, sec^{-1}
...	...	2.95	13.3	...	4.95
Pyridine	4.8	3.63	13.3	0.005	4.74
	6.6	4.07	13.3	0.010	4.33
	9.6	4.62	13.3	0.020	4.06
	13.3	4.95	13.3	0.025	3.90
	18.4	6.00	13.3	0.050	4.02
	21.5	7.78	13.3	0.050	3.92
	21.5	7.90	13.3	0.10	4.11
2,6-Lutidine	27.5	3.04			
	55.0	3.30			

[a] Temperature 0.4°; pH 6.00; titrant 0.1 N Na_2HPO_4.

We measured the second-order rate constant, k_{OH}, for reaction between acetic anhydride and hydroxide ion at 0.4° using a pH-Stat, because for reaction at higher temperatures there are considerable discrepancies between the rate constants measured with a flow apparatus and those measured using either pH-Stat, chemical analysis, or spectrophotometrically.[3,4,6]

Our results for the alkaline hydrolysis of acetic anhydride (Table V) do not agree with those of Koskikallio,[6] whose rate constants are *ca.* 30 times greater than those determined at 25° by Kirsch and Jencks,[4] and those determined at 0.4° in this work. From our value of $k_{OH} = 158$ l. mole^{-1} sec^{-1}, at 0.4°, and the value of 967 l. mole^{-1}/sec^{-1}, at 25° of Kirsch and Jencks[4] we calculate approximate values of $E = 11.5$ kcal mole^{-1} and $\Delta S^* = -4$ eu. The value of the entropy of activation is close to those generally found for ion–molecule reactions in solution.[7]

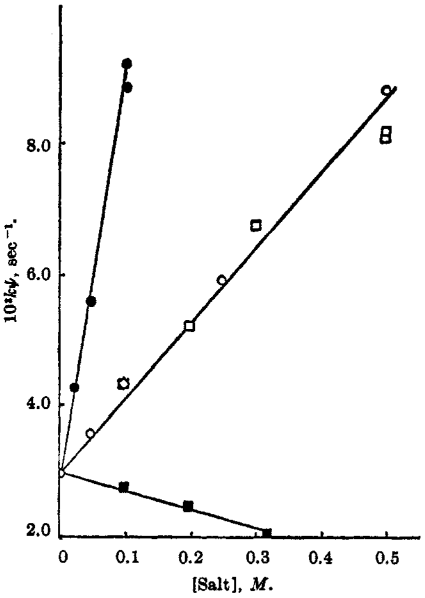


Figure 3.—Effects of salts of weak acids upon the hydrolysis of acetyl fluoride. ●, HCO_2Na, pH 6; ■, CH_3CO_2Na, pH 5.5; ○, NaF, pH 6; □, pH 5.5; ◇, pH 4.5.

Table V

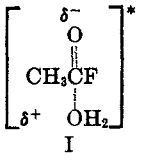
Hydrolysis of Acetic Anhydride at pH 8–10.1[a]

pH	10^4k_ψ, sec^{-1}
8.0	6.55
9.0	7.80
9.6	12.9
9.8	16.5
10.0	24.0
10.1	27.8

[a] Temperature 0.4°; titrant 0.1 N Na_2PO_4.

Discussion

Spontaneous Hydrolysis.—The hydrolysis of acetyl fluoride in water is *ca.* 14 times faster than in acetone–water (50:50, v/v) where at 0.5° $k_\psi = 2.2 \times 10^{-4}$ sec^{-1}. This solvent effect is similar to those found for hydrolyses of carboxylic anhydrides in water and in aqueous organic solvents;[6,8,9] *e.g.*, for acetic anhydride hydrolysis at 0° the corresponding solvent effect is 15. (from 10^4 $k_\psi = 4.7$ sec^{-1} in water, and the interpolated value for acetone–water (50:50, v/v) of 10^4 $k_\psi = 0.28$ sec^{-1}).[6] Such solvent effects are to be expected for hydrolyses in which the transition state I is highly polar and is stabilized by hydrogen bonding with a hydroxylic solvent.[9,10]



$$\left[\begin{array}{c} \delta^- \\ O \\ \| \\ CH_3CF \\ | \\ \delta^+ \quad OH_2 \end{array}\right]^*$$

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[6] J. Koskikallio, *Ann. Acad. Sci. Fennicae, Ser. A II*, **57**, 1 (1954).

[7] A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1961, p 147.

[8] V. Gold, *Trans. Faraday Soc.*, **44**, 506 (1948).

[9] C. A. Bunton, N. A. Fuller, S. G. Perry, and V. J. Shiner, *J. Chem. Soc.*, 2918 (1963).

[10] C. A. Bunton and V. J. Shiner, *J. Am. Chem. Soc.*, **83**, 3207 (1961).

In initially neutral solution acetyl fluoride is more reactive than acetic anhydride, but much less reactive than acetyl chloride.[11] In water at 0° the reactivities relative to acetic anhydride are acetyl fluoride 6 (8) and acetyl chloride 280. [The figure in parentheses refers to the relative reactivities in acetone–water (50:50, v/v[1,6]).] Swain and Scott have discussed the unreactivity of acid fluorides relative to the chlorides in terms of the strength of the carbon fluorine bond.[1]

The Arrhenius parameters for hydrolysis of acetyl fluoride are similar to those for acetic anhydride, where in water ΔS^* is *ca.* −35 eu, and E is *ca.* 11 kcal mole^{-1}.[6,8,9] The corresponding values for acetyl chloride are not known, but generally speaking the activation energy is higher, and the entropy less negative for solvolyses of acid chlorides than of acid fluorides or carboxylic anhydrides, although variations in solvent composition complicate these comparisons.[12]

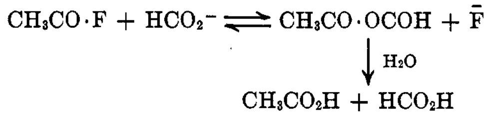
The evidence suggests that bond making is more important than bond breaking in hydrolyses of acid anhydrides, and apparently also of acid fluorides, whereas for acid chlorides, as for alkyl halides in SN2 reactions, both bond making and breaking are important.[12,13]

Salt Effects on the Spontaneous Hydrolysis.—Salts of the strong acids affect the hydrolyses of acetic anhydride and acetyl fluoride similarly. Both reactions are retarded by sodium chloride and perchlorate and assisted by sulfate.[14] For hydrolyses of carboxylic anhydrides in water determination of the activity coefficient of the anhydride shows that these salt effects depend in part upon a specific destabilisation of the initial state by an anion of high charge density, such as sulfate, or a specific stabilisation by an anion of low charge density such as perchlorate, and in part upon a destabilization of the polar transition state.[14] The effects of salts of the strong acids upon the hydrolysis of acetyl fluoride probably have a similar origin, but the reactivity of acetyl fluoride makes it difficult to test this point. Chloride ions in water do not act as nucleophiles and convert acetyl fluoride into the more reactive chloride, in accord with Wiberg's generalization that in the absence of electrophilic catalysis one nucleophile will not displace a better nucleophile in a substitution at a carbonyl center.[15]

Effects of Nucleophiles and Bases.—Hydroxide ions are very reactive toward acid fluorides, both in aqueous organic solvents,[1] and in water (Table I, Figure 1). For reactions in water our value of k_{OH}, calculated from results at pH >6.5, of 5.7×10^4 l. mole^{-1} sec^{-1}, is much larger than that reported by Swain and Scott, for reaction in acetone–water (50:50, v/v), where $k_{\mathrm{OH}} = 250$ l. mole^{-1} sec^{-1}. However, they used borate buffers in aqueous acetone to control the hydroxide ion concentration, and the two sets of data may therefore not be strictly comparable, because of effects of the borate ion. The apparent large difference between k_{OH} in water and aqueous acetone is surprising, because generally the nucleophilicity of small highly solvated anions is increased by the addition of polar organic solvents to water.[16]

Acetyl fluoride is *ca.* 360 times more reactive than acetic anhydride towards hydroxide ion at 0.4°. This result is readily understandable in view of the powerful electron withdrawal by a fluorine atom,[1] and the reactivity of acetyl fluoride, relative to acetic anhydride, toward hydroxide ion is very much greater than toward water.

Sodium formate can act as a nucleophilic catalyst and convert acetyl fluoride into the more reactive formic acetic anhydride in the same way that it catalyzes the hydrolysis of acetic anhydride.[17]



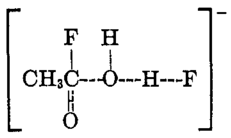
$$\begin{array}{c} CH_3CO{\cdot}F + HCO_2^- \rightleftharpoons CH_3CO{\cdot}OCOH + \bar{F} \\ \quad\quad\quad\quad\quad\quad\quad \downarrow{\scriptstyle H_2O} \\ \quad\quad\quad\quad\quad\quad\quad CH_3CO_2H + HCO_2H \end{array}$$

The rate constant of hydrolysis of formic acetic anhydride is 38.7×10^{-4} sec^{-1}, at 0°, in acetone–water (50:50, v/v),[18] and by comparison with the solvent effects upon hydrolyses of acetic anhydride and acetyl fluoride we should expect it to be *ca.* 15 times more reactive in water, with $k_\psi \approx 600 \times 10^{-4}$ sec^{-1}. Therefore, its hydrolysis should be much faster than its formation from acetyl fluoride and formate ions, and in these solutions where the fluoride ion concentration is very low it should be hydrolyzed by water as soon as it is formed. If we assume that all the rate enhancement caused by sodium formate arises from this nucleophilic catalysis, we can estimate the second-order rate constant for attack of formate ion upon acetyl fluoride as 0.09 l. mole^{-1} sec^{-1}, compared with 5.7×10^4 for the hydroxide ion. Although sodium formate is a catalyst sodium acetate slightly retards hydrolysis of acetyl fluoride, probably because it converts it to a small extent into the less reactive acetic anhydride. (The strong catalysis by formate ion suggests that the negative salt effects of carboxylate ions are small and are probably similar to the electrolyte effects of inorganic anions.)

$$CH_3CO{\cdot}F + CH_3CO_2^- \rightleftharpoons (CH_3CO)_2O + \bar{F}$$

However, a detailed kinetic analysis of the effects of carboxylate ions is difficult, because they can act as basic catalysts as well as nucleophiles.

Fluroride ion cannot act as a nucleophilic catalyst, and it must therefore be acting as a general base, just as acetate ion does in catalyzing the hydrolysis of acetic anhydride.[16,19] General base catalyzed hydrolyses have been observed with a large number of carboxylic



II

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[11] V. Gold and J. Hilton, *J. Chem. Soc.*, 838 (1955).

[12] R. F. Hudson and J. E. Wardill, *ibid.*, 1729 (1950); B. L. Archer, R. F. Hudson, and J. E. Wardill, *ibid.*, 888 (1953).

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[16] A. J. Parker, *Quart. Rev.* (London), **16**, 163 (1962).

[17] M. Kilpatrick, *J. Am. Chem. Soc.*, **50**, 2891 (1928).

[18] V. Gold and E. G. Jefferson, *J. Chem. Soc.*, 1416 (1953).

[19] (a) A. R. Butler and V. Gold, *ibid.*, 2305 (1961); 2212 (1962). (b) S. L. Johnson, *J. Am. Chem. Soc.*, **84**, 1729 (1962).

esters,[4,20] and an explanation is that the base is removing a proton from the incoming water molecule II.[19b,21]

The fluoride ion is an effective general base catalyst for enolizations and related reactions, and Bell has noted that these small basic anions of high charge density are much better general bases than those which have a delocalized negative charge.[22]

Models other than II have been written for the transition state,[19a,20] and equilibrium hydration steps could be followed by slow proton transfers. In so far as all these transition state models include the substrate, the base, and the nucleophile, and transition state formation involves strong hydrogen-bonding interactions, it is difficult to differentiate between them.

For both formate and fluoride ion catalysis the rate constant varies linearly with salt concentration (Figure 3), whereas generally for electrolyte effects there is a logarithmic relation between activity coefficient, and hence rate constant, and salt concentration (*cf.* Figure 2 and ref 23).

Pyridine is a very effective nucleophilic catalyst for the hydrolysis of acetic anhydride,[24] which it converts rapidly and reversibly into the acetyl pyridinium ion, whereas a sterically hindered tertiary amine such as 2,6-lutidine is an ineffective catalyst despite its higher basicity (*cf.* ref 24).

We observe this same behavior for the hydrolysis of acetyl fluoride, where addition of 2 × 10^{-4} *M* pyridine more than doubles the rate of hydrolysis, but 2,6-lutidine has no effect (Table IV).

The probable mechanism is

$$\begin{array}{l} \mathrm{CH_3COF} + \mathrm{C_5H_5N} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{CH_3{\cdot}CO{\cdot}\overset{+}{N}C_5H_5} + \bar{\mathrm{F}} \\ \qquad\qquad\qquad\qquad\quad k_2 \Big\downarrow \mathrm{H_2O} \\ \qquad\qquad\qquad\quad \mathrm{CH_3CO_2H} + \mathrm{C_5H_5N} + \overset{+}{\mathrm{H}} \end{array}$$

(Pyridine is not extensively protonated at pH 6, where these particular hydrolyses were followed.)

The formation of the acetylpyridinium ion from acetyl fluoride and pyridine should be reversible, and in the presence of appreciable amounts of fluoride ion this reverse reaction can compete with the hydrolysis of the acetylpyridinium ion. At the same time the fluoride ion is catalyzing the spontaneous hydrolysis of acetyl fluoride (Table III and Figure 3), and therefore the values of k_ψ for hydrolysis in the presence of 1.33 × 10^{-4} *M* pyridine go through a shallow minimum on addition of fluoride ion (Table IV). It is, therefore, necessary to separate these two effects of the fluoride ion, and the kinetic equation is

$$[\mathrm{C_5H_5N}]/(k_\psi - k_\mathrm{F}) = k_{-1}[\bar{\mathrm{F}}]/k_1k_2 + 1/k_1 \qquad (1)$$

(In eq 1 k_F is the observed first-order rate constant of hydrolysis in the presence of a given concentration of fluoride ion and with no pyridine present.)

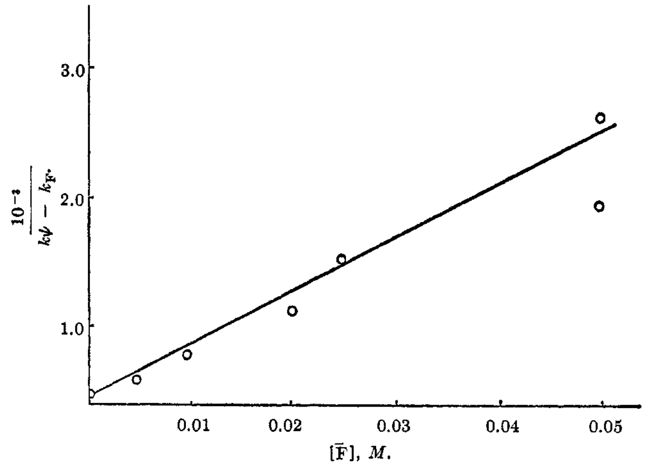

Figure 4.—Effects of fluoride ion on the pyridine-catalyzed hydrolysis of acetyl fluoride.

The concentration of pyridine was maintained at 1.33 × 10^{-5} *M*, and that of fluoride ion was varied. For fluoride ion concentrations of 0.09 *M* or greater the pyridine catalysis is completely suppressed, and $k_\psi = k_\mathrm{F}$ (Table IV). For lower concentrations of fluoride ion the results fit eq 1 reasonably well, with considerable scatter when $k_\psi \approx k_\mathrm{F}$, as shown by the linearity of the plot of $1/(k_\psi - k_\mathrm{F})$ *vs.* [F] in Figure 4. The value of k_1, the second-order rate constant for reaction between acetyl fluoride and pyridine is *ca.* 15 l. sec^{-1} mole^{-1}, and k_{-1}/k_2 = 80 l. mole^{-1}. (In estimating these values we assume that fluoride ion in these low concentrations will not act as a general base and appreciably catalyze the hydrolysis of the acetylpyridinium ion.)

This treatment allows us to compare the nucleophilicities of hydroxide ion, formate ion, and pyridine toward acetyl fluoride, and at 0.4° the second-order rate constants are, respectively, 5.7 × 10^4, 0.09, and 15 l. sec^{-1} mole^{-1}. We can also compare the relative reactivities of fluoride and acetate ion and water toward the acetylpyridinium ion, because this same ion can be generated by the attack of pyridine upon acetic anhydride.[24]

$$\begin{array}{l} \mathrm{(CH_3CO)_2} + \mathrm{C_5H_5N} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{CH_3CO{\cdot}\overset{+}{N}C_5H_5} + \mathrm{CH_3CO_2^-} \\ \qquad\qquad\qquad\qquad\qquad\quad k_2 \Big\downarrow \mathrm{H_2O} \\ \qquad\qquad\qquad\qquad \mathrm{CH_3CO_2H} + \mathrm{C_5H_5N} + \overset{+}{\mathrm{H}} \end{array}$$

With 0.5 *M* sodium acetate at 0° the rate v_2 of step 2 is *ca.* 25 times that of v_{-1}, *i.e.*, $k_{-1}/k_2 \approx 50$ l. mole^{-1}.[25] This value was obtained by studying radioactive exchange, at a relatively high ionic concentration, which could affect the ratio of k_{-1}/k_2, but it suggests that fluoride ion is slightly more reactive than acetate towards the acetylpyridinium ion.

We have already shown that uni-univalent salts of the strong acids retard hydrolysis, and suggest that this negative salt effect is in part caused by a decrease in the activity coefficient of the initial state.[14] Added sodium perchlorate also retards the fluoride ion catalyzed hydrolysis, as shown in Figure 2, where we plot log k_ψ and log k_F *vs.* ionic strength for the spontaneous and fluoride ion catalyzed hydrolyses. The similarity of the salt

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effects upon the spontaneous and fluoride ion catalyzed hydrolysis of acetyl fluoride means that the ratios of the activity coefficients of the initial and transition states must be similar, and analogy with the behavior of acetic anhydride suggests that the salt effects upon the initial state are specific, and on the transition state nonspecific.

Electrophilic Catalysis.—The hydrolysis of benzoyl fluoride is catalyzed by acids in aqueous acetone,[26] although it was not known whether the catalysis was specific or general.

Our values of k_ψ vary linearly with $[\overset{+}{H}]$, and there is an appreciable acid-catalyzed hydrolysis even at pH 2. Acetyl fluoride is, therefore, very much more sensitive to acid than is acetic anhydride. The acid hydrolysis of acetic anhydride is relatively insignificant unless the acid concentration is >2 *M*. The value of k_H for the hydrolysis of acetic anhydride in aqueous sulfuric acid at 0° is *ca.* 1.2×10^{-3} l. mole^{-1} sec^{-1}, with some uncertainty because of the electrolyte effect of the acid upon the spontaneous hydrolysis,[27] and is very much less than that of 0.66 for acetyl fluoride, reflecting the strength of the hydrogen–fluorine relative to the hydrogen–oxygen bond. A reasonable mechanism involves protonation of acetyl fluoride followed by a rate-limiting attack of water upon the conjugate acid.

$$CH_3COF + \overset{+}{H} \rightleftharpoons CH_3CO\overset{+}{F}H \qquad \text{(fast)}$$

$$CH_3CO\overset{+}{F}H + H_2O \longrightarrow CH_3CO_2 + HF \qquad \text{(slow)}$$

These hydrolyses at low pH had a good first-order kinetic form, with no autocatalysis by the hydrogen fluoride produced, suggesting that general acids are not effective catalysts for this reaction.

Metallic cations will often coordinate with electronegative atoms, and so act as electrophilic catalysts,[28] but neither copper nor magnesium ions have other than a small salt effect on the hydrolysis of acetyl fluoride. These observations suggest that breaking of the carbon–fluorine bond has made much progress in the transition state, because one might expect a partially formed fluoride ion to interact strongly with a cation. It may be that other inorganic cations will catalyze the hydrolysis of acid fluorides in water, but the use of a pH-Stat restricts our choice of cation.

Acknowledgment.—Support by the National Science Foundation under G.P. 2889 is gratefully acknowledged.

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The Chemistry of Hexafluoropropene Epoxide

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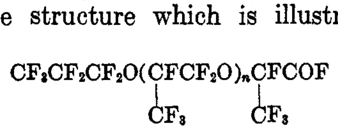
Hexafluoropropene epoxide was treated with a number of organic and inorganic (protic) reagents resulting in the synthesis of a series of α-substituted perfluoropropionic acids and their derivatives. The structures of the products indicated that in all cases the opening of the epoxide ring was initiated by a nucleophilic attack on the secondary carbon atom. The ability of some organic bases to isomerize the epoxide to perfluoropropionyl fluoride was observed and discussed.

Very little information has appeared in the literature concerning the synthesis and the chemical behavior of halo-substituted epoxide rings. However, the epoxides of perfluorinated olefins have been recently described. Tetrafluoroethylene epoxide has been prepared by the oxidation of C_2F_4, induced by electromagnetic radiations;[1,2] hexafluoropropene epoxide, formerly obtained by electrochemical fluorination of epichlorohydrin,[3] more recently has been directly synthesized by chemical[4] or photochemical[2,5] oxidation of hexafluoropropene.

Unlike tetrafluoroethylene epoxide, which was found to isomerize spontaneously even below room temperature to CF_3COF,[1] hexafluoropropene epoxide is quite a stable compound, being thermally converted to perfluoropropionyl fluoride only at high temperature.[4]

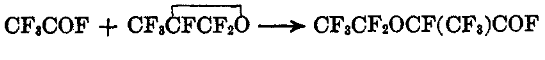
As far as we know only a few reactions of hexafluoropropene epoxide have been described and these only in the patent literature. In addition to the above-mentioned thermal isomerization to the acyl fluoride, the epoxide was found to undergo another type of isomerization, yielding hexafluoroacetone under the catalytic action of antimony pentafluoride.[6]

Other known reactions of the epoxide can be summarized as follows: (1) oligomerization,[7] catalyzed by active carbon or by fluoride ion, which gives polyethers of the structure which is illustrated below;



$$CF_3CF_2CF_2O(\underset{\displaystyle CF_3}{\underset{|}{C}}FCF_2O)_n\underset{\displaystyle CF_3}{\underset{|}{C}}FCOF$$

(2) addition to perfluorinated acid fluorides,[8] to give 2-perfluoroalkoxyperfluoropropionyl fluorides, as *e.g.*



$$CF_3COF + CF_3\overbrace{CFCF_2O} \longrightarrow CF_3CF_2OCF(CF_3)COF$$

(3) copyrolysis with halothiocarbonyl compounds,[9] to form fluorinated thiiranes.

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