87. *Acylation. Part VIII.* The Mechanism of the Acid-catalysed Solvolysis of Acyl Derivatives: the Fluorides as a Special Case?*

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The rate of the acid-catalysed solvolysis of acetyl, butyryl, and benzoyl fluoride in dioxan–water mixtures is dependent on the stoicheiometric acid concentration rather than on h_0. The mechanism of the catalysed solvolysis of acyl fluorides in aqueous media therefore differs from that of alkyl fluorides. The mechanism of the former solvolysis is described and proposed as a general model for the solvolyses of other acyl derivatives dependent on $[H_3O^+]$.

IN acetone–water mixtures, the solvolysis of benzoyl fluoride exhibits Brønsted-acid catalysis and is the only reported example of such catalysis concerning acyl halides in aqueous media.[1,2] Alkyl fluorides also undergo Brønsted acid-catalysed solvolyses in aqueous media and, for benzyl fluoride at least, the catalysed rate shows dependence on h_0.[3] While the solvolyses of some *acyl* derivatives (*e.g.*, anhydrides) show an h_0 dependence, those of others (*e.g.*, esters) have rates more closely dependent on $[H_3O^+]$. It, therefore, seemed of interest to examine the apparently special case of solvolysis of acyl fluorides from this viewpoint.[4] The previous measurements with benzoyl fluoride are insufficient to permit a distinction between dependence on h_0 and on $[H_3O^+]$. For that reason we have studied the solvolysis at different perchloric acid concentrations in 60 : 40 (v/v) dioxan–water mixtures (for which h_0 data exist [5]). We have studied likewise acetyl and butyryl fluoride for the first time. Our results are in the Table. For each compound the catalysed rate is directly proportional to the stoicheiometric acid concentration (and dissociation will be complete) but increases much less rapidly than h_0 demands. With an excess of solvent the observed first-order loss of acyl derivative (see Experimental section) can be represented as:

$$-d[R\cdot COF]/dt = (k_0 + k_c[H_3O^+])[R\cdot COF] = k_{obs}[R\cdot COF]$$

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* Part VII, *J.*, 1962, 1906.

[1] Bevan and Hudson, *J.*, 1953, 2187.

[2] Bender, *Chem. Rev.*, 1960, **60**, 53.

[3] Swain and Spalding, *J. Amer. Chem. Soc.*, 1960, **82**, 6104; Coverdale and Kohnstam, *J.*, 1960, 3806.

[4] See, *e.g.*, Long and Paul, *Chem. Rev.*, 1957, **57**, 935.

[5] Bunton, Ley, Rhind-Tutt, and Vernon, *J.*, 1957, 2327.

Solvolysis of acyl fluorides in dioxan–water mixtures at 25°. Initial acyl fluoride concentration = 0·08M; k_{obs} = observed first-order rate constant.

Benzoyl fluoride.

$HClO_4$ (M)	0	0·24	0·46	0·86	1·38
$10^3 k_{obs}$ (min.$^{-1}$)	2·02	5·08	6·64	11·1	16·4
H_0 *	—	1·90	1·48	0·90	0·34

Acetyl fluoride.

$HClO_4$ (M)	0	0·24	0·46	0·86
$10^2 k_{obs}$ (min.$^{-1}$)	2·65	5·80	8·63	15·0
H_0	—	1·90	1·48	0·90

Butyryl fluoride.

$HClO_4$ (M)	0	0·46	0·86	1·38
$10^2 k_{obs}$ (min.$^{-1}$)	1·02	4·70	7·26	11·4
H_0	—	1·48	0·90	0·34

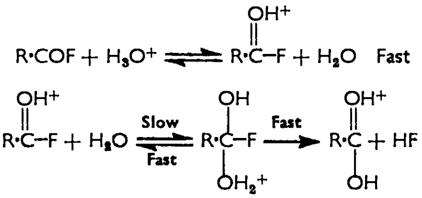
* Interpolated from ref 5.

The values of the second-order catalytic constants, k_c, are 14×10^{-2}, $7{\cdot}4 \times 10^{-2}$, and $10{\cdot}4 \times 10^{-3}$ l. mole^{-1} min.$^{-1}$ for acetyl, butyryl, and benzoyl fluoride, respectively, while the corresponding spontaneous rates, k_0, are $2{\cdot}65 \times 10^{-2}$, $1{\cdot}02 \times 10^{-2}$, and $2{\cdot}02 \times 10^{-3}$ min.$^{-1}$. Two conclusions emerge at once: (*a*) the overall reactivity, both spontaneous and catalysed, is in the order acetyl > butyryl > benzoyl; and (*b*) the detailed mechanism is probably unlike that operative for benzyl fluoride.

For alkyl fluorides, while the very fact of acid catalysis must mean that the separation of the fluoride ion is assisted in some way by some form of positively charged hydrogen, the observed h_0 dependence probably implies a catalytic mechanism broadly as follows:[3,4]

$$\begin{aligned} RF + H_3O^+ &\rightleftharpoons RFH^+ + H_2O && \text{Fast} \\ RFH^+ &\longrightarrow R^+ + HF && \text{Slow} \\ R^+ + 2H_2O &\longrightarrow ROH + H_3O^+ && \text{Fast} \end{aligned}$$

Proton-assisted removal of fluoride must therefore be a possibility for acyl fluorides also. It has indeed been assumed to be the sole origin of their catalysis.[1,2] The proton could, however, be received by oxygen, as shown below:



$$\begin{aligned} &R{\cdot}COF + H_3O^+ \rightleftharpoons R{\cdot}C(=OH^+){-}F + H_2O \quad \text{Fast} \\ &R{\cdot}C(=OH^+){-}F + H_2O \underset{\text{Fast}}{\overset{\text{Slow}}{\rightleftharpoons}} R{\cdot}C(OH)(OH_2^+){-}F \xrightarrow{\text{Fast}} R{\cdot}C(=OH^+){-}OH + HF \end{aligned}$$

(I)

This scheme satisfies the kinetic dependence on $[H_3O^+]$ and also the substituent effects noted under (*a*), which imply that nucleophilic approach of solvent is kinetically important.[6] It is a scheme, involving as it does an intermediate symmetrical with respect to oxygen, which would normally commend itself to Bender, but even he dismisses it in the present context.[2] This is presumably because only acyl fluorides, and not chlorides, bromides, or iodides, exhibit catalysis and, while only fluorine forms unusually strong hydrogen bonds, any catalysis via protonated oxygen might reasonably be expected to intrude also for the other halogens. (Their inductive effects, which reduce the electron density on oxygen and so protonation, are not so very different.) Therefore, such catalysis probably does not intrude at all for acyl halides. We concur. Moreover, we consider that the catalysis exhibited by fluorides probably does not constitute a special case and should not be thought different in kind, but only in degree, from any experienced by chlorides, bromides, and

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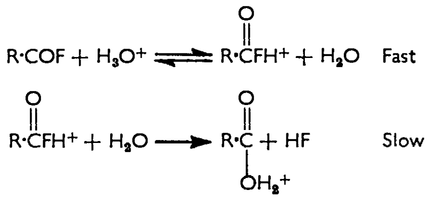
[6] Satchell, *J.*, 1960, 1752.

iodides (see following papers). We go further in thinking that acidic solvolyses of other acyl derivatives generally will not differ in principle from those of acyl halides, and that the important catalytic assistance is perhaps always more likely to occur at the leaving group than elsewhere, though exceptions may exist.[7] The following type of mechanism, probable for fluorides, is possible, and seems to us likely at least to contribute, in other examples exhibiting [H_3O^+]-dependence.



$$\mathrm{R{\cdot}COF + H_3O^+ \rightleftharpoons R{\cdot}\overset{\overset{O}{\|}}{C}FH^+ + H_2O} \quad \text{Fast}$$
$$\mathrm{R{\cdot}\overset{\overset{O}{\|}}{C}FH^+ + H_2O \longrightarrow R{\cdot}\underset{\underset{OH_2^+}{|}}{\overset{\overset{O}{\|}}{C}} + HF} \quad \text{Slow} \qquad (2)$$

However, any acid-catalysed oxygen exchange concurrent with solvolysis must involve a scheme based on (1). Where catalysed exchange has been established, then part, at least of the catalysed solvolysis will surely also involve such a scheme, but not necessarily all of it. And where catalysed exchange is not, or has not yet been, found (which is for most types of acyl derivative) scheme (2) suffices. Conversely, if (2) is the only (detectable) acid-catalysed route to solvolysis, as we suggest for the halides, then little oxygen exchange is likely to occur under similar conditions. It will be interesting to see if acyl halides do exhibit acid-catalysed oxygen exchange.

The probability that schemes such as (2) are important in acid-catalysed solvolyses is increased by the fact that such catalysis often leads to solvolysis by way of acylonium ions—a process hardly possible for most acyl derivatives except with protonation of the leaving group. There seems no reason to suppose that the proton will be placed there only for such unimolecular solvolyses. We therefore feel that Bender, who regards schemes such as (1) as almost universal for bimolecular sovolysis, overstates the case, at least so far as acid-catalysis is concerned.

EXPERIMENTAL

Materials.—The acyl fluorides were prepared by Mashentsev's method.[8] Complete solvolysis, followed by tritation for fluoride, showed them all to contain >96% of the theoretical amount of fluorine (benzoyl fluoride contained 99·8%.) Dioxan was purified by Vogel's method.[9] Perchloric acid was of "AnalaR" grade. The perchloric acid–dioxan–water mixtures were made up as described by Bunton *et al.*[5]

Kinetic Measurements.—Reaction was initiated by adding a small, known volume of acyl fluoride to a large excess of the solvent mixture, contained in a volumetric flask and kept at 25° in a thermostat-bath. Samples of solution were withdrawn at appropriate intervals and added to a dioxan–water mixture containing sufficient sodium hydroxide almost to neutralise their acid contents. This quenched the reaction. Titration for fluoride followed. Thus the rate of loss of acyl derivative was found. Good first-order plots were usually obtained. At the lowest catalyst concentrations the reaction was autocatalytic owing to the hydrogen fluoride produced. When necessary initial slopes were used in calculating the rate. The first-order constants are in the Table.

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[7] See, *e.g.*, Aksnes and Prue, *J.*, 1959, 103.

[8] Mashentsev, *J. Appl. Chem.* (*U.S.S.R.*), 1941, **14**, 816.

[9] Vogel, "Practical Organic Chemistry," Longmans, Green and Co., London, 1948.