755. *The Kinetics of the Hydrolysis of Triphenylmethyl Fluoride in Aqueous Acetone.*

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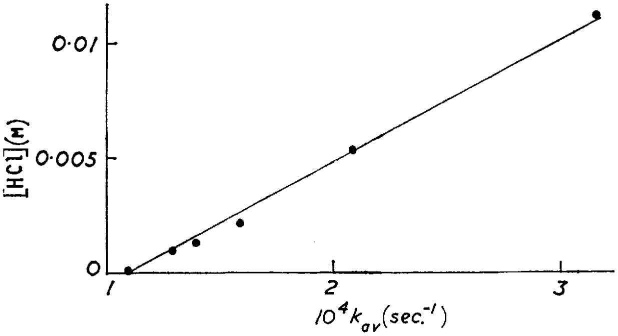
The reaction of triphenylmethyl fluoride with 70% aqueous acetone is subject to autocatalysis. Added hydrochloric acid accelerates the hydrolysis considerably, but sodium chloride and fluoride have no effect on the rate. The observations are consistent with the view that molecules of hydrofluoric acid are responsible for most, if not all, of the autocatalysis; hydrogen-ion catalysis only becomes significant when strong acids are added to the reaction mixture. It seems likely that both catalysts assist the heterolysis of the C–F linkage by virtue of their ability to form strong bonds with fluorine.

ORGANIC fluorides undergo nucleophilic substitution much more slowly than the corresponding chlorides,[1-7] and the solvolysis reaction is generally catalysed by hydrogen ions.[3,4b,6] Autocatalysis has also been reported for the solvolysis,[4b] but it is not clear whether this arises from the direct intervention of hydrofluoric acid or from the hydrogen ions produced by its dissociation. Little quantitative evidence is available (see, however, ref. 4*b*, 6) and we now report an attempt to obtain further information about the catalysis from a study of the reaction between triphenylmethyl fluoride and 70% (v/v) aqueous acetone. Swain and his co-workers had already studied the hydrolysis in a more aqueous solvent and found no evidence for autocatalysis or hydrogen-ion catalysis,[5] but preliminary measurements in connection with another investigation showed that this did not apply in the present systems.

The hydrolysis of *ca.* 0·015—0·030M-triphenylmethyl fluoride was studied in 70% aqueous acetone, and also in the presence of hydrochloric acid (0·001—0·01M), sodium chloride (0·003—0·01M), and sodium fluoride (0·006—0·01M). The reactions were followed by noting the development of acidity, after check experiments had shown that the hydrolysis went to completion and that the attack of hydrofluoric acid on the solvent and on the glass reaction vessels was negligibly small during the course of the reaction.

[1] Ingold and Ingold, *J.*, 1928, 2249.
[2] Cooper and Hughes, *J.*, 1937, 1183.
[3] Miller and Bernstein, *J. Amer. Chem. Soc.*, 1948, **70**, 3600.
[4] Chapman and Levy, *J.*, 1952, (*a*) 1673, (*b*) 1677.
[5] (*a*) Swain, Esteve, and Jones, *J. Amer. Chem. Soc.*, 1949, **71**, 965; Swain and Moseley, *ibid.*, 1955, **77**, 3727; (*b*) Swain, Scott, and Lohmann, *ibid.*, 1953, **75**, 136.
[6] Bevan and Hudson, *J.*, 1953, 2187.
[7] Bathgate and Moelwyn-Hughes, *J.*, 1959, 2642.

The present reactions appeared to be subject to autocatalysis; in all the systems investigated the integrated first-order rate coefficients (k) increased by 0·12—0·22 × 10^{-4} sec.$^{-1}$ over the course of the reaction (for examples, see Table 1). Hydrochloric acid exerted a strong catalytic effect. It can be seen in the Fig. that the rate is increased approximately threefold in the presence of 0·01M-acid, and that the average rate coefficients vary linearly with the acid concentration. Deviations from the straight line in the Fig.



The effect of hydrochloric acid on the rate of hydrolysis of triphenylmethyl fluoride in 70% *aqueous acetone at* 40·00°.

The rate coefficients, $k_{av.}$, are the mean integrated first-order rate coefficients at each concentration of hydrochloric acid.

TABLE 1. *Kinetic data for the reaction of triphenylmethyl fluoride with* 70% *aqueous acetone at* 40·00°.

t in sec., k in sec.$^{-1}$, titres in ml.

(i) Run 7, no additions, 4·18 ml. samples titrated with 0·01000N-NaOH. Titre at t_∞ = 7·65

$10^{-3}t$	0·000	2·298	2·910	3·536	4·530	4·875	5·195	5·478	5·850	6·350
Titre	0·64	2·12	2·48	2·84	3·32	3·49	3·64	3·76	3·93	4·13
10^4k obs.	—	1·032	1·046	1·048	1·064	1·070	1·075	1·075	1·083	1·085
10^4k calc., eqn. 1 *	—	1·039	1·053	1·066	1·080	1·086	1·094	1·098	1·104	1·110
10^4k calc., eqn. 2 †	—	1·041	1·056	1·062	1·078	1·083	1·088	1·092	1·097	1·104

$10^{-3}t$	6·960	7·850	8·665	9·595	10·070	10·740	11·755	12·585	13·490	14·160
Titre	4·37	4·71	4·96	5·28	5·44	5·56	5·82	6·00	6·18	6·32
10^4k obs.	1·091	1·107	1·105	1·130	1·146	1·127	1·204	1·150	1·158	1·175
10^4k calc., eqn. 1 *	1·118	1·129	1·138	1·147	1·152	1·158	1·166	1·173	1·179	1·184
10^4k calc., eqn. 2 †	1·113	1·124	1·134	1·145	1·151	1·158	1·169	1·177	1·185	1·191

(ii) Run 28, [NaCl] = 0·00328, 4·18 ml. samples titrated with 0·01020N-NaOH. Titre at t_∞ = 12·65

$10^{-3}t$	0·000	2·400	3·020	3·625	4·540	5·068	5·700	6·695	7·665	8·970
Titre	0·67	3·28	4·04	4·60	5·52	6·10	6·61	7·20	7·95	8·70
10^4k obs.	—	1·032	1·104	1·110	1·153	1·204	1·214	1·190	1·236	1·254
10^4k calc., eqn. 1 *		1·074	1·095	1·114	1·138	1·151	1·166	1·186	1·203	1·224
10^4k calc., eqn. 2 †		1·065	1·085	1·104	1·131	1·147	1·165	1·191	1·215	1·246

(iii) Run 25, [HCl] = 0·00135, 4·18 ml. samples titrated with 0·001020N-NaOH. Titre at t_∞ = 11·26

$10^{-3}t$	0·000	1·020	1·230	1·525	1·992	2·813	3·360	3·900	4·340	4·920	5·460
Titre	1·54	2·74	3·02	3·32	3·78	4·61	5·13	5·53	5·92	6·32	6·71
10^4k obs.	—	1·293	1·346	1·326	1·355	1·380	1·373	1·355	1·380	1·375	1·390
10^4k calc., eqn. 1 *	—	1·245	1·253	1·262	1·273	1·296	1·308	1·319	1·327	1·339	1·348
10^4k calc., eqn. 2 †	—	1·288	1·295	1·305	1·318	1·345	1·360	1·375	1·386	1·402	1·415

(iv) Run 39, [NaF] = 0·00969, 4·18 ml. samples titrated with 0·00839N-NaOH. Titre at t_∞ = 11·60

$10^{-3}t$	0·000	1·800	2·400	2·940	3·360	4·140	5·100
Titre	0·97	2·82	3·32	3·78	4·17	4·80	5·47
10^4k obs.	—	1·063	1·042	1·043	1·067	1·079	1·079
10^4k calc., eqn. 1 *	—	0·868	0·872	0·875	0·878	0·882	0·887
10^4k calc., eqn. 2 †	—	1·042	1·055	1·067	1·076	1·092	1·111

$10^{-3}t$	5·700	6·480	7·740	9·180	10·800	12·120	13·500
Titre	5·95	6·44	7·26	7·92	8·76	9·24	9·68
10^4k obs.	1·108	1·115	1·157	1·156	1·222	1·242	1·268
10^4k calc., eqn. 1 *	0·890	0·894	0·900	0·906	0·912	0·917	0·922
10^4k calc., eqn. 2 †	1·122	1·136	1·159	1·182	1·205	1·224	1·241

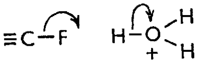
* $10^4k_0' = 0·845$, $10^2k_{H^+}' = 2·06$, $10^4K_{HF}' = 2·91$.

† $10^4k_0 = 0·954$, $10^3k_{HF} = 2·31$, $10^2k_{H^+} = 1·81$.

probably arise from the use of average rate coefficients which depend on the extent of the autocatalysis at the times when readings were taken; this, in turn, depends on the initial concentration of the substrate and the extent of the reaction. Sodium chloride and fluoride had little, if any, effect on the rate (see Table 1).

DISCUSSION

The observation that hydrochloric acid exerts a strong catalytic effect, while sodium chloride and fluoride leave the rate virtually unaltered, suggests that the hydrolysis of triphenylmethyl fluoride is catalysed by hydrogen ions, like the hydrolysis of other fluorides.[3,4b,6] This conclusion contradicts a previous report that strong acids do not alter the rate of hydrolysis of the present compound.[5] No explanation can be advanced to account for this discrepancy but we have been unable to explain the results shown in the Fig. except on the assumption of catalysis by hydrogen or chloride ions; chloride-ion catalysis is excluded by the results observed in the presence of sodium chloride. The catalysis probably arises from partial covalent binding between fluorine and a hydrated hydrogen ion (I) which assists the heterolysis of the C–F linkage,[3,4b] analogously to other examples of electrophilic catalysis in nucleophilic substitution.[8]



(I)

It is attractive to consider that the autocatalysis observed in the present reactions arises from the hydrogen ions which are produced by the electrolytic dissociation of the hydrofluoric acid formed during hydrolysis. On this view, the rate of hydrolysis is always given by

$$d[Ph_3C{\cdot}OH]/dt = -d[Ph_3CF]/dt = [Ph_3CF]\{k_0' + k_{H^+}'[H^+]\}$$

which, on integration, yields

$$k = \frac{1}{t}\ln\frac{[Ph_3CF]_{t=0}}{[Ph_3CF]_{t=t}} = k_0' + \frac{k_{H^+}'}{t}\int_0^t [H^+]\cdot dt \qquad . \ . \ . \ . \quad (1)$$

The hydrogen-ion concentration can be obtained from the concentrations of any added hydrogen and fluoride ions, the concentration of the hydrofluoric acid, and its dissociation constant in concentration units, K_{HF}'. Combination of the results for reaction with the pure solvent and in the presence of 0·0112M-hydrochloric acid yields the values of k_0', k_{H^+}', and K_{HF}' which are shown in the footnote of Table 1 (for details, see p. 3810). Rate coefficients calculated by the substitution of these values in eqn. (1) are compared with those observed in some typical runs in Table 1, and the average deviation of the ratio $k_{calc.}/k_{obs.}$ from unity is given in Table 2 for each series of experiments. It can be seen that eqn. (1) gives good agreement with the experimental observations when electrolytes have not been added and when sodium chloride is present, but that the calculated rate coefficients are, on the average, 3·5% too low in the presence of hydrochloric acid and 21% too low in the presence of sodium fluoride.* Since both hydrogen and fluoride ions depress the ionisation of hydrofluoric acid, it must be concluded that the autocatalysis arises mostly, if not entirely, from some cause other than the production of hydrogen ions as the reaction proceeds. This conclusion is supported by the value of $2{\cdot}91 \times 10^{-4}$ required for K_{HF}' on the basis of this approach. This value is about one-half of the dissociation constant in

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* K_{HF}' was assumed to have the same value in all these experiments. Even an overestimate of the variation of this constant with changing ionic strength (by accepting Debye's limiting law for the ionic activity coefficients) does not alter the result that the rate coefficients calculated from eqn. (1) are, on the average, lower than those observed in the presence of hydrochloric acid, and much lower than those found when sodium fluoride is present.

[8] Ingold, " Structure and Mechanism in Organic Chemistry," G. Bell and Sons, London, 1953, p. 357.

water,[9] but results for other weak acids in organic solvent–water mixtures [10] suggest that K_{HF}' should be reduced at least 1000-fold on changing from water to the present solvent.

TABLE 2. *Comparison of observed rate coefficients with those calculated from equations* (1) *and* (2).

		$100\{(k_{\mathrm{calc.}}/k_{\mathrm{obs.}})_{\mathrm{mean}} - 1\}$	
Additions	*n* *	Eqn. (1)	Eqn. (2)
None	103	$0{\cdot}0 \pm 0{\cdot}2_5$	$0{\cdot}0 \pm 0{\cdot}2_4$
NaCl (0·003—0·01M)	40	$-0{\cdot}3 \pm 0{\cdot}4_5$	$-0{\cdot}1 \pm 0{\cdot}4_7$
HCl (0·001—0·01M)	85	$-3{\cdot}5 \pm 0{\cdot}3_8$	$-0{\cdot}6 \pm 0{\cdot}3_0$
NaF (0·006—0·01M)	52	$-20{\cdot}8 \pm 0{\cdot}4_4$	$-0{\cdot}6 \pm 0{\cdot}3_3$

* Number of separate determinations of *k*.

An alternative explanation of the autocatalysis arises from the fact that hydrofluoric acid can form strong bonds with fluoride ions, and this acid can therefore also be capable of acting as an electrophilic catalyst in the heterolysis of the C–F linkage. On this view, the rate of hydrolysis is given by

$$\mathrm{d}[\mathrm{Ph_3C{\cdot}OH}]/\mathrm{d}t = -\mathrm{d}[\mathrm{Ph_3CF}]/\mathrm{d}t = [\mathrm{Ph_3CF}]\{k_0 + k_{\mathrm{HF}}[\mathrm{HF}] + k_{\mathrm{H^+}}[\mathrm{H^+}]\}$$

If K_{HF}' is one-thousandth of its value in water, the last term is only significant when hydrochloric acid has been added, and the hydrogen-ion concentration is then virtually constant at the concentration of this acid. Thus, on integration

$$k = \frac{1}{t}\ln\frac{[\mathrm{Ph_3CF}]_{t=0}}{[\mathrm{Ph_3CF}]_{t=t}} = k_0 + k_{\mathrm{H^+}}[\mathrm{HCl}] + \frac{k_{\mathrm{HF}}}{t}\int_0^t [\mathrm{HF}]\,.\,\mathrm{d}t \quad . \quad . \quad . \quad (2)$$

Values of k_0 and k_{HF} were obtained from the results of reaction with the pure solvent and are given in the footnote of Table 1 together with the value of $k_{\mathrm{H^+}}$ which was obtained from the runs with 0·0112M-hydrochloric acid (for details, see p. 3811). Substitution of these values in eqn. (2) yields rate coefficients which are always in good agreement with those observed.* This is illustrated in Table 1 where the observed and calculated rate coefficients are compared for some typical runs, and in Table 2 where the average deviations of $k_{\mathrm{calc.}}/k_{\mathrm{obs.}}$ from unity are recorded for the various series. The present findings are thus fully consistent with the view that the hydrolysis of triphenylmethyl fluoride is catalysed by hydrofluoric acid molecules as well as by hydrogen ions. Autocatalysis arises mainly, if not entirely, from the undissociated acid but the results are not sufficiently accurate to permit the complete exclusion of a small contribution from the hydrogen ions produced by the dissociation of this acid.

EXPERIMENTAL

Materials.—Triphenylmethyl fluoride was prepared by a method similar to that employed by Swain and his co-workers.[5b] Triphenylmethyl chloride was dissolved in hydrofluoric acid (Imperial Smelters, purity better than 99·5%) at −15° and stored for 1 hr. Most of the excess of acid was removed at 60—80° in a stream of dry nitrogen, the residue dissolved in dry ether, and the remaining acid removed by the careful addition of potassium hydrogen fluoride. Triphenylmethyl fluoride was obtained from the filtered solution by adding five volumes of light petroleum (b. p. 40—60°) and cooling to −15°. The material was further purified by

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* It seems most likely that the uncatalysed reaction [represented by k_0 in eqn. (2)] occurs by mechanism $S_{\mathrm{N}}1$. Added electrolytes should therefore accelerate hydrolysis by the ionic-strength effect,[11] and sodium fluoride should, in addition, invoke a retarding mass-law effect.[11] No allowance was made for the operation of these effects since they were likely to be negligibly small at the low electrolyte concentrations employed (0·01M), and with " common-ions " which are poor nucleophilic reagents.

[9] Broene and de Vries, *J. Amer. Chem. Soc.*, 1947, **69**, 1644.

[10] Harned and Owen, " The Physical Chemistry of Electrolytic Solutions," Reinhold, New York, 1951, p. 581.

[11] Bateman, Church, Hughes, Ingold, and Taher, *J.*, 1940, 979.

crystallisation from ether–light petroleum; it had m. p. 103—104°. The hydrolysable fluoride was 99·3% of the theoretical amount.

Acetone was purified as previously described,[12] and 70% aqueous acetone was prepared by adding 7 vol. of pure acetone to 3 vol. of distilled water which had also been passed through a mixed ion-exchange column.

Rate Measurements and Analytical Methods.—Reaction rates were measured at 40·00° by using the sealed ampoule technique. The total acid concentration of a 4·18 ml. sample was usually determined by dissolving it in 200 ml. of neutral acetone to which 1 ml. of 0·1M-calcium chloride had been added and titrating with alkali, lacmoid being the indicator. This method gave poor end-points when additional fluoride ions were present, and samples from runs with added sodium fluoride were therefore dissolved in 10 ml. of benzene, extracted three times with 5 ml. portions of " equilibrium " water, and the combined aqueous extracts titrated with alkali to a standard colour with Methyl Red–Bromocresol Green as indicator; [13] the colour was matched instrumentally. Check experiments showed that triphenylmethyl fluoride was not hydrolysed significantly during the extraction, and that rates determined by this technique for reaction in the absence of added electrolytes were the same as those obtained by the simpler method.

Hydrofluoric acid did not react with the solvent or with the product of hydrolysis. The titres of *ca.* 0·02M-solutions of this acid in 70% aqueous acetone, and in the presence of 0·02M-triphenylmethanol, did not alter during 20 hr. at 40°; this corresponds to ten " half-lives " of the solvolysis.

Any reaction between hydrofluoric acid and the glass containers would not have altered the observed titres since fluorosilicate ions were completely hydrolysed during titration with alkali in water and in acetone. Such a reaction would, however, have had serious effects on the kinetics of a process catalysed by hydrogen ions, since fluorosilicic acid can be expected to be almost completely dissociated in 70% aqueous acetone. 0·02M-Solutions of hydrofluoric acid in this solvent were therefore kept at 40° for three " half-lives " of the solvolysis, boiled with sodium carbonate after the acetone had been evaporated, acidified, and analysed for silica by the " molybdenum blue " method,[14] a Spekker absorptiometer being used. Sodium metasilicate was employed as the reference substance, and the reliability of the method was demonstrated with standard solutions of sodium fluorosilicate. It was found that the concentration of silica in the solutions of hydrofluoric acid was never greater than 10^{-5}M, corresponding to 2×10^{-5}M as the upper limit for the hydrogen ions resulting from reaction with the glass containers. The production of this quantity of hydrogen ions during a kinetic run has a negligibly small effect on the integrated rate coefficient, k, and even this represents an overestimate since few reactions were followed over three " half-lives " and since the concentration of hydrofluoric acid was well below 0·02M in the early stages of solvolysis.

Calculations.—(a) *Catalysis by hydrogen ions only.* If the hydrolysis of triphenylmethyl fluoride is catalysed by hydrogen ions only, a knowledge of the concentration of these ions is essential before the rate coefficients k_0' and k_{H^+}' can be determined from eqn. (1). It was assumed that hydrofluoric acid is a weak acid and that

$$(1 + x)^{\frac{1}{2}} = 1 + x/2 \text{ for } x < 1 \qquad \ldots\ldots\ldots \qquad (3)$$

Eqn. (1) then takes the following forms:

(ii) Sodium chloride or no electrolyte added:

$$k = k_0' + k_{\mathrm{H}}'(K_{\mathrm{HF}}')^{\frac{1}{2}} \cdot \frac{1}{t}\int_0^t [\mathrm{HF}]^{\frac{1}{2}} \,.\, \mathrm{d}t \qquad \ldots\ldots \qquad (4)$$

(ii) Hydrochloric acid added, with $[\mathrm{HCl}]^2 > 4K_{\mathrm{HF}}'[\mathrm{HF}]$:

$$k = k_0' + k_{\mathrm{H}^+}'\left\{[\mathrm{HCl}] + \frac{K_{\mathrm{HF}}'}{[\mathrm{HCl}]} \cdot \frac{1}{t}\int_0^t [\mathrm{HF}] \,.\, \mathrm{d}t\right\} \qquad \ldots\ldots \qquad (5)$$

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[12] Bensley and Kohnstam, *J.*, 1956, 287.

[13] Banks, Cuthbertson, and Musgrave, *Analyt. Chim. Acta*, 1955, **13**, 442.

[14] Vogel, " Quantitative Inorganic Analysis," Longmans, Green and Co., London, 1951, p. 669.

(iii) Hydrochloric acid added, with $[\mathrm{HCl}]^2 < 4K_{\mathrm{HF}}'[\mathrm{HF}]$:

$$k = k_0' + k_{\mathrm{H}^+}'\left\{\frac{[\mathrm{HCl}]}{2} + (K_{\mathrm{HF}}')^{\frac{1}{2}}\cdot\frac{1}{t}\int_0^t[\mathrm{HF}]\,.\,\mathrm{d}t + \frac{[\mathrm{HCl}]^2}{8(K_{\mathrm{HF}}')^{\frac{1}{2}}}\cdot\frac{1}{t}\int_0^t\frac{\mathrm{d}t}{[\mathrm{HF}]}\right\} \quad . \quad (6)$$

(iv) Sodium fluoride added, with $[\mathrm{NaF}] > 4K_{\mathrm{HF}}'[\mathrm{HF}]$:

$$k = k_0' + \frac{k_{\mathrm{H}^+}'\,.\,K_{\mathrm{HF}}'}{[\mathrm{NaF}]}\cdot\frac{1}{t}\int_0^t[\mathrm{HF}]\,.\,\mathrm{d}t \quad . \; . \; . \; . \; . \; . \; . \quad (7)$$

Once K_{HF}' had been evaluated, it was found that eqn. (5) applied when $[\mathrm{HCl}] \geqslant 0{\cdot}005$, eqn. (6) when $[\mathrm{HCl}] \leqslant 0{\cdot}0025$, and eqn. (7) to all the experiments with added sodium fluoride. All these equations involve eqn. (3) and are therefore subject to the errors which arise from the fact that this equation is only approximate. These errors are largest for $[\mathrm{HCl}] = 0{\cdot}00542$, but even then the average error in k is less than 1% over the course of a kinetic run.

The application of the method of least squares to the results from reaction in the absence of added electrolytes gave k_0' and $k_{\mathrm{H}^+}'(K_{\mathrm{HF}}')^{\frac{1}{2}} = 0{\cdot}845 \times 10^{-4}$ and $3{\cdot}52 \times 10^{-4}$, respectively—as the intercept and slope of the " best " straight line of the observed rate coefficient, k, against $(1/t)\int_0^t[\mathrm{HF}]^{\frac{1}{2}}\,.\,\mathrm{d}t$, from eqn. (4). When $[\mathrm{HCl}] = 0{\cdot}0112$ the variable term in eqn. (5) is never more than 0·1% of the value of k* and can therefore be neglected.† The average of the rate coefficients under these conditions yields $10^2k_{\mathrm{H}^+}' = 2{\cdot}06$, whence $10^4K_{\mathrm{HF}}' = 2{\cdot}91$. Substitution of these values in eqns. (4)—(7) gave the " integrated first-order rate coefficients calculated from eqn. (1) " which are quoted in Tables 1 and 2; all integrals were evaluated by graphical methods.

(b) *Catalysis by hydrogen ions and by hydrofluoric acid.* The rate coefficients k_0 and k_{HF} were obtained by the method of least squares from the results observed in the absence of added electrolytes as the intercept and slope of the " best " straight line of the observed coefficients, k, against $(1/t)\int_0^t \mathrm{HF}\,.\,\mathrm{d}t$, from eqn. (2): $10^4k_0 = 0{\cdot}954$, $10^3k_{\mathrm{HF}} = 2{\cdot}31$. These values gave $10^2k_{\mathrm{H}^+} = 1{\cdot}81$ from the results observed in the presence of 0·0112M-hydrochloric acid.

The integrated first-order rate coefficients, k, calculated from eqn. (2) with the aid of these values were, on the average, slightly less than those observed for reaction in the presence of hydrochloric acid (see Table 2). This may well have arisen from a small error in k_{H^+}, which was evaluated from relatively few measurements in the most acid solutions. The fact that $k_{\mathrm{calc.}}$ was, on the average, 0·6% less than $k_{\mathrm{obs.}}$ for reaction in the presence of sodium fluoride (see Table 2) may have resulted from the neglect of the ionic-strength effect [11] which accelerates solvolysis—the average ionic strength of the solutions in this series of reactions was considerably greater than in any of the other series studied. It is, however, noteworthy that any significant formation of hydrogen difluoride ions from fluoride ions and hydrofluoric acid would have resulted in calculated rate coefficients larger than those observed. Since this was not found, it can be concluded that the equilibrium constant for the formation of hydrogen fluoride ions is not nearly as sensitive to changes in the solvent composition as the dissociation constant of hydrofluoric acid. This is only to be expected for a process in which reactants and products carry the same number of formal electric charges.

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* This can be demonstrated *a posteriori* once K_{HF}' has been evaluated.

† On this view, no autocatalysis should have been observed when $[\mathrm{HCl}] = 0{\cdot}0112$. A slight upward drift of the integrated rate coefficients, k, was observed as the reaction proceeded by the relatively large value of k (*ca.* 3×10^{-4}) made it impossible to decide whether this drift was genuine or whether it arose fortuitously from the experimental errors; normally, 10^4k increased by 0·12—0·22 over the course of solvolysis.