$CCl_2FCCl_2CF_3$. An ampoule was charged with 12.0 g., 0.08 mole, of $CF_3CH=CClF$, 18.0 g., 0.25 mole, of Cl_2, and 10 ml. of water which was added to dissolve HCl formed during the reaction. The ampoule was irradiated with two 15 watt fluorescent lamps (General Electric 360 BL) for 19 days at 35°. On opening the ampoule excess chlorine was the only low boiling material found. The organic product was taken up in ether and the ether solution washed with sodium thiosulfate solution, dried over $MgSO_4$ and distilled. A solid distillate, 16.5 g., b.p. 109–112°, 79% yield calculated as $C_3Cl_4F_4$, was obtained. This material was redistilled to yield: (1) 2.0 g., b.p. to 110.5° (729 mm.); (2) 3.7 g., b.p. 110.5–111.5° (729 mm.); (3) 8.0 g., b.p. 111.5° (728 mm.); (4) 2.0 g. of residue.

The properties of fraction 3, $CCl_2FCCl_2CF_3$, were b.p. 111.5° (729 mm.), m.p. 41–43°, mixed melting point with a 1:1 ratio of an authentic sample of $CCl_2FCCl_2CF_3$ 42-44°. The infrared curves in the region 2–15 μ for the two samples were superimposable; reported[33] for $CCl_2FCCl_2CF_3$: m.p. 41.74°, b.p. 112.4° (760 mm.).

Reaction of Chloride Ion with 3,3-Dichloro-1,1,3-trifluoropropene.—An ampoule was charged with 11.5 g., 0.07 mole, of $CCl_2FCH=CF_2$, 50 g. of acetone and 4.0 g., 0.10 mole, of lithium chloride. The solution was shaken for one day at 27°. The ampoule was opened and the contents poured into 1 liter of ice-water. The resulting water-insoluble material was dried over $MgSO_4$ and distilled. The distillate, b.p. 53–55° (736 mm.), showed infrared peaks at 5.71 and 5.94 μ which indicated a mixture of starting material and rearranged product $CClF_2CH=CClF$.

It was believed that insufficient time had been allowed for the reaction. Accordingly, 8.0 g. of additional CCl_2F-$CH=CF_2$ and 4.0 g. of the mixed product obtained above, a total of 0.073 mole, was treated as before but the reaction time was increased to 48 hours at 42 ± 2°. Simple distillation of the crude material yielded 7.1 g., 59%, of CCl-$F_2CF=CClF$. Redistillation yielded: (1) 5.4 g., b.p. 56–58° (734 mm.); (2) 1.0 g. of residue. The properties of fraction 1, $CClF_2CH=CClF$, were: b.p. 56–58° (734 mm.), $n^{20}\text{D}$ 1.3701, *d* 1.459 (Densitometer at 27.5°); calcd. for $C_3Cl_2F_4$ mol. wt. 165, found mol. wt. 167 (Dumas). An infrared absorption peak was observed only at 5.94 μ in the $C=C$ region.

Stability of $CF_2=CHCCl_2F$ in Acetone Solution.[32]—Two tubes were filled with 2.5 g. of olefin and 10 ml. of dry acetone and sealed under vacuum. Each tube was held at 65° for 45 hours. The contents of each tube was then separately drowned in ice-water to yield 2.3 g., 92%, and 2.2 g., 88%, of water-insoluble material. This was shown to be unchanged olefin by refractive index and infrared spectra.

Reaction of Iodide Ion with 3,3-Dichloro-1,1,3-trifluoropropene.—A solution containing 11.5 g., 0.07 mole, of $CCl_2FCH=CF_2$, 30.0 g., 0.20 mole, of NaI and 105 g. of acetone was sealed in a glass ampoule and shaken at 60 ± 2° for 45 hours. The ampoule was opened and the contents were drowned in 1.5 liters of ice-water. The resulting insoluble material was washed with 50 ml. of ice-water, separated, and dried over $MgSO_4$, to yield 13.0 g. of product, $n^{20}\text{D}$ 1.4639. Distillation yielded: (1) 3.0 g. of Dry Ice trap condensate, water soluble and presumed to be acetone; (2) 0.5 g., b.p. 40–43° (70 mm.), $n^{20}\text{D}$ 1.4673; (3) 8.3 g., b.p. 43° (70 mm.), $n^{20}\text{D}$ 1.4682; (4) 1.0 g. of residue. Fractions 2–4 represented a 55% yield of $CClF=CHCF_2I$.

Fraction 3 was combined with material from another run decolorized with mercury and redistilled. The physical properties of this fraction, $CF_2ICH=CClF$, were b.p. 51° (100 mm.), formed a glass in liquid nitrogen, $n^{20}\text{D}$ 1.4681, d^{20}_4 2.0894; calcd. for $CF_2ICH=CClF$: *MR*D 33.5, chlorine plus iodine 63.3%; found: *MR*D 34.1, chlorine plus iodine, 62.9% (total silver halide precipitate). Redistillation yielded a center cut, b.p. 51° (100 mm.), $n^{20}\text{D}$ 1.4688.

The infrared absorption spectra of $CF_2ICH=CClF$ prepared by the dehydrochlorination of $CCl_2FCH_2CF_2I$ and of fraction 3 obtained by reacting NaI with $CCl_2FCH=CF_2$ were compared in the region 2–15 μ and found to be superimposable.

A further reaction of $CCl_2FCH=CF_2$ with NaI in acetone was carried out at 61 ± 1° for 24 hours. This was not sufficient time to obtain equilibrium. After distillation and removal of acetone by washing with ice-water there was obtained a fraction, 19%, whose infrared absorption spectrum in the region 2–15 μ was identical with that of the starting $CCl_2FCH=CF_2$. The only other product isolated in 52% yield, based on unrecovered $CCl_2FCH=CF_2$, was CF_2ICH-$=CClF$. This result showed that under the conditions utilized reaction with chloride ion produced in the reaction to form $CClF_2CH=CClF$ did not take place to an appreciable extent.

Difluoroiodoacetamide.—The olefin, 12.5 g., 0.05 mole, $CF_2ICH=CClF$, prepared by treating $CCl_2FCH=CF_2$ with NaI in acetone, was oxidized with $KMnO_4$, in solution buffered by $NaHCO_3$.[29] The resulting acid was converted to its ethyl ester. The ester was not isolated, but a solution of the ester in ethanol was treated with anhydrous ammonia. Ethanol was removed under vacuum and the residue, which failed to crystallize, was passed through a 10 × 0.8 cm. column containing Magnesol–Celite 1:1. The eluent was diethyl ether–petroleum ether (b.p. 30–60°). Evaporation of the solvent yielded 2.9 g. of a solid m.p. 91–96°, 27% yield of CF_2ICONH_2. Two recrystallizations from benzene–petroleum ether, gave needles, m.p. 100.6-101.1° (cor.); calcd. for CF_2ICONH_2: iodine 57.4%; found: iodine 57.7%.

ITHACA, N. Y.

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(33) A. L. Henne and A. M. Whaley, THIS JOURNAL, **64**, 1157 (1942).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

Solvent and Chain Length Effects in the Non-catalyzed Hydrolysis of Some Alkyl and Aryl Trifluoroacetates

BY ARLO MOFFAT AND HERSCHEL HUNT

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The chain length effects on the rates of hydrolysis of the *n*-alkyl and *sec*-alkyl trifluoroacetates parallel those which are observed in base-catalyzed hydrolysis of esters of non-catalyzed hydrolyses also parallel the solvent effects which are observed for the base-catalyzed hydrolyses. An explanation is presented to account for the very large differences which are observed between acid-catalyzed and base-catalyzed acyl–oxygen cleavage as far as chain length effects and solvent effects are concerned. Chain length effects and reactivity are related through a function of the reciprocal of the mass of the intermediate involved. It is suggested that a possible explanation for this mass relationship might lie in the effect of chain length upon bond amplitudes or bond vibrations.

Introduction

We have shown that the non-catalyzed hydrolysis of the *n*-alkyl trifluoroacetates is very closely related to the base-catalyzed hydrolysis of the *n*-alkyl benzoates[1,2] as far as chain length *versus* structure is concerned. It was found that re-

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(1) A. Moffat and H. Hunt, THIS JOURNAL, **79**, 54 (1957).

(2) E. Tommila, *Ann. Acad. Sci. Fennicae*, **A59**, No. 3, 3 (1912).

activity could be related to structure by

$$\ln k = a/M + b \qquad (1)$$

where k is the rate constant (pseudo first-order rate constant for the *n*-alkyl trifluoroacetates and second-order rate constant for the *n*-alkyl benzoates); a and b are constants and M is the molecular weight of the *n*-alkyl group, R', in RCO_2R'.

One of the purposes of this research was to investigate the effect of chain length upon the rates of hydrolysis of *sec*-alkyl trifluoroacetates. Another purpose was to see if increasing the water concentration of the solvent had the same effect upon the rates of hydrolysis of primary and secondary alkyl trifluoroacetates as it does upon the alkaline hydrolysis of esters. The effects of aryl groups upon the non-catalyzed hydrolysis of some aryl trifluoroacetates were also investigated.

In order to substantiate the conclusions which were drawn as to the differences between substituent and solvent effects in the acid- and base-catalyzed acyl–oxygen cleavage, lithium alkoxides were added to alkyl trifluoroacetates to determine the effect of structure upon the amount of addition which occurred.

Experimental

The *sec*-alkyl and *n*-alkyl trifluoroacetates were prepared from the corresponding alcohols and a slight excess of trifluoroacetic acid using concentrated sulfuric acid as a catalyst. They were purified as described previously.[1]

TABLE I

PROPERTIES OF THE ESTERS

Ester	B.p. °C.	B.p. Mm.	$n^{20}D$[a]	Sapon. equiv.
$CF_3CO_2C_3H_7$(iso)	73	749	1.3178	156
$CF_3CO_2C_4H_9$(*sec*)	94.2	749	1.3330	171
$CF_3CO_2C_5H_{11}$(*sec*)	114	750	1.3460	185
$CF_3CO_2C_6H_{13}$(*sec*)	53	35	1.3569	199
CF_3CO_2-phenyl	67	40	1.4226	190
CF_3CO_2-*m*-tolyl	87.5	40	1.4297	203
CF_3CO_2-*p*-tolyl	88.5	40	1.4292	204
CF_3CO_2-*o*-tolyl	81	40	1.4270	204

[a] Abbé.

The aryl trifluoroacetates were prepared from trifluoroacetic anhydride and the corresponding aryl alcohol. Purification consisted of fractional distillation through a glass packed column under reduced pressure. The aryl trifluoroacetates were not washed with water before distillation since water reacts very rapidly with these esters.

The hydrolysis procedure which was used for the *sec*-alkyl trifluoroacetates is similar to the one described previously[1] except that 99 ml. of the solvent (70.7% aqueous acetone) and one ml. of the ester were mixed at 25°, and the cells were filled with the resultant mixture and transferred to their respective baths (at 25, 35 or 45°).

The additions of alkoxides to the alkyl trifluoroacetates were carried out approximately as described by Bender,[3] except that the transfer of reagents was done in an inert atmosphere of argon.

The solvent, di-*n*-butyl ether was refluxed[3] over sodium for 6 to 8 hours and then distilled through a Todd-type, glass-packed column. The fraction collected boiled at 52–53° (26 mm.). Its refractive index was 1.3983.

The ethyl and *n*-butyl alcohols were dried for 2 days over anhydrous magnesium sulfate and calcium hydride. The alcohols were then refluxed with magnesium turnings and I_2[4] and distilled through the column. The boiling points of ethyl and *n*-butyl alcohols were, respectively, 78.3° and 117.5° at a pressure of 750 mm.

The lithium alkoxides were prepared from corresponding alcohols and lithium. The lithium butoxide was prepared at approximately 60° in an atmosphere of argon.

The infrared spectra were determined using a Perkin-Elmer model 21 double beam recording infrared spectrophotometer. A sodium chloride liquid absorption cell of approximately 0.1 mm. in thickness was used since matched cells were not available. Standard solutions of each ester were used to determine the Beer law relationship for the calculation of the unknown ester concentrations. The very sharp carbonyl absorption band which occurs at approximately 1790 cm.$^{-1}$ was used for the determination of ester concentrations.

The initial ester concentration was 0.10 molar and a 1:1 ratio of dry alkoxide to ester was employed as described by Bender.

Usually 25 to 30 minutes elapsed between the time of mixing and the time of analysis. No appreciable change in the amount of addition occurred when a given sample was analyzed 30 minutes after mixing and 60 minutes after mixing.

Isopropyl trifluoroacetate was hydrolyzed in 70.7, 65, 60 and 55% aqueous acetone solutions (by volume). Ethyl trifluoroacetate was hydrolyzed in 70.7 and 60% aqueous acetone (by volume). All of the acetone–water solutions were prepared at approximately 25°.

Experimental Results and Discussion

All of the hydrolyses which were studied in this project were found to be first order. Acid catalysis seemed to become important after approximately 40 to 50% of the *sec*-alkyl trifluoroacetates had reacted and in the aryl trifluoroacetates no acid catalysis was observed. This result is to be expected since an aryl group is a far better electron-withdrawing group than an alkyl group.

Rate constants were calculated as described previously.[5]

Entropies of activation were calculated using

$$\Delta S^{\ddagger} = R\,[\ln k_1 - \ln(kT/h) + E/RT - 1] \qquad (2)$$

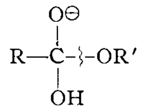
where k_1 is the rate constant in sec.$^{-1}$ and E is the Arrhenius energy of activation.

The rate constants, activation energies and activation entropies for the esters which were studied are listed in Table II. Table III demonstrates the effect of solvent (water concentration) upon the rates of hydrolysis of ethyl and isopropyl trifluoroacetates. Table IV lists the percentage addition of lithium alkoxides to alkyl trifluoroacetates.

If in the *n*-alkyl trifluoroacetates the methyl ester is considered as a special case[6] the reaction rates for the other members of the *n*-alkyl series can be related by an intrinsically and physically more satisfying equation which indeed may have an important theoretical significance. This equation is

$$\ln k = a/\mu + b \qquad (3)$$

where k is the rate constant, a and b are constants and μ is the reduced mass, *i.e.* in the intermediate



$$R{-}\overset{\displaystyle O^{\ominus}}{\underset{\displaystyle OH}{C}}{-}\wr{-}OR' \qquad (4)$$

$$\mu = (M_1M_2)/(M_1 + M_2)$$

where M_1 is the mass of the group to the left of the bond which is broken and M_2 is the mass of the

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[3] M. L. Bender, THIS JOURNAL, **75**, 5986 (1953).

[4] L. F. Fieser, "Experiments in Organic Chemistry," D. Heath and Co., New York, N. Y., 1941, p. 359.

[5] K. J. Laidler, "Chemical Kinetics," McGraw–Hill Book Co., Inc., New York, N. Y., 1950, p. 94.

[6] J. E. Leffler, private communication.

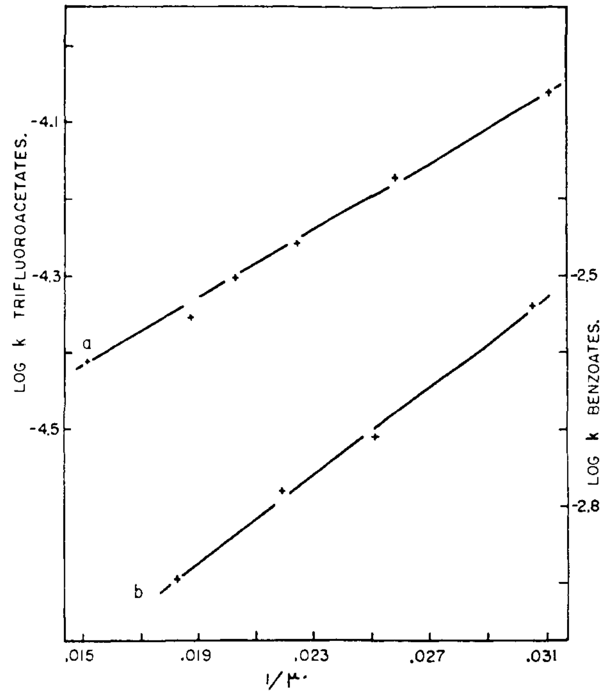


Fig. 1.—Log *k versus* $1/\mu$ for *n*-alkyl trifluoroacetates and benzoates: (a), trifluoroacetates at 44.9°; (b) benzoates at 25°.

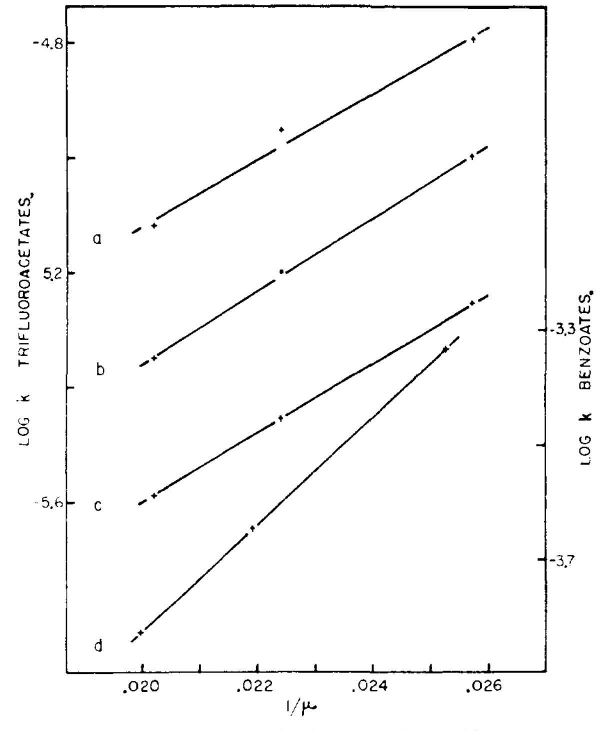


Fig. 2.—Log *k versus* $1/\mu$ for *sec*-alkyl trifluoroacetates and benzoates: trifluoroacetates at (a) 45°, (b) 35°, and (c) 25°; (d) benzoates at 25°.

—OR′ group. The applicability of equation 3 is demonstrated in Fig. 2, and equation 3 can also be applied to a large number of other reaction series.

TABLE II

RATE CONSTANTS, ACTIVATION ENERGIES AND ACTIVATION ENTROPIES FOR THE *sec*-ALKYL AND ARYL TRIFLUOROACETATES

Ester	$k \times 10^6$, sec.$^{-1}$[a]	E, kcal.	$\Delta S^{\ddagger}$, e.u.
$CF_3CO_2C_3H_7$	(a) 5.67	9.80	−51.7
	(b) 10.0		
	(c) 16.1		
$CF_3CO_2C_4H_9$	(a) 3.50	10.88	−49.1
	(b) 6.28		
	(c) 11.1		
$CF_3CO_2C_5H_{11}$	(a) 2.56	10.29	−51.7
	(b) 4.45		
	(c) 7.63		
$CF_3CO_2C_6H_{13}$	(a) 2.59	10.45	−51.1
	(b) 4.63		
	(c) 7.86		
	$k \times 10^2$, sec.$^{-1}$		
Phenyl-	(a) 1.67	6.85	−45.9
	(b) 2.47		
	(c) 3.46		
m-Tolyl-	(a) 1.00	7.21	−45.6
	(b) 1.49		
	(c) 2.15		
p-Tolyl-	(a) 0.839	6.82	−47.2
	(b) 1.21		
	(c) 1.73		
o-Tolyl-	(a) 0.455	7.59	−45.8
	(b) 0.716		
	(c) 1.02		

[a] (a) 25°, (b) 35°, (c) 45°.

TABLE III

THE EFFECT OF THE WATER CONCENTRATION UPON THE RATE OF HYDROLYSIS OF ISOPROPYL TRIFLUOROACETATE AND ETHYL TRIFLUOROACETATE

Ester	Water (by vol.),[a] %	$k_{25} \times 10^6$, sec.$^{-1}$
$CF_3CO_2C_3H_7$(*iso*)	29	5.57 ± 0.13
	35	8.30 ± .16
	40	11.9 ± .4
	45	15.9 ± .5
$CF_3CO_2C_2H_5$	29	39.9 ± 1.8
	50	257 ± 13

[a] Aqueous acetone.

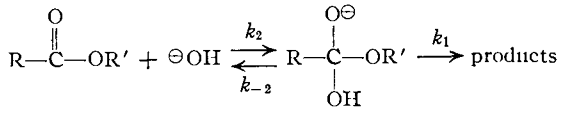
TABLE IV

PERCENTAGE ADDITION OF ALKOXIDES TO ALKYL TRIFLUOROACETATES AT APPROXIMATELY 25°[a]

Ester	Addition (ethoxide), %	Addition (butoxide), %
Ethyl-	72 ± 2	75 ± 2
Butyl-	72 ± 2	73 ± 2
Hexyl-	70 ± 2	....
Isopropyl-	54 ± 2	....
sec-Butyl-	47 ± 2	....
2-Pentyl-	65 ± 2	....
t-Butyl-	51 ± 2	....

[a] Solvent, di-*n*-butyl ether.

If the reduced mass relationship represented by equation 3 is to have any real significance then the effect of increasing chain length should be felt primarily in the rate of cleavage of the acyl–oxygen bond. This does not mean, however, that the rate of cleavage of the acyl–oxygen bond is the slow or rate-controlling step. It can be shown using the mechanism.



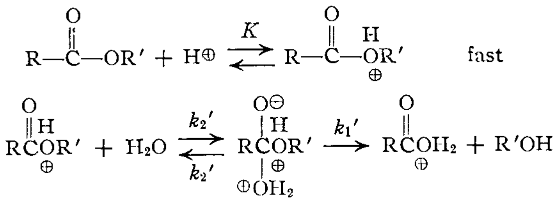
$$\mathrm{R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}OR'} + {}^{\ominus}\mathrm{OH} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \mathrm{R{-}\overset{\overset{\displaystyle O^{\ominus}}{|}}{\underset{\underset{\displaystyle OH}{|}}{C}}{-}OR'} \xrightarrow{k_1} \text{products}$$

that the rate constant, k for the over-all reaction is

$$k = k_1k_2/(k_1 + k_{-2}) \qquad (5)$$

where the step involving k_2 is very likely the rate-controlling step.[3] If $k_1 >> k_{-2}$ then a change in k_1 should have very little effect upon the over-all rate constant, k; but if $k_{-2} >> k_1$ then any change in k_1 would cause proportionally the same change in k.

A similar line of reasoning, using the mechanism[7] for acid



$$\mathrm{R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}OR'} + \mathrm{H}^{\oplus} \overset{K}{\rightleftharpoons} \mathrm{R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}\underset{\oplus}{\overset{H}{O}}R'} \qquad \text{fast}$$

$$\mathrm{\underset{\oplus}{\overset{\overset{\displaystyle O}{\|H}}{RCOR'}}} + \mathrm{H_2O} \underset{k_2'}{\overset{k_2'}{\rightleftharpoons}} \mathrm{\underset{\underset{\displaystyle {}^{\oplus}OH_2}{|\oplus}}{\overset{\overset{\displaystyle O^{\ominus}}{|H}}{RCOR'}}} \xrightarrow{k_1'} \mathrm{\underset{\oplus}{\overset{\overset{\displaystyle O}{\|}}{RCOH_2}}} + \mathrm{R'OH}$$

leads to

$$k' = k_1'k_2'K/(k_1' + k'_{-2}) \qquad (6)$$

where the step involving k_2' is very likely the rate-controlling step. Thus if $k_1' >> k'_{-2}$ then any change in k_1' will not affect the value of k'.

Theoretically, the energy of interaction between the ion and the dipole of a neutral molecule will be greater in a solvent of lower dielectric constant,[8] and thus the rate of reaction between an ion and a neutral molecule will be larger in the solvent of lower dielectric constant. Since both the acid- and the base-catalyzed acyl–oxygen cleavage involve the reaction of a neutral molecule with an ion in the rate-controlling step, both reactions would be expected to behave similarly under the influence of solvent changes. This, however, is not the case. The acid-catalyzed acyl–oxygen cleavage of methyl acetate[9] and the *t*-butyl acetate,[10] for example, are found to decrease slightly as the water concentration is increased. This seems to be at least qualitatively in agreement with ion–dipole interaction predictions.

For the base-catalyzed acyl–oxygen cleavage an entirely different solvent effect is observed. Tommila and Hietala[11] have shown that the alkaline hydrolysis of the ethyl esters of acetic, propionic and butyric acids is increased very markedly by small increases in the water concentration using aqueous ethyl alcohol as a solvent.

It was found in this project that the hydrolyses of the *n*-alkyl and *sec*-alkyl trifluoroacetates are also increased very markedly by small increases in the water concentration using aqueous acetone as a solvent (see Table III).

A comparison of solvent effects in acid- and base-catalyzed hydrolyses seems to indicate that some step other than the rate-controlling step is primarily responsible for the solvent effects which are observed in the base-catalyzed cleavage. In other words equations 5 and 6 might reduce, respectively, to

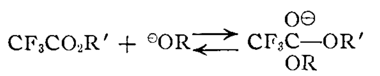
$$k = k_1k_2/k_{-2} \qquad (5a)$$

and

$$k' = k_2'K \qquad (6a)$$

Since the attack by a water molecule in acid catalysis is not responsible for the diminished chain length effects which are observed,[1] then it appears that the steps involving k_2' and k_2, respectively, for acid and base catalysis are fairly insensitive to chain length. Therefore, it appears that some step other than the rate-controlling step is primarily responsible for the chain length effects which are observed in base-catalyzed acyl–oxygen cleavage. This step may also be the one which accounts for the observed solvent effects.

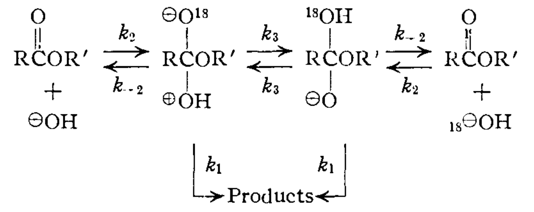
In an attempt to check upon the conclusions which lead to equation 5a, a procedure used by Bender[3] was employed to determine the effect of chain length upon the addition of alkoxides to alkyl trifluoroacetates (Table IV). Although the



$$\mathrm{CF_3CO_2R'} + {}^{\ominus}\mathrm{OR} \rightleftharpoons \mathrm{CF_3\overset{O^{\ominus}}{\underset{OR}{C}}{-}OR'}$$

reaction is heterogeneous and a very complex equilibrium may be involved, it is interesting to note that the percentage addition for the *n*-alkyl trifluoroacetates is constant and (depending upon a more detailed study of these heterogeneous equilibria) seems to substantiate equation 5a, *i.e.*, the chain length effects are not primarily felt in the rate-controlling step, k_2.

In considering the effect of structure upon reactivity, the basicity of the anion being displaced should be mentioned.[12] Thus hydroxide ions would be expected to be lost in preference to alkoxide ions, *i.e.*, $k_{-2} >> k_1$. Bender's conclusions, based upon the relative rates of hydrolysis and O^{18} exchange,[13] are that alkoxide ions are lost in preference to the hydroxide ion. It can be shown using the mechanism[13] that the ratio of the initial



$$\begin{matrix} \mathrm{\overset{\overset{\displaystyle O}{\|}}{RCOR'}} \\ + \\ {}^{\ominus}\mathrm{OH} \end{matrix} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \mathrm{\underset{\underset{\displaystyle {}^{\ominus}OH}{|}}{\overset{\overset{\displaystyle {}^{\ominus}O^{18}}{|}}{RCOR'}}} \underset{k_3}{\overset{k_3}{\rightleftharpoons}} \mathrm{\underset{\underset{\displaystyle {}^{\ominus}O}{|}}{\overset{\overset{\displaystyle {}^{18}OH}{|}}{RCOR'}}} \underset{k_2}{\overset{k_{-2}}{\rightleftharpoons}} \begin{matrix} \mathrm{\overset{\overset{\displaystyle O}{\|}}{RCOR'}} \\ + \\ {}_{18}{}^{\ominus}\mathrm{OH} \end{matrix}$$

$$\xrightarrow{k_1} \text{Products} \xleftarrow{k_1}$$

rate of hydrolysis to the initial rate of exchange is

$$k_h/k_e = k_1(k_1 + k_{-2} + 2k_3)/(k_3k_{-2}) \qquad (7)$$

In order for Bender's conclusions to be justified, k_3 would have to be very much larger than k_1 and k_{-2}.

Arnold[14] has demonstrated that the rate constant for the exchange of a proton in the reaction

$$\mathrm{C_2H_5OH} + {}^{\ominus}\mathrm{OH} \xrightarrow{k(\mathrm{C_2H_5OH})} \mathrm{H_2O} + \mathrm{C_2HO_5}^{-}$$

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(7) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953, pp. 265-266.

(8) A. A. Frost and R. J. Pearson, *ibid.*, pp. 135-138.

(9) G. J. Burrows, *J. Chem. Soc.*, **115**, 1230 (1919).

(10) C. A. Bunton and J. L. Wood, *ibid.*, 1522 (1955).

(11) E. Tommila and S. Hietala, *Acta Chim. Scand.*, **8**, 257 (1954).

(12) J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1956, p. 274.

(13) M. L. Bender, THIS JOURNAL, **73**, 1626 (1951).

(14) J. T. Arnold, *Phys. Rev.*, **102**, 136 (1956).

is approximately 1×10^6 sec.$^{-1}$. If k_3 is assumed to be of the same order of magnitude, then it can be shown using

$$k_1 = (kT/h)e^{\Delta S^{\ddagger}/R}e^{-\Delta H_1^{\ddagger}/RT} \quad (8)$$

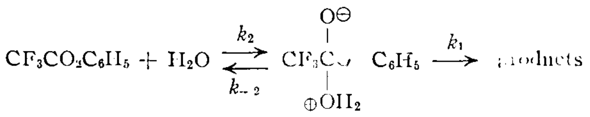
that in order for k_1 to be greater than k_3, $\Delta H_1^{\ddagger}$ could be approximately 8 kcal., or less (assuming a reasonable value for $\Delta S^{\ddagger}$). In the alkaline hydrolysis of ethyl benzoate[2] which has an activation energy of 14.56 kcal., there could be an energy barrier of approximately 8 kcal. for the unstable intermediate and k_1 could still be greater than k_3.

Thus it is very possible that the life of the unstable intermediate is too short for the two oxygen atoms to become completely equivalent by proton transfer.

An explanation for equation 3 might be found in the effect of chain length upon the amplitude of the –C–OR bond vibrations or upon the probability that the bond will obtain the requisite energy for the reaction. Theimer[15] has shown, for example, that the relative intensities of the terminal modes in straight chain *n*-paraffins decrease with increasing chain length, *i.e.*, a linear relationship is obtained when the relative intensities, $I(\nu)$, are plotted against $1/N$ where N is the number of carbon atoms. Morino and co-workers[16] have shown that the potential energy of both bonded and non-bonded atom pairs is related directly to the reciprocal of the reduced mass of the atoms.

The rates of hydrolysis of the aryl trifluoroacetates are qualitatively dependent upon the basicity of the ArO–group.

It was found, at least qualitatively, that the rate of hydrolysis of phenyl trifluoroacetate was very dependent upon the water concentration. This suggests that a possible mechanism for the non-catalyzed hydrolysis of this ester might be



$$CF_3CO_2C_6H_5 + H_2O \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} CF_3\overset{\overset{O^{\ominus}}{|}}{\underset{\underset{\oplus OH_2}{|}}{C}}C_6H_5 \xrightarrow{k_1} \text{products}$$

and thereby k_{-2} could be greater than or approximately the same as k_1; thus, the effect of the ionization step, k_1, could be felt in the over-all rate constant.

[15] O. Theimer, *J. Chem. Phys.*, **27**, 1041 (1957).

[16] Y. Morino, *et al.*, *ibid.*, **21**, 1927 (1953).

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF NORTHWESTERN UNIVERSITY]

Overlap Control of Carbanionoid Reactions. II.[1] The Stereochemistry of the Perkin Reaction and Related Condensation Reactions

BY HOWARD E. ZIMMERMAN AND LEO AHRAMJIAN

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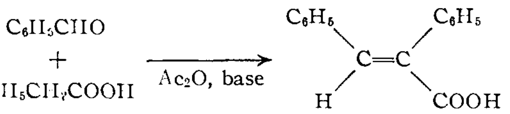
The Perkin reaction of aromatic aldehydes with phenylacetic acids has been known for quite some time to afford preferentially the α-phenylcinnamic acid stereoisomer with *cis*-phenyl groups but an unhindered carboxyl group. The nature of the stereochemical driving force has now been elucidated. Evidence is presented that the initial condensation step is not reversible and that the reaction stereochemistry is eliminatively controlled. The role of overlap control in affording condensation products with unhindered electron delocalizing groups is discussed.

It has been known for some time that the Perkin condensation of aromatic aldehydes with phenylacetic acids affords the α-phenylcinnamic acid stereoisomer with *cis*-phenyl groups.



(1)

This knowledge derives mainly from the work of Stoermer and co-workers[2] and Bakunin.[3]

Recently, Crawford and Moore[4] have emphasized the generality of this reaction stereochemistry[5] and commented on the enigma of a reaction which leads preferentially to a product with *cis*-phenyl groups. To account for the observed reaction course a mechanism was proposed which involved preferential formation of the *erythro*[9]-3-hydroxy-2,3-diphenylpropionic acid anhydride intermediate[10] (Ib, R = Ac) followed by *trans* elimination of acetic acid

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[1] For paper I in this series see H. E. Zimmerman, L. Singer and B. S. Thyagarajan, THIS JOURNAL, **81**, 108 (1959).

[2] R. Stoermer, *Ann.*, **409**, 15 (1915); R. Stoermer and L. Prigge, *ibid.*, **409**, 20 (1915); R. Stoermer and G. Voht, *ibid.*, **409**, 36 (1915).

[3] M. Bakunin, *Gazz. chim. ital.*, **27**, II, 34 (1897); *Chem. Zentr.*, **68**, II, 662 (1897).

[4] M. Crawford and G. W. Moore, *J. Chem. Soc.*, 3445 (1955).

[5] The configurations of the various α-phenylcinnamic acids are firmly established. The evidence includes the stereospecific decarboxylation to the stilbene of the same configuration (ref. 1), the much greater rate of esterification of α-phenyl-*trans*-cinnamic than of α-phenyl-*cis*-cinnamic acid (ref. 6) as would be expected from the less hindered carboxyl group of the former, the ready cyclization of only the α-phenyl-*cis*-cinnamic acid to the corresponding indone (ref. 7), the similar cyclization of the related nitrile stereoisomer to the indone contrasted with the non-reactivity of the α-phenyl-*trans*-cinnamonitrile (ref. 8), the Pschorr reaction of α-phenyl-*trans*-o-aminocinnamic acid compared with the formation of 3-phenylcoumarin from α-phenyl-*cis*-o-aminocinnamic acid on diazotization (ref. 2).

[6] J. J. Sudborough and L. L. Loyd, *J. Chem. Soc.*, 81 (1898); J. J. Sudborough and D. J. Roberts, *ibid.*, 1851 (1905).

[7] M. Bakunin, *Gazz. chim. ital.*, **30**, II, 340 (1900); *cf. Chem. Zentr.*, **71**, II, 1276 (1900).

[8] P. Pfeiffer, H. Kübler and H. Rüping, *J. prakt. Chem.*, [2] **121**, 85 (1929).

[9] It is convenient to assign the *erythro* and *threo* designations on the basis of similarity of relative size of groups rather than similarity of functionality. On this basis the *erythro* diastereomer will be the more stable one, since as has been pointed out by both D. J. Cram, F. D. Greene and C. H. DePuy, THIS JOURNAL, **78**, 790 (1956), and D. H. R. Barton and R. C. Cookson, *Quart. Rev.*, **10**, 48 (1956), it has available to it a low energy conformation in which not only the large groups (L and L$'$,) have an *S-trans* arrangement but also the medium groups (M and M$'$,).

[10] The suggestion that the stereochemistry of condensation reactions is controlled by preferential formation of the more stable *erythro*