309. *Nucleophilic Displacement of Fluorine from Organic Compounds. Part III.* Acid-catalysed Solvolysis of Alkyl Fluorides in Aqueous Ethanol.*

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Graphs illustrating the course of reaction in the acid-catalysed solvolysis in 80% aqueous ethanol of primary, secondary, and tertiary alkyl fluorides are presented. Solvolyses of tertiary fluorides are of the first order with respect to fluoride. The reaction involves attack by a solvated proton on the fluorine, and a process very similar to the unimolecular solvolysis of alkyl chlorides and bromides. Apparent zeroth-order reactions are sometimes observed, but these are thought to be fortuitous. The solvolyses of secondary and primary alkyl fluorides are autocatalytic when the initial acid concentration is low, by virtue of the generated hydrofluoric acid. The variation with structure of mean rate of reaction is far greater in solvolyses of alkyl fluorides than in reactions with ethanolic sodium ethoxide. Alkyl fluorides are often much more stable to heat in ethanolic solution, even in the presence of ethoxide ions, than in the liquid or gaseous phase.

Solvolysis of alkyl and arylalkyl chlorides and bromides has been very widely investigated (numerous papers by Hughes and Ingold and their co-workers, *J.*, 1940, 1946, 1948), but the solvolysis of alkyl fluorides has received hardly any attention. Cooper and Hughes (*J.*, 1937, 1183) briefly discussed the solvolysis of *tert.*-butyl fluoride, and Bernstein and Miller (*J. Amer. Chem. Soc.*, 1948, **70**, 3600) recorded the percentage reaction after a given time when substituted benzyl fluorides are heated under reflux with 70% aqueous ethanol containing various concentrations of hydrogen chloride. The rate of reaction depends on the initial concentration of hydrochloric acid, in contrast with Olivier and Berger's observations (*Rec. Trav. chim.*, 1922, **41**, 637) with benzyl, *n*-butyl, and *iso*butyl chloride, the solvolyses of which were unaffected by added hydrochloric acid. The present communication records studies of the overall reaction in the solvolysis of a series of alkyl monofluorides, with and without added hydrochloric acid. For reasons to be discussed later, the results are presented graphically in Figs. 2—6, and no attempt has

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* Part II, preceding paper.

been made to attribute velocity coefficients to the various reactions, except in a few special cases, and then only approximately.

EXPERIMENTAL

Materials.—Alkyl fluorides were prepared, and ethanol was purified, as recorded in Part II (*loc. cit.*).

Procedure.—Thermostats were as described previously. Reactions were followed by titration with aqueous sodium hydroxide (phenolphthalein) of the total acidity produced when aqueous-ethanolic alkyl fluorides, with or without added hydrochloric acid, were heated in a thermostat for definite times. The samples were enclosed in sealed " Pyrex " bulbs with minimum " free " space: bulbs of the same glass and nearly the same dimensions were used throughout.

TABLE 1. *Reaction of* tert.*-amyl fluoride with* 80% *aq.* EtOH *at* 79·8° *in the presence of* 0·0148N-*hydrochloric acid.* Initial [$C_5H_{11}F$] = 0·1949M (cf. Fig. 2, *B*).

Time (sec.) × 10^{-3}	2·70	5·82	9·00	12·84	17·46	21·72	25·80
Decompn. (uncorr.), %	7·5	15·4	22·9	29·4	40·1	48·9	51·9
Decompn. (corr.), %	8·8	18·1	26·9	34·6	47·2	57·5	61·0
10^5k (sec.$^{-1}$) (uncorr.)	2·92	2·88	2·90	2·72	2·95	3·09	2·83
10^5k (sec.$^{-1}$) (corr.)	3·40	3·42	3·47	3·30	3·65	3·94	3·64

Mean k, uncorr. = 2·90 × 10^{-5}; mean deviation = 0·09.
Mean k, corr. = 3·54 × 10^{-6}; mean deviation = 0·17.

Results.—Our observations, for the most part, do not permit us to determine velocity coefficients for the reactions, so a selection of the results is presented graphically in Figs. 2—6.

FIG. 1.

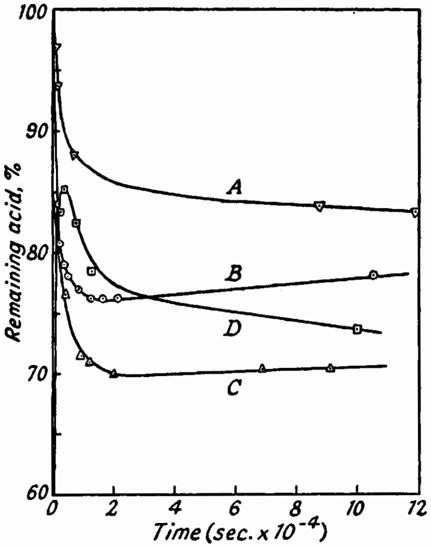


FIG. 2.

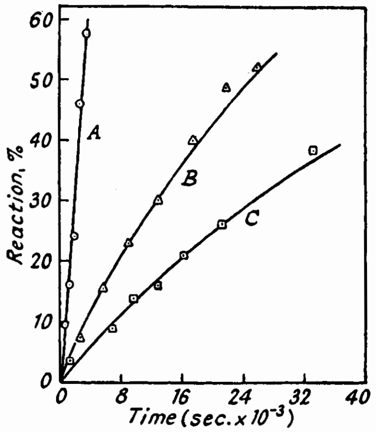


FIG. 1. *Reaction of* HF *in* 80% *aqueous ethanol with " Pyrex " glass.*

	Temp.	*Initial* [HF]	*Initial* [HCl]
A	80°	0·576M	—
B	139·1	1·150M	—
C	138·4	0·457M	0·0742M
D	89·8	*Illustrative example in* Bu^{t}F *solvolysis, zero of time being taken as " infinite " time in the solvolytic reaction.*	

FIG. 2. *Reaction of* tert.*-amyl fluoride in* 80% *aqueous ethanol at* 79·8°.

	A	*B*	*C*
Initial [tert.-$C_5H_{11}F$] (M)	0·894	0·1949	0·1123
Initial [HCl] (M)	0·0742	0·0148	0·0074

In Table 1 results are given in detail for one of the reactions approximating to first-order behaviour and of special importance (cf. p. 1681). These results are given both with and without a correction for loss of hydrofluoric acid by reaction with glass. The correction has been made by assuming that the hydrofluoric acid formed is always in equilibrium with the glass (cf. below), and utilising the appropriate curve from Fig. 1.

The loss of acidity due to reaction of hydrofluoric acid with glass is displayed in Fig. 1, and that due to interaction of ethanol and hydrochloric acid is shown Table 2.

TABLE 2.

Temp.	80°	120°	140°	160°
HCl at equilibrium, %	95	~70—80	27	16
Time reqd. for equilibrn. (sec.)	~3×10^5	—	~3×10^4	—

Occasionally the solvolyses were conducted in the presence of powdered glass (~3 g. per bulb) without significant influence on the results.

DISCUSSION

Preliminary experiments, summarised in Fig. 1, showed that, when aqueous ethanolic hydrofluoric acid is heated in sealed bulbs at ~80° and ~140°, equilibrium, at which some 70—85% of the initial titratable acidity remains (depending on the temperature), is established within ~330 minutes, *i.e.*, the mean rate of attainment of this equilibrium is large relatively to those of most of the reactions studied. In any given solvolysis the apparent rate of the reaction, as illustrated in Figs. 2—6, depends on the true rate of

FIG. 3.

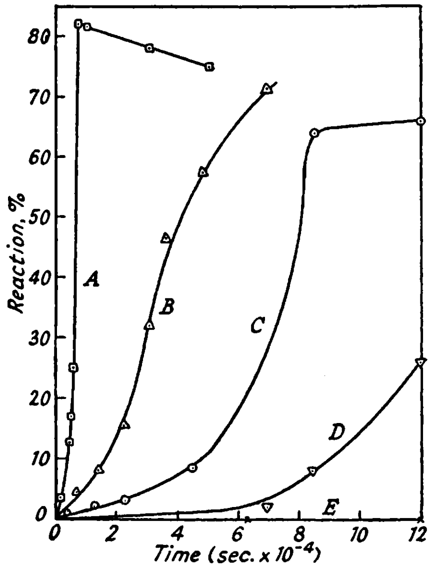


FIG. 4.

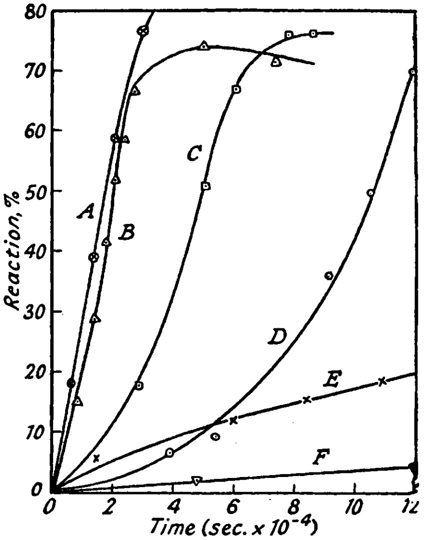


FIG. 3. *Reactions of* tert.*-amyl fluoride in aqueous ethanol at* 79·8°.

	Initial [tert.-$C_5H_{11}F$]	*Solvent*	*Initial* [HCl]
A	0·863M	80% EtOH	0·0074M
B	0·795M	,,	*Nil*
C	0·1488M	70% EtOH	*Nil* + 0·126M-NaCl
D	0·1650M	,,	*Nil*
E	0·843M	100% EtOH	,,

FIG. 4. *Reactions of* cyclo*hexyl fluoride in* 80% *aqueous ethanol at* 138·4°.

	Initial [$C_6H_{11}F$]	*Initial* [*acid*]		*Initial* [$C_6H_{11}F$]	*Initial* [*acid*]
A	0·731M	0·0814N-H_2SO_4	*D*	0·684M	0·0074M-HCl
B	0·983M	0·0742M-HCl	*E*	0·1834M	,,
C	0·698M	0·0296M-HCl	*F*	0·773M	0·094N-H_3PO_4

production of acid in solvolysis and the rate of loss of acid by reaction with the glass. Therefore, apart from the most rapid solvolyses, the form of the various curves in Figs. 2—6 will not be significantly affected relatively to each other because of the action on glass of the hydrofluoric acid formed. There is also a loss of acidity due to interaction of ethanol and added hydrochloric acid (cf. Table 2). This has been allowed for by using the acid value of the first sample titrated in any experiment as zero, or by making appropriate corrections from blank experiments. Also this loss of acid is always relatively small, since the initial concentration of hydrochloric acid is $\not>$10% of that of the hydrofluoric acid produced in the reaction. In specifying the concentration of added hydrochloric acid, no account has been taken of interaction with the ethanol. The total likely errors, being small and all in the same sense, are not such as to obscure the considerable differences between the various curves. Consequently, while we regard our results as relatively valid among themselves, the calculation of rate coefficients is not generally warranted. Moreover, we have made no correction for the loss of hydrofluoric acid by reaction with glass in plotting the curves which summarise our results, because a correction is of importance only where reactions approximate to a first-order law. Table 1 shows that making the maximum correction does not cause serious divergence from first-order behaviour (mean deviations of ~3% and ~5% for uncorrected and corrected values of k).

FIG. 5.

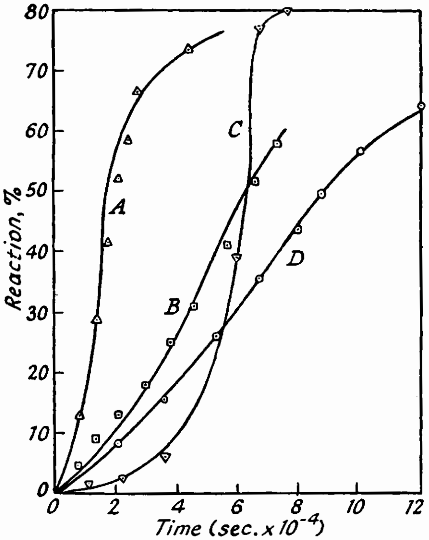


FIG. 6.

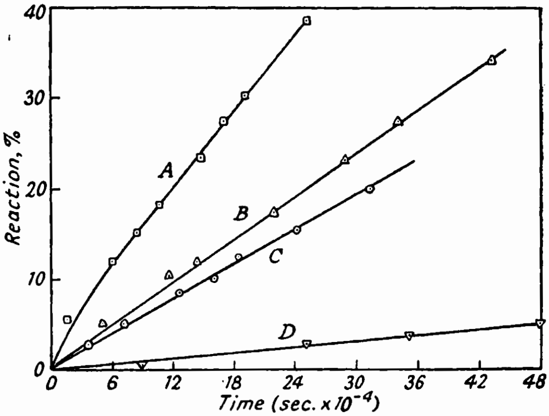


FIG. 5. *Reactions of* cyclo*hexyl fluoride : solvent and temperature effects.*

	Initial [$C_6H_{11}F$]	*Initial* [HCl]	*Solvent*	*Temp.*
A	0·983M	0·0742M	80% EtOH	138·4°
B	0·910M	,,	70% EtOH	119·5
C	0·867M	0·1236M	100% EtOH	139·7
D	0·904M	0·0742M	80% EtOH	119·8

FIG. 6. *Reactions of alkyl fluorides with* 80% *aqueous ethanol.*

	Initial [AlkF]	*Initial* [HCl]	*Temp.*
A. cyclo*Hexyl*	0·1534M	0·0074M	138·4°
B. sec.-*Amyl*	0·1680M	,,	,,
C. n-*Amyl* *	0·420M	0·037M	159·5
D. 2-*Methyl*-n-*butyl*	0·172M	0·0074M	138·4

* *In* 70% EtOH.

The variation of mean rate of reaction with structure is far greater in solvolysis of alkyl fluorides than in overall reactions with ethanolic sodium ethoxide. Thus with *n*-amyl fluoride, even at 160° in the presence of 0·0741N-hydrochloric acid, only ~5%

reaction has occurred after 4·8 × 10^5 seconds, whereas with *tert.*-amyl fluoride and the same hydrochloric acid concentration at 80°, 5% reaction has occurred after ~400 seconds. As an increase in temperature of 20° increases the rate roughly four times, the mean rate ratio is of the order of 10^5—10^6, compared with ~40 for the overall reaction with ethanolic sodium ethoxide.

From the standpoint of kinetic form, the solvolyses of alkyl fluorides are divisible into three main classes: (*a*) approximately first-order reactions, (*b*) apparently zeroth-order reactions, (*c*) autocatalytic reactions. The first and last are of considerable theoretical significance; the second class is probably fortuitous in origin. The first-order reactions constitute the key to the mechanism.

The reactions of *tert.*-butyl and *tert.*-amyl fluorides with 80% ethanol containing hydrochloric acid (0·007—0·07N) show increasing acidity obeying approximately a first-order law (Figs. 2 and 3 and Table 1)—first order in alkyl fluoride—and the velocity coefficients are, within experimental error, directly proportional to the initial concentration of hydrochloric acid (Table 3).

It is improbable that there is any consumption of acid in the reactions, apart from the hydrofluoric acid destroyed by the glass, since the corrected final acid concentrations approximately correspond stoicheiometrically to the initial alkyl fluoride and added hydrochloric acid. Moreover, if the hydrochloric acid is replaced by sodium chloride the reaction assumes a quite distinct form (Fig. 3). Hence we conclude that the rate-determining step involves the alkyl fluoride and the hydrogen ion, which is, however, not consumed in the reaction.

TABLE 3. *Reactions of* tert.*-butyl and* tert.*-amyl fluoride with* 80% *ethanol at* 79·8° *with added hydrochloric acid.*

Added HCl	Initial Bu^tF	10^5k_1	$10^3k/[HCl]$	Initial *tert.*-$C_5H_{11}F$	10^5k_1	$10^3k_1/[HCl]$
0·00742M	0·192M	1·1	1·5	0·112M	1·4	1·9
0·0148M	0·180M	1·9	1·3	0·195M	2·9	1·9
0·0742M	0·811M	12	1·5	0·894M	18	2·4

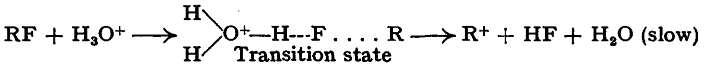
It seems most likely that we are dealing with acid-catalysed solvolysis in these reactions. The kinetic results do not distinguish between unimolecular and bimolecular solvolysis, since the latter reactions become pseudo-unimolecular. However, the facts that solvolysis is most rapid, and only approximates closely to a first-order law, for tertiary fluorides make it very probable that the mechanism of this acid-catalysed solvolysis is fundamentally similar to that of unimolecular solvolysis of alkyl bromides and chlorides. It is clear that the hydrofluoric acid produced in the solvolysis has very little effect on the observed rate for tertiary fluorides. Two factors probably account for this: (*a*) much of the hydrofluoric acid is converted, by reaction with the glass, into fluorosilicic and fluoroboric acid, with a consequent reduction in the concentration of free acid; and (*b*) hydrofluoric acid is a weak acid (pK_a ~5 for water at 25°). Similar behviour is shown by phosphoric acid, also weak ($pK_a = 2·1$ for water at 25°) (cf. Fig. 4). Thus the first-order reaction persists as the reaction proceeds because the rate of the reaction due to hydrofluoric acid is insignificant compared to that due to hydrochloric acid. With relatively high initial fluoride concentrations the hydrofluoric acid becomes significant, and the reactions assume apparent zeroth-order character, even with tertiary halides. It is noteworthy in this connection that Swain, Esteve, jnr., and Jones (*J. Amer. Chem. Soc.*, 1949, **71**, 965) found that the solvolysis of triphenylmethyl fluoride in aqueous methanol and in methanol–acetone was of the first order and unaffected by variation in pH. They worked with a fluoride concentration of 0·001M.

The apparent obedience to a zeroth-order law in the solvolysis of primary fluorides and of secondary fluorides in the presence of hydrochloric acid (Figs. 2, 4, and 6) we regard as fortuitous and arising from a combination of a first-order reaction and significant autocatalysis by the hydrofluoric acid formed. We do not think it conceivable that the rate-determining process can be localised in such a way as to exclude the fluoride molecule in view of the strength of the bond broken and the rapidity of proton transfers.

Autocatalytic reactions are observed in solvolysis in initially neutral solutions or when the ratio of the initial concentration of alkyl fluoride to that of hydrochloric acid exceeds 100 (Figs. 3, 4, and 5). In either case the rate increases with increasing concentration of hydrofluoric acid formed : in the former it is the only acid present, in the latter the hydrochloric acid, being in relatively low concentration, no longer dominates the situation as in previous examples (p. 1681). The solvolyses of secondary alkyl fluorides are either apparently of zeroth order or autocatalytic. At relatively low initial concentrations of hydrochloric acid, the reactions are autocatalytic : at higher concentrations of zeroth order, *i.e.*, probably of first order with superimposed autocatalysis.

The stability of alkyl fluorides to solvolysis in initially neutral anhydrous ethanol is very considerable : thus no detectable reaction occurs when M-*cyclo*hexyl fluoride in ethanol is heated at 140° for 200 hours. Even with M-ethanolic *tert.*-amyl fluoride at 120° no reaction is observable after 4 hours, although after 22 hours 85% reaction has occurred. Pure alkyl fluorides, however, especially *tert.*-butyl and *tert.*-amyl fluoride, are thermally unstable at their boiling points.

The ultimate cause of the acid catalysis in these solvolyses is the great affinity of fluorine for protons, even when solvated (cf. Bernstein and Miller, *loc. cit.*). This behaviour is unique among alkyl halides, but finds an analogy in the solvolyses of other alkyl halides "catalysed" by mercuric and silver salts, where the metallic ions have powerful affinity for the halogen. In contrast with reactions in alkaline media, the driving force of these reactions is an attack on halogen by an electrophilic reagent. However, the overall process may be regarded as a nucleophilic substitution, since the substituting agents are weakly nucleophilic, *viz.*, water and ethanol. The most likely mechanism for these reactions is :



$$RF + H_3O^+ \longrightarrow \underset{\text{Transition state}}{\overset{H\diagdown}{\underset{H\diagup}{}}\!\!>O^+\text{—}H\text{---}F \ldots\ldots R} \longrightarrow R^+ + HF + H_2O \text{ (slow)} \quad . \quad . \quad . \quad (1)$$

$$R^+ + 2H_2O \longrightarrow ROH + H_3O^+ \text{ (rapid)} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

The hydrogen fluoride formed will, of course, be partly dissociated. Variants may be suggested, especially one involving rapid and reversible complex-formation between the fluoride and a solvated proton. However, we have at present no experimental evidence to distinguish these mechanisms, so we confine ourselves to the above. Again, as we have no relevant experimental evidence, we have not considered Swain's "push-pull" mechanism (*J. Amer. Chem. Soc.*, 1948, **70**, 1119).

It is clear from this and the preceding paper that the displacement of fluorine from alkyl fluorides is dominated by three characteristic features of fluorine : ability to form hydrogen bonds, ability to form very strong bonds with carbon, and a high degree of solvation of the incipient fluoride ion.

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