195. *Tracer Studies in Ester Hydrolysis. Part IX.* Phenyl and Diphenylmethyl Trifluoroacetate.*

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The acyl–oxygen bond is broken during hydrolysis of phenyl trifluoroacetate in acid, alkaline, or initially neutral aqueous dioxan. The kinetic forms of the hydrolysis are similar to those observed for methyl trifluoroacetate. The rate of acid hydrolysis is at a maximum when the concentration of acid is *ca.* 1·5M.

The alkaline hydrolysis of diphenylmethyl trifluoroacetate is by mechanism $B_{Ac}2$. Tracer and kinetic experiments prove the existence of mechanisms $B_{Ac}2$ and $B_{Al}1$ for hydrolysis in initially neutral solution, and of mechanisms $A_{Ac}2$ and $A_{Al}1$ for acid hydrolysis.

Hydrolysis of methyl trifluoroacetate is very rapid in alkaline solution.[1] It is not strongly catalysed by hydrogen ions, in comparison with unfluorinated esters, and the rate begins to level off at $[HClO_4] > 1M$, this unusual kinetic form being thought to be caused by a negative salt effect of the fully ionised perchloric acid. The acyl–oxygen bond was broken in acid, alkaline, and initially neutral solution.

Although we found exclusive acyl–oxygen fission for hydrolysis it is possible to observe bimolecular attack upon the methyl group by methoxide ion in absolute methanol. Traynham and Battiste [2] reported the rapid formation of a gas, thought to be dimethyl ether, in this reaction, and one of us has confirmed this by the use of gas–liquid chromatography. The mechanism must be $B_{Al}2$. Another example of alkyl–oxygen fission, probably with carbonium-ion formation, is the elimination of olefins during solvolyses of t-alkyl trifluoroacetates.[3]

The hydrolyses of phenyl and diphenylmethyl trifluoroacetate were studied by the methods applied to the methyl ester,[1] *i.e.*, determination of the kinetic forms of hydrolysis and of the position of bond fission. Because the mechanisms are strikingly different for

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* Part VIII, *J.*, 1960, 3364.

[1] Bunton and Hadwick, *J.*, 1958, 3248.

[2] Traynham and Battiste, *J. Org. Chem.*, 1957, **22**, 1551.

[3] Moffat and Hunt, *J. Amer. Chem. Soc.*, 1958, **80**, 2985.

differing alkyl groups, we discuss the results for the phenyl and the diphenylmethyl ester separately.

Phenyl Trifluoroacetate.—Hydrolysis is by acyl–oxygen bond fission (see p. 952). This position of bond fission appears to be universal for hydrolyses of phenyl esters. The rate of hydrolysis is increased by addition of alkali or acid, but whereas the effect of acid is comparatively small that of alkali is so great that the reaction in the presence of sodium hydrogen carbonate is too fast for measurement by conventional methods (see p. 951). The kinetic effects of added salts and acids are given in Table 1. Neutral salts decrease the rate, as was found for methyl trifluoroacetate.[1] The negative salt effects are in the sequence, sodium toluene-*p*-sulphonate > lithium perchlorate > potassium trifluoroacetate. Although the mechanism of this retardation is not completely understood, these salts will decrease the activity of the water and probably reduce the activity coefficient of the ester[4] (*i.e.*, " salt in " the ester).

TABLE 1. *Rates of hydrolysis of phenyl trifluoroacetate.*

Solvent: dioxan–water (70 : 30 v/v). Temp. 0°. Titration method (1), unless otherwise specified.

Initially neutral:

10^3k_1 (sec.$^{-1}$) 5·27, 5·59, 5·66, 5·85,[a] 5·96,[a] 6·15,[a] 11·4[b] (mean value 10^3k_1 = 5·55 sec.$^{-1}$).

Effect of added salt:

[$LiClO_4$] (M)...	1·03	1·54	[p-$C_6H_4Me{\cdot}SO_3Na$] (M)	0·384	0·565	[$CF_3{\cdot}CO_2K$] (M)	0·715	1·01
10^3k_1 (sec.$^{-1}$)	3·50	2·19	10^3k_1 (sec.$^{-1}$)...............	3·24	2·80[c]	10^3k_1 (sec.$^{-1}$) ...	4·91	4·39

Acid solutions:

[$HClO_4$] (M)...	0·202	0·503	0·540	0·573	0·923	1·47	1·81	2·39	2·69	3·29	4·90
10^3k_1 (sec.$^{-1}$)	7·92	11·5[a]	10·4	8·64[d]	11·7	11·3[a]	8·18	6·00[a]	3·68	1·89	0·32
[p-$C_6H_4Me{\cdot}SO_3H$] (M)...	0·450	0·578	0·814	1·80	2·53	2·53					
10^3k_1 (sec.$^{-1}$)	9·21	8·62[a]	9·21	11·7	7·05[a]	7·67					

[a] Titration method (2). [b] Temp. 13·7°. Slight pptn. during run. [d] [$LiClO_4$] 0·765 M.

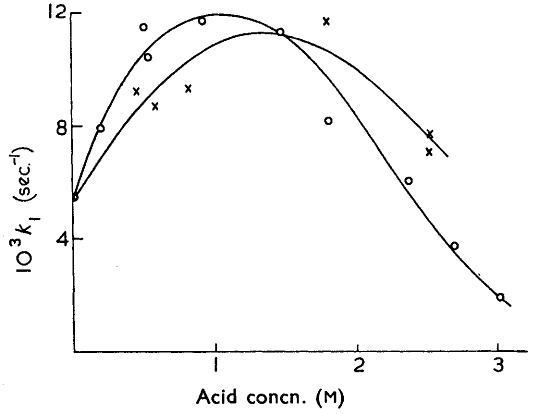

FIG. 1. *Hydrolysis of phenyl trifluoroacetate at 0°.*
○ *Perchloric acid.*
× *Toluene-*p*-sulphonic acid.*

The kinetic form in acid is very similar to that observed for the hydrolysis of methyl trifluoroacetate, but, because our analytical method allowed rate measurements at comparatively high concentrations of acid, we were able to demonstrate the existence of a maximum rate of hydrolysis at [$HClO_4$] or [$C_6H_4Me{\cdot}SO_3H$] *ca.* 1·5M (Fig. 1). Because neutral salts decrease the rate of the neutral hydrolysis, it is difficult to calculate the rate constant for the acid-catalysed component of the hydrolysis. The ions of the added acids will have a negative salt effect upon the neutral hydrolysis, and probably also upon the acid hydrolysis. We were able to treat the hydrolysis of methyl trifluoroacetate semi-quantitatively, by assuming that the negative salt effects of perchloric acid were the same

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[4] Long and McDevitt, *Chem. Rev.*, 1952, **51**, 119; Waind, *J.*, 1954, 2879.

as those of sodium perchlorate, and that these effects varied linearly with salt concentration over a limited range of concentration.[1] These approximations are less satisfactory for the experiments on phenyl trifluoroacetate in which we use concentrations of acid up to *ca.* 3M. An additional complication is that we were unable to estimate the initial slope of a plot of the first-order rate constant, k_1, against the acid concentration (Fig. 1) with precision, because the values of k_1 are scattered. Therefore we used an alternative method of calculation which is described in an Appendix. We assume that the logarithm of the rate of the acid and the neutral hydrolyses will be a linear function of ionic strength,[5] and that the negative salt effects upon the neutral hydrolysis will be the same for perchloric acid as for lithium perchlorate. This calculation, as applied to the acid hydrolysis of methyl trifluoroacetate, gives values for the rate constants close to those calculated earlier.[1]

The values of k_a (the second-order rate-constant for acid hydrolysis) are for perchloric $10^3k_a = 21$ (sec.$^{-1}$ mole^{-1} l.), and for toluene-*p*-sulphonic acid $10^3k_a =$ *ca.* 16 (sec.$^{-1}$ mole^{-1} l.). The smaller catalysis by toluene-*p*-sulphonic acid accords with the observation that it is weaker than perchloric acid in water,[6] and it may not be fully dissociated in aqueous dioxan.

The Arrhenius equation for the neutral hydrolysis in dioxan–water (70 : 30 v/v) is $k_1 = 10^{4\cdot4} \exp(-8300/\boldsymbol{R}T)$ sec.$^{-1}$. The corresponding equations for the neutral hydrolyses of the methyl esters are: in dioxan–water (70 : 30 v/v) $k_1 = 10^{3\cdot6} \exp(-10{,}500/\boldsymbol{R}T)$ sec.$^{-1}$; and in dioxan-water (60 : 40 v/v) $k_1 = 10^{3\cdot8} \exp(-10{,}200/\boldsymbol{R}T)$ sec.$^{-1}$. (In an earlier paper incorrect values were given for the non-exponential Arrhenius parameter.[1])

Electron-withdrawal by the fluorine atoms should reduce the energy of activation for nucleophilic attack upon the acyl-carbon atom. The low value of the non-exponential Arrhenius parameter, corresponding to a negative entropy of activation ($\Delta S^* = -40$ e.u. for hydrolysis of phenyl trifluoroacetate), suggests that there is considerable orientation of water molecules in the transition state, more than in the initial state. This is probably because the transition state is akin to that for addition to a carbonyl carbon atom.[7]

Diphenylmethyl Trifluoroacetate.—Because of the known stability of the diphenylmethyl cation,[8] we expected to observe at least some alkyl–oxygen fission in acid and neutral hydrolyses of this ester (cf. refs. 9 and 10).

The position of bond fission was determined by isolating diphenylmethanol after hydrolysis with water enriched in oxygen-18. A base, 2,6-lutidine, was added for the neutral hydrolyses, to suppress the exchange between diphenylmethanol and water which would be catalysed by trifluoroacetic acid liberated during reaction. (2,6-Lutidine is one of several tertiary amines which can be used as non-nucleophilic buffers.[11])

The acid hydrolysis is faster than the oxygen exchange of diphenylmethanol, and a small correction for the latter, based on control experiments, was applied. Our tracer experiments (Table 2) show that the acyl–oxygen bond is broken during alkaline hydrolysis, but mixed bond fission is found for hydrolysis in acid and initially neutral solution. The position of the bond fission depends, not only upon the nature of the reagent, but also upon the temperature and the solvent, and for an understanding of the mechanisms it is necessary to consider the bond fission and the kinetic form together. We discuss the mechanisms of neutral and acid hydrolysis separately.

The first-order rate constants, k_1, for the neutral hydrolyses are given in Table 3. These refer to two concurrent reactions with different positions of bond fission; the amount

[5] Frost and Pearson, " Kinetics and Mechanism," Chapman and Hall, London, 1953, p. 140.

[6] Bascombe and Bell, *J.*, 1959, 1096.

[7] Bender, *J. Amer. Chem. Soc.*, 1951, **73**, 1626; 1953, **75**, 5986.

[8] Ingold, " Structure and Mechanism in Organic Chemistry," Bell, London, 1953, p. 325.

[9] Davies and Kenyon, *Quart. Rev.*, 1955, **9**, 203; Harvey and Stimson, *J.*, 1956, 3629; Bunton and Hadwick, *J.*, 1957, 3043.

[10] Bunton, Day, Flowers, Sheel, and Wood, *J.*, 1957, 963.

[11] Long and Pritchard, *J. Amer. Chem. Soc.*, 1957, **79**, 2365.

of alkyl–oxygen fission varies from 6% in dioxan–water (60 : 40 v/v) at 25·0°, to 37% in this solvent at 72·9° (Table 2). We can expect the unimolecular alkyl–oxygen fission, $B_{\mathrm{Al}}1$, to be favoured relatively to the bimolecular acyl–oxygen fission, $B_{\mathrm{Ac}}2$, by the factors which favour carbonium-ion formation. Those relevant to our experiments are temperature and solvent composition. Many, though not all, unimolecular processes have higher activation energies than their bimolecular counterparts, and the extent of alkyl–oxygen bond fission increases, as expected, with increasing temperature (Table 2). Somewhat similarly, the amount of alkyl–oxygen bond fission increases with increasing water content of the solvent, because carbonium-ion formation, with charge separation, is facilitated.[12]

TABLE 2. *Bond fission for diphenylmethyl trifluoroacetate.*

The enrichments of the control samples are given in parentheses.*

Neutral solution: Isotopic abundance of solvent water = 0·863 atom % excess.

Solvent (Dioxan vol. %)	Temp.	Isotopic abundance of product (atom % excess)	Alkyl–oxygen fission (%)
40	72·9°	0·275 (0·014)	30[a, b]
60	,,	0·336 (0·016)	37[b]
,,	44·6	0·117 (0·017)	12
,,	25·0	0·060 (0·011)	6
70	72·9	0·220 (0·020)	23[b]

[a] Ester only partially soluble. [b] For experiments at 72·9° the warming-up time is not negligible relatively to the half-life of reaction. These values therefore underestimate the amount of alkyl–oxygen bond fission.

Perchloric acid: in dioxan–water (60 : 40 v/v).

Temp.	[HClO$_4$] (M)	Isotopic abundances (atom % excess) H$_2$O	ROH	Alkyl–oxygen fission (%)
25°	1·0	0·776	0·368 (0·038)	42
,,	2·0	0·680	0·428 (0·104)	48
44·6	1·0	0·776	0·531 (0·055)	62

Alkaline hydrolysis: in water.

Isotopic abundance of water 0·863, of product 0·014 atom % excess.

* For the control tests the diphenylmethanol, with the equivalent amount of trifluoroacetic acid, was kept under the hydrolysis conditions for *ca.* 6 half-lives of the hydrolysis.

TABLE 3. *Rates of hydrolysis of diphenylmethyl trifluoroacetate.*

Dioxan–water (60 : 40 v/v), unless otherwise specified.

Initially neutral solution:

Temp.	0°	10·4°	25·0°	35·8°	42·5°
[Salt] (M)	—	—	—	—	—
$10^5 k_1$ (sec.$^{-1}$)	0·627	2·10	9·14, 9·44	30·2	72·5

Temp.	25°							
[Salt] (M)	CF$_3$·CO$_2$K	0·202	0·561	1·00	LiClO$_4$	0·194	0·820	—
$10^5 k_1$ (sec.$^{-1}$)		10·1	8·83	7·54		14·4	32·0	2·81[a]

Acid solution: (Temp. 25° unless otherwise specified.)

[HClO$_4$] (M)	0·197	0·365	0·784	0·983	1·02	1·36	1·63	2·00	0·936	1·69	1·06	1·49	1·80
$10^5 k_1$ (sec.$^{-1}$)	24·2	35·3	84·8	160[b]	121	180	253	383	7·95[c]	15·0[c]	60·5[a]	104[a]	160[a]

[a] Dioxan–water (70 : 30 v/v). [b] 0·51M-LiClO$_4$ added. [c] At 0°.

The temperature-dependence of the bond fission shows that the unimolecular mechanism, $B_{\mathrm{Al}}1$, has a higher activation energy than the bimolecular mechanism, $B_{\mathrm{Ac}}2$, and a plot of log k_1 against the reciprocal of the absolute temperature is not a straight line, but a smooth curve with slope increasing with temperature. This can be seen from the variation of the values of E (the Arrhenius activation energy) with temperature. The following

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[12] Ref. 8, p. 345.

values are calculated over the preceding 10° for neutral hydrolysis in dioxan–water (60 : 40 v/v):

Temp.	10°	20°	30°	40°
E (kcal. mole^{-1})	17·2	18·3	19·5	20·6

These activation energies are considerably greater than those for the neutral hydrolyses of methyl [1] and phenyl trifluoroacetates (p. 945).

It should be possible, in principle, to use the temperature-dependence of the bond fission to calculate the difference in activation energies for the two mechanisms. This has not been done here, because the fastest measured reaction rate corresponds to only 12% of alkyl–oxygen bond fission, and this figure is uncertain because we do not know whether 2,6-lutidine affects the rate, and we know that trifluoroacetate ions, formed during reaction, do (p. 946). However it is clear that the activation energy for the unimolecular mechanism, $B_{\mathrm{Al}}1$, must be considerably greater than 21 kcal. mole^{-1}, as expected for such a reaction.

The effects of added neutral salts confirm this picture of two simultaneous reactions. Azide ions intervene by trapping diphenylmethyl ions formed during hydrolysis by mechanism $B_{\mathrm{Al}}1$ (Table 4); the extent of intervention in the hydrolysis of diphenylmethyl chloride is given there for comparison.

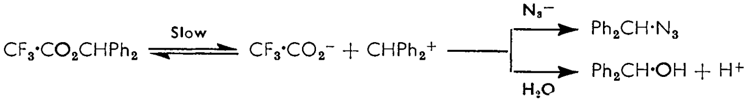

TABLE 4. *Azide intervention.*

Solvent dioxan–water (60 : 40 v/v), unless otherwise specified.

Temp.	25°			72·9°	100°	
[NaN$_3$] (M)	0·38	0·31 *	0·38 *	0·33	0·30	0·16
[Ph$_2$CH·N$_3$] (mole %)	14	62	65	35	37	26 †

* Ph$_2$CHCl. † Dioxan–water (70 : 30 v/v).

Just as an increase in temperature increases the extent of alkyl–oxygen bond fission, so it increases carbonium-ion capture by azide ions. There are two reasons for this; first the proportion of reaction by mechanism $B_{\mathrm{Al}}1$ increases with increasing temperature, and, secondly, there is a difference of *ca.* 4 kcal. mole^{-1} between the activation energies for carbonium-ion capture by azide ions and by water,[13] *i.e.*, azide ion is a more effective competitor at higher temperatures. For a given temperature, the extent of azide-ion intervention is greater for the more aqueous solvent, with its greater component of $B_{\mathrm{Al}}1$. (The competitive efficiency of the azide ion is little affected by changes in the water content of the solvent.)

It should also be possible, in principle to use these intervention experiments to calculate the proportion of mechanism $B_{\mathrm{Al}}1$, by finding the competitive efficiency of azide, relative to water, from the experiments on a diphenylmethyl halide. Comparison between the extents of azide intervention in hydrolysis of the chloride and the trifluoroacetate (Table 4), suggests that there is *ca.* 20% of carbonium-ion formation for hydrolysis of the latter at 25°, in the presence of 0·38M-sodium azide. This is much larger than the amount of alkyl–oxygen fission (with carbonium-ion formation), as determined by use of ^{18}O, in the absence of sodium azide (Table 2). It is probable that this salt is favouring carbonium-ion formation, by an ionic-strength effect, and at the same time it may retard hydrolysis by mechanism $B_{\mathrm{Ac}}2$, because neutral salts retard the neutral hydrolysis of methyl and phenyl trifluoroacetates by mechanism $B_{\mathrm{Ac}}2$ (p. 944).

Lithium perchlorate and trifluoroacetate both have kinetic salt effects upon the neutral hydrolysis. Their forms are very different from those observed for methyl [1] and phenyl trifluoroacetate (p. 944), whose neutral hydrolyses were retarded by these salts. Lithium

[13] Hawdon, Hughes, and Ingold, *J.*, 1952, 2499.

perchlorate increases the total rate of neutral hydrolysis of diphenylmethyl trifluoroacetate. Increase in ionic strength will facilitate the charge formation which occurs during neutral hydrolysis, and this accelerating effect must outweigh any negative salt effect upon mechanism $B_{Ac}2$.

The behaviour of lithium trifluoroacetate is more complex. The rate of hydrolysis first increases, and then decreases, on addition of this salt (Table 3). Such behaviour has been observed with chloride ions in the S_N1 solvolysis of 2,3-dichlorodioxan,[14] and it was thought to be the result of an ionic-strength acceleration predominating, at low ion concentration, over a retarding common-ion effect. Such an explanation is probably correct for our results, although we have the complication of an extra component of reaction ($B_{Ac}2$) which will show no common-ion retardation.

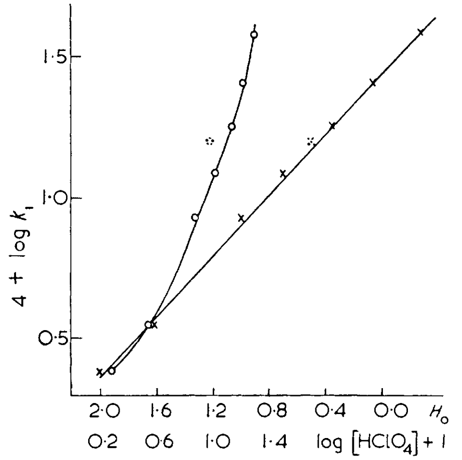

FIG. 2. *Acid-catalysed hydrolysis of diphenylmethyl trifluoroacetate at* 25°.

○ *Plot of* log k_1 *against* log [$HClO_4$].
× *Plot of* log k_1 *against* H_0.
0·51M-$LiClO_4$ *present for broken circle and cross.*

The extent of acid catalysis (relative to the neutral rate) is not large by comparison with that usually found for ester hydrolyses, but it is greater than for hydrolyses of other trifluoroacetates (ref. 1 and p. 944). The isotopic results again show two simultaneous reaction paths, one with acyl–oxygen and the other with alkyl–oxygen bond fission (Table 2). As for neutral hydrolysis, the extent of alkyl–oxygen bond fission increases with temperature, and it seems that mechanisms $A_{Al}1$ and $A_{Ac}2$ co-exist, the former having the higher activation energy.

It is usually found that the rates of specific hydrogen-ion catalysed hydrolyses are, to a first approximation, proportional to the acid concentration in bimolecular or to Hammett's acidity function, h_0, in unimolecular reactions[15] (although intermediate kinetic forms are known). Our acid hydrolyses fit neither of these limiting forms: the plot of log k_1 against the logarithm of perchloric acid concentration is a curve of continually increasing slope, always greater than unity; whilst against $-H_0$ it is a straight line of slope 0·55 (Fig. 2). From the bond-fission results this must be an example of two simultaneous reactions of different kinetic forms. The unimolecular mechanism $A_{Al}1$ should increase in relative importance at higher acid concentrations (where h_0 diverges from [$HClO_4$]), and the rate of the bimolecular mechanism, $A_{Ac}2$ may increase more slowly than does [$HClO_4$]. [This behaviour is observed for the acid hydrolyses of the methyl[1] and phenyl trifluoroacetate (Fig. 1).]

Tracer experiments (Table 2) prove that the relative importance of mechanism $A_{Al}1$ increases with increasing [$HClO_4$]. If we could measure the rate at acid concentrations

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[14] Salomaa, *Acta Chem. Scand.*, 1954, 8, 744.
[15] Long and Paul, *Chem. Rev.*, 1957, **57**, 935.

$>$ *ca.* 3M, we should expect to find the rate varying linearly with h_0. Unfortunately our dilatometric method fails at *ca.* 2M-$HClO_4$ and we could not test this point. However, we found that at a lower temperature (0°) the slope of log k_1 against $-H_0$ was only 0·3 (from results in Table 3); this is understandable because reaction $A_{Al}1$, whose rate follows h_0, will be relatively unimportant at this temperature.

It has been suggested that the values of the entropy, ΔS^*, or the energy, E, of activation provide a test of molecularity, and in particular that ΔS^* is negative for bimolecular reactions, and near to zero, or positive, for unimolecular ones.[16]

We find changes in the values of ΔS^* and E in the expected direction, with increasing acid concentration:

$[HClO_4]$ (M)	E (kcal. mole^{-1})	ΔS^* (e.u.)
0·936	16·8	$-18·2$
1·69	18·9	$-10·0$

(These values are calculated from the overall rate of reaction; subtraction of the neutral rates changes them insignificantly.) The actual numerical values have no particular significance, because the relative amounts of reactions $A_{Al}1$ and $A_{Ac}2$ are changing with temperature, acid concentration, and ionic strength.

The isotopic and the kinetic method both show that the extent of the unimolecular mechanism, $A_{Al}1$, increases relative to that of $A_{Ac}2$ with increasing temperature and perchloric acid concentration.

The rate of acid hydrolysis of diphenylmethyl trifluoroacetate in dioxan-water (70 : 30 v/v) (by mechanism $A_{Ac}2$) is very similar to that of diphenylmethyl formate, and much greater than that of the acetate.[10] The effect of the fluorine atom in decreasing the basicity of diphenylmethyl trifluoroacetate is therefore offset by an increased rate of decomposition of the conjugate acid.

Relative Rates of Hydrolyses.—Comparison of the relative rates of hydrolysis of methyl, phenyl, and diphenylmethyl trifluoroacetate is complicated by the fact that hydrolysis of diphenylmethyl trifluoroacetate in neutral and acid solution has extra reaction paths ($B_{Al}1$ and $A_{Al}1$) over those available to the other esters. We can, however, make qualitative comparison between the reactivities of these three esters by choosing conditions in which there is little alkyl-oxygen fission of diphenylmethyl trifluoroacetate, *i.e.*, low temperatures and low concentrations of acid. The numerical values which we quote depend upon the temperature, because the hydrolyses of these esters have different activation energies [1] (and p. 945 and above).

For hydrolysis in initially neutral dioxan-water (70 : 30 v/v) at 0°, the relative rates of mechanism $B_{Ac}2$ are: diphenylmethyl 1; methyl 10; phenyl, 2600. The relatively low reactivity of the diphenylmethyl ester may be caused by steric hindrance by the phenyl groups to the incoming water molecule. The hydrolyses in alkaline solutions of sodium carbonate or sodium hydrogen carbonate have (qualitatively) the same sequence of rates.

The rate constants for the acid hydrolysis of methyl and phenyl trifluoroacetate cannot be determined very accurately, because a small acid-catalysis is superimposed upon a neutral hydrolysis, and both are subject to negative salt effects. We compare the rates of acid hydrolysis at 0°, because at this temperature, and at a low acid concentration, the hydrolysis of all three esters should be by the same mechanism, $A_{Ac}2$. (The value for diphenylmethyl trifluoroacetate is calculated from rate constants at 25°, by using a value of E of 14 kcal. mole^{-1}; cf. above.)

The values of the second-order rate constants, 10^5k_a, in units of sec.$^{-1}$ mole^{-1} l., are: diphenylmethyl — (6); methyl 30 (47); phenyl, 2100. [The comparison is for the solvents dioxan-water (70 : 30 v/v), with values for the 60 : 40 mixture in parentheses.]

Where comparison is possible the rates are greater in the more aqueous solvent (see

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[16] Taft, *J. Amer. Chem. Soc.*, 1952, **74**, 5372; Long, Pritchard, and Stafford, *ibid.*, 1957, **79**, 2362.

also ref. 1 and Table 3), because in it the protonating power of the acid is greater.[17,18] The structural factors which affect the rate of a specific hydrogen-ion catalysed reaction are the basicity of the neutral molecule and the reactivity of the conjugate acid. The sequence of the basicities of the three esters is probably: methyl > diphenylmethyl > phenyl. This is not the sequence of the acid rates, and it seems that the ease of breakdown of the conjugate acid is the more important factor.

Comparison between the hydrolyses of diphenylmethyl formate, acetate, and trifluoroacetate shows that the powerful electron-attracting fluorine atoms facilitate both bimolecular attack upon the acyl-carbon atom, and unimolecular alkyl-oxygen bond fission;[19] there is, however, no striking enhancement of the latter relative to the former. The $B_{Ac}2$ mechanism is accelerated much more than the acid mechanisms $A_{Ac}2$ and $A_{Al}1$; *e.g.*, the hydrolysis of diphenylmethyl trifluoroacetate in alkaline solution is very rapid, whereas that of diphenylmethyl formate can be followed by acid–base titration;[10] the acid hydrolyses have similar rates (p. 949). To this extent the trifluoroacetates are similar to the esters of the tetra-alkylammonio-acetic acids, whose alkaline hydrolysis is very rapid and whose acid hydrolysis is slow relative to those of acetates.[20]

The kinetic forms for methyl and phenyl trifluoroacetate are very similar, *e.g.*, both show a levelling off, or a maximum, in the rate of hydrolysis in acid, at $[H^+]$ *ca.* 1·5M, which is not associated with complete protonation. So far as we know, the only other examples of this behaviour are the acid hydrolyses of some aryl phosphates.[21] In all these reactions the acyl–oxygen bond (or the equivalent bond in the phosphates) is broken. Diphenylmethyl trifluoroacetate, with appreciable alkyl–oxygen fission in acid solution, shows no such effects (Fig. 2).

Somewhat similarly, increase in ionic strength decreases the rates of neutral and acid hydrolysis of methyl[1] and phenyl trifluoroacetate, and increases those of diphenylmethyl trifluoroacetate (Tables 1 and 3).

EXPERIMENTAL

Materials.—Phenyl trifluoroacetate, prepared from phenol and trifluoroacetic anhydride,[22] and fractionated through a 30 cm. helix-packed column, had b. p. 149° and n_D^{25} 1·4247.

Diphenylmethyl trifluoroacetate was prepared by the reaction of diphenylmethanol (0·25 mole) with trifluoroacetic anhydride (0·25 mole) in sodium-dried ether. The solution was cooled and stirred vigorously. On the following day the volatile materials were removed *in vacuo*, and the ester was distilled under reduced pressure. Diphenylmethyl trifluoroacetate had b. p. 93°/2·5 mm., n_D^{25} 1·500 (Found: C, 63·6; H, 4·0%; equiv., 282. $C_{15}H_{11}F_3O_2$ requires C, 64·2; H, 3·9%; equiv., 280).

The solvent was aqueous dioxan as already described.[1]

Kinetic Measurements.—*Phenyl trifluoroacetate.* The solvent was dioxan–water (70 : 30 v/v). The reaction was followed by estimating the phenol produced,[23] by means of a stock solution of bromine (bromine 8 c.c., sodium acetate trihydrate 120 g., and acetic acid 100 c.c., made up to 1 l. with water). The concentration of sodium acetate was always sufficient to neutralise the acid present in the reaction solution, and that formed in the bromination, and for runs at high acid concentration extra sodium acetate was added.

Two procedures were used. (1) Samples (5 c.c.) of the reaction solution were added as rapidly as possible to a mixture (5 c.c.) of the bromine solution and carbon tetrachloride. The flask was shaken vigorously for 7 sec., and an excess of potassium iodide then added with shaking. This time of 7 sec. was sufficient for complete bromination, and no further reaction of phenol occurred after addition of the iodide. The carbon tetrachloride reduces the volatility

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[17] Braude and Stern, *J.*, 1948, 1976.
[18] Bunton, Ley, Rhind-Tutt, and Vernon, *J.*, 1957, 2327.
[19] Cf. Anbar, Dostrovsky, Samuel, and Yoffe, *J.*, 1954, 3603.
[20] Bell and Lindars, *J.*, 1954, 4601.
[21] Vernon, *Chem. Soc. Spec. Publ.*, 1957, No. 8, p. 17; unpublished results by Barnard, Silver, and Welch; Holbrook and Ouellet, *Canad. J. Chem.*, 1958, **36**, 698.
[22] Clark and Simons, *J. Amer. Chem. Soc.*, 1953, **75**, 6305.
[23] Waters, *J.*, 1936, 1014.

of bromine, and also stops the hydrolysis by extracting the ester from the aqueous phase. There is thus some uncertainty in time, depending upon the vigour of the shaking.

For this reason an alternative procedure (2) was used to test the method. Instead of carbon tetrachloride, purified dioxan (10 c.c.) was present during the bromination, which took place in homogeneous solution. Excess of potassium iodide was added 5 sec. after addition of the reaction solution. This method gave slightly higher results than the first (see Table 1 and Fig. 1), probably because hydrolysis continued during the 5 sec. before addition of the iodide.

The iodine liberated was titrated with 0·05N-sodium thiosulphate; no indicator was used. The copious precipitate formed during titrations, for runs catalysed by perchloric acid, did not appear to affect the results. An example of a kinetic run at 0° is given:

$[HClO_4]$ 0·54M, $[CF_3{\cdot}CO_2Ph]$ *ca.* 0·05M. Titration method 1.

Time (sec.)	36	63	90	116	142	165	∞
Titre (c.c.)	29·6	23·9	19·9	17·8	16·0	14·6	9·49, 9·42

$10^3k_1 = 10{\cdot}4$ (sec.$^{-1}$), calc. graphically from the integrated first-order rate equation.

The alkaline hydrolysis, even with sodium hydrogen carbonate in dioxan–water (60 : 40 v/v) at 0°, was too fast for measurement by our methods.

Diphenylmethyl Trifluoroacetate.—Hydrolysis in initially neutral solution was followed titrimetrically by the method used for methyl trifluoroacetate.[1] The acid produced was estimated by the reaction:[24] $6H^+ + 5I^- + IO_3^- \longrightarrow 3I_2 + 3H_2O$.

Stoppered flasks were used at all temperatures except 45·2° (at which sealed tubes were used). Slight autocatalysis was observed in the neutral hydrolysis, as for the methyl ester; therefore initial values are quoted.

An example of a run in initially neutral dioxan–water (60 : 40 v/v) at 25° is given.

Ester *ca.* 0·03M. Concns. given in c.c. of 0·025N-sodium thiosulphate per 5 c.c. portion.

Time (min.)	4	30	60	92	120	150	203
[Ester]	5·85	5·15	4·20	3·40	2·75	2·25	1·50

$10^5k_1 = 9{\cdot}44$ sec.$^{-1}$ (initial rate constant); at time = 200 min.

$10^5k_1 = 15{\cdot}3$ sec.$^{-1}$. Both constants evaluated graphically, from the integrated first-order rate equation.

The intervention of azide ions was used as a test for carbonium-ion formation during neutral hydrolysis. The amount of acid produced after complete reaction was estimated by acid–base titration (phenolphthalein indicator); reactions in which sodium azide was present gave a milky emulsion, probably of diphenylmethyl azide. Most of these intervention experiments (Table 4) were made at the higher temperatures, because here carbonium-ion formation is of most importance. Unfortunately much reaction occurred while the solution was coming to thermostat temperature; *e.g.*, at 72·9° the half-life is *ca.* ½ min. These intervention experiments may therefore underestimate the extent of carbonium-ion formation.

The acid-catalysed reaction was followed dilatometrically, and the first-order rate constants were calculated by Guggenheim's method.[25] An example is given:

Solvent: dioxan–water (60 : 40 v/v). 25·0°. $[HClO_4]$ 0·365M.
[Ester] *ca.* 0·03M. Alternate points are quoted.

Time (min.)	10	20	30	40	50	60	70	80	90
h_t (mm.)	18·43	16·66	15·11	13·86	12·91	12·12	11·49	11·01	10·59
$h_{t+\tau}$ (min.)	10·29	9·89	9·81	9·62	9·43	9·35	9·28	9·18	9·10

$10^5k_1 = 35{\cdot}3$ (sec.$^{-1}$), calculated graphically.

Alkaline hydrolysis with sodium hydroxide was too fast for measurement by conventional methods; we therefore followed the reaction with sodium hydrogen carbonate at 17°, in dioxan–water (60 : 40 v/v). With [Ester] = 0·032M, $[NaHCO_3]$ = 0·0415N, $t_{1/2} \approx 7$ min. The hydrolysis is therefore much slower than those of methyl[1] and phenyl trifluoroacetate.

The values for Hammett's acidity function for perchloric acid in aqueous dioxan have been reported earlier.[18]

Tracer Experiments.—Reactions were taken to completion in solvent with the water enriched in ^{18}O.

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[24] Gorrin, Pierce, and McBee, *J. Amer. Chem. Soc.*, 1953, **75**, 5622.

[25] Guggenheim, *Phil. Mag.*, 1926, **2**, 538.

Phenyl trifluoroacetate. The acid and neutral hydrolyses were made under kinetic conditions at 0°. After hydrolysis, the acid was neutralised with potassium hydroxide, any precipitate filtered off, the solution made slightly acid, and the phenol extracted with ether. The recrystallised phenol was dried over phosphoric oxide.

Neutral hydrolysis: Phenol, isotopic abundance 0·021 atom % excess, was isolated from hydrolysis with the abundance of water 0·595 atom % excess.

Acid hydrolysis: Phenol isolated had 0·017 and the water 0·385 atom % excess; hydrolysis was with [$HClO_4$] = 2·4M. The alkaline hydrolysis was in aqueous 0·7M-sodium hydroxide at room temperature. After complete reaction the solution was acidified, and the phenol isolated as described. The abundances were phenol 0·016 and water 0·595 atom % excess.

Diphenylmethyl Trifluoroacetate.—Diphenylmethanol was isolated after the reaction was complete and purified by recrystallisation from light petroleum. For hydrolysis under neutral conditions an excess of 2,6-lutidine was added to the solvent; [11] it was assumed that this base would not affect the reaction. Control tests were made with diphenylmethanol in the isotopically enriched solvent containing 2,6-lutidine, and a correction applied.

The acid hydrolysis was made under kinetic conditions; control experiments were made on the exchange between diphenyl methanol and water, and a correction was applied.

The alkaline hydrolysis was made by shaking the ester with $H_2{}^{18}O$ containing 0·5M-sodium hydroxide.

Isotopic abundances of phenol and diphenylmethanol were determined by pyrolysis to carbon monoxide, over red-hot carbon *in vacuo*, and mass-spectrometric analysis of this gas. All the isotopic abundances were expressed in atom % excess above normal.

APPENDIX

Calculation of the Rate Constants for the Acid-catalysed Hydrolysis of Phenyl Trifluoroacetate.—Because the extent of acid-catalysis is small, and because of uncertainty in the initial slope of Fig. 1, it is difficult to estimate k_a, the second-order rate constant for acid hydrolysis, where $\mu \longrightarrow 0$. The following extrapolation procedure was used. For ionic strengths (μ) outside the Debye–Hückel region the relation between rate (v) and ionic strength approximates to: [5]

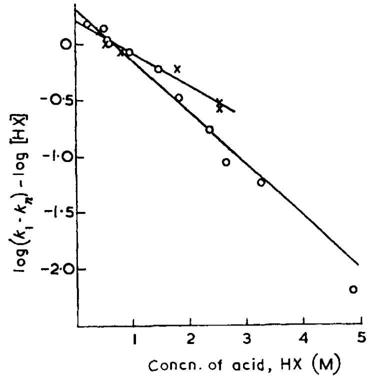

FIG. 3. *Calculation of rate constants for acid-catalysed hydrolysis of phenyl trifluoroacetate.*
○ *Perchloric acid.*
× *Toluene-*p*-sulphonic acid.*

$$v = v_0 \exp(-\beta\mu)$$

We assume that the salt effects upon the neutral rate of perchloric and toluene-*p*-sulphonic acid will be approximately the same as those of their lithium and sodium salts respectively; thus for the neutral hydrolysis in perchloric acid $\beta = 0{\cdot}19$, and for that in toluene-*p*-sulphonic acid $\beta = 0{\cdot}56$. Thus at any acidity we can estimate k_n, the first-order rate constant for the neutral hydrolysis. This value of k_n, subtracted from the overall first-order rate constant, k_1, gives the first-order rate for the acid hydrolysis. This will be related to k_n by

$$(k_1 - k_n) = k_a[HX] \exp(-\beta_x\mu)$$

or

$$\log(k_1 - k_n) - \log k_a - \log[HX] = -\beta_X\mu/2{\cdot}3$$

(and μ = [HX]).

A plot of the acid concentration against {log $(k_1 - k_n)$ − log [HX]} should be a straight line, and extrapolate to log k_a for [HX] = 0 (Fig. 3). The points for perchloric and toluene-*p*-sulphonic acid do not coincide, the slope being less for the latter. The calculated values of k_a are: perchloric acid $10^3k_a = 21$ (sec.$^{-1}$ mole^{-1} l.), and toluene-*p*-sulphonic acid $10^3k_a =$ *ca.* 16 (sec.$^{-1}$ mole^{-1} l.), at 0°.

The most serious uncertainty in this calculation is the assumption that a strong acid and its salt have similar negative salt effects upon a reaction. This is not reasonable for high ionic strengths, if only because the acid will reduce the activity of the water more than does the salt; by an extrapolation to zero acid concentration we reduce the effect of this uncertainty.

We have applied this calculation to the acid hydrolysis of the methyl ester, and find reasonable agreement with our original values (in parentheses):

dioxan–water (60 : 40 v/v); $10^4k_a = 4{\cdot}6$ (sec.$^{-1}$ mole^{-1} l.) (4·7)
dioxan–water (40 : 60 v/v); $10^4k_a = 13$ (sec.$^{-1}$ mole^{-1} l.) (12·7)

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