[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, PURDUE UNIVERSITY]

The Effect of Substituents upon the Rates of Hydrolysis of Fluorinated Esters

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n-Alkyl esters of straight chain, perfluorinated acids were hydrolyzed in a mixture of acetone (70% by volume) and water. It was found that the pseudo first-order rate constants for the *n*-alkyl trifluoroacetates can be related quantitatively to the molecular weight of the *n*-alkyl group. The pseudo first-order rate constants for the ethyl esters of trifluoroacetic, pentafluoropropionic and heptafluorobutyric acids can be related quantitatively to molecular weight differences.

Introduction

A large amount of information is available concerning the effect of substituents upon the hydrolysis (alkaline or acid) of esters. This information allows the qualitative prediction (in most cases) of the effect of structure upon hydrolysis rates.

The object of this study was to determine the effect of chain length of both the acid and the alcohol component upon the neutral hydrolysis of *n*-alkyl esters of perfluorinated acids. The esters studied were the methyl, ethyl, *n*-propyl, *n*-butyl, *n*-pentyl, *n*-hexyl and *n*-decyl trifluoroacetates, ethyl pentafluoropropionate and ethyl heptafluorobutyrate. It is hoped that this study will aid in clarifying both the qualitative and the quantitative effect of structure upon reactivity.

Experimental

The esters, which were prepared from the corresponding acids and alcohols, were (1) washed with an excess amount of dilute sodium carbonate solution followed by washings with distilled water, (2) dried with anhydrous magnesium sulfate, (3) passed through a Vigreux column to collect a fraction with a two degree boiling point range (or less), (4) rectified through an 18-plate Todd column (reflux ratio approximately 10/1) to obtain the sample used in this project. Boiling point ranges of 0.1° were obtained for all esters except hexyl trifluoroacetate.

TABLE I

PROPERTIES OF FLUORINATED ESTERS

Esters	B.p., °C. (750 mm.)	n^{20}_{D}[a]	Sapon. equiv.
$CF_3CO_2CH_3$	43	1.29073	129.0
$CF_3CO_2C_2H_5$	61.3	1.30725	141.6
$CF_3CO_2C_3H_7$	81.9	1.32382	157.0
$CF_3CO_2C_4H_9$	104.0	1.33923	171.0
$CF_3CO_2C_5H_{11}$	125.0	1.35194	183.4
$CF_3CO_2C_6H_{13}$	146.0–.5	1.36253	200.4
$CF_3CO_2C_{10}H_{21}$	229.5 (744 mm.)	1.3911 (Abbe)	254.6
$C_2F_5CO_2C_2H_5$	76.5	1.30110	. . .
$C_3F_7CO_2C_2H_5$	96.6	1.30254	241

[a] Determined using a Bausch and Lomb refractometer, precision ±0.00005.

Acetone (C.P. grade from Commercial Solvents Corp.) was treated with $KMnO_4$ and solid KOH followed by distillation using a Vigreux column.

The 70% acetone solution was prepared from 290 ml. of conductance water[1] and 700 ml. of acetone.

Trifluoroacetic acid (Minnesota Mining and Manufacturing Co.) was distilled through an 18-plate Todd column and the fraction collected boiled at 71.4° (750 mm.).

A Wheatstone bridge was used to follow the reactions by taking advantage of the change in specific conductance during a reaction. The Wheatstone bridge consisted of a vacuum tube oscillator (1000 cycle), a Kohlrausch slide wire, a Leeds and Northrup resistance box, an amplifier, earphones and Washburn conductivity cells. Cell constants for the cells used were in the vicinity of two cm.$^{-1}$.

A 100-ml. volumetric flask was filled with 70.7% acetone solution, placed in a constant temperature bath and allowed to reach the temperature of the bath. One ml. of the water–acetone mixture was removed from the volumetric flask and replaced by one ml. of ester. A clean conductance cell was removed from the constant temperature bath, washed twice with the acetone–water–ester solution, filled with this solution, and placed into the constant temperature bath. A period of at least 200 seconds was allowed for cell and contents to reach the temperature of the bath before the first reading was taken. The cells were sealed to eliminate evaporation. The specific conductance at infinite time was determined after letting the cell and contents stand (usually at some higher temperature) until the specific conductance reached a constant value.

TABLE II

HYDROLYSIS RATE CONSTANTS, ACTIVATION ENERGIES AND ln *PZ* FACTORS

Ester		$k \times 10^5$[a]	*E* (kg.-cal./mole)	ln *PZ*
$CF_3CO_2CH_3$	(a)	12.8 ± 1.2	7.8	3.40
	(b)	19.5 ± 0.5		
	(c)	29.4 ± 0.3		
$CF_3CO_2C_2H_5$	(a)	3.99 ± 0.18	7.3	0.53
	(b)	5.43 ± .22		
	(c)	8.64 ± .26		
$CF_3CO_2C_3H_7$	(a)	2.69 ± 0.10	8.7	2.17
	(b)	3.95 ± .14		
	(c)	6.74 ± .13		
$CF_3CO_2C_4H_9$	(a)	2.28 ± 0.05	8.3	1.68
	(b)	3.44 ± .10		
	(c)	5.50 ± .15		
$CF_3CO_2C_5H_{11}$	(a)	1.95 ± 0.13	8.8	2.04
	(b)	3.02 ± .18		
	(c)	4.97 ± .13		
$CF_3CO_2C_6H_{13}$	(a)	1.75 ± 0.05	8.7	1.93
	(b)	2.71 ± .17		
	(c)	4.41 ± .11		
$CF_3CO_2C_{10}H_{21}$	(a)	1.33 ± 0.08	10.1	3.70
	(b)	2.29 ± .08		
	(c)	3.90 ± .26		
$C_2F_5CO_2C_2H_5$	(a)	0.272 ± 0.014	11.7	4.92
	(b)	.469 ± .013		
	(c)	.871 ± .012		
$C_3F_7CO_2C_2H_5$	(a)	0.131 ± 0.005	12.2	5.20
	(b)	.233 ± .008		
	(c)	.447 ± .023		

[a] (a) 24.9°C.; (b) 34.9°C.; (c) 44.9°C.

Experimental Results and Discussion

All of the reactions studied in this project were found to follow a pseudo first-order relationship. Specific reaction rate constants were calculated from

$$k = [1/(t_2 - t_1)] \ln [(C_\infty - C_1)/(C_\infty - C_2)] \quad (1)$$

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[1] S. Glasstone, "Textbook of Physical Chemistry," D. Van Nostrand and Company, Inc., New York, N. Y., 1946, p. 891.

where C_∞ is the specific conductance at infinite time, C_1 is the specific conductance at time t_1, and C_2 is the specific conductance at time t_2.

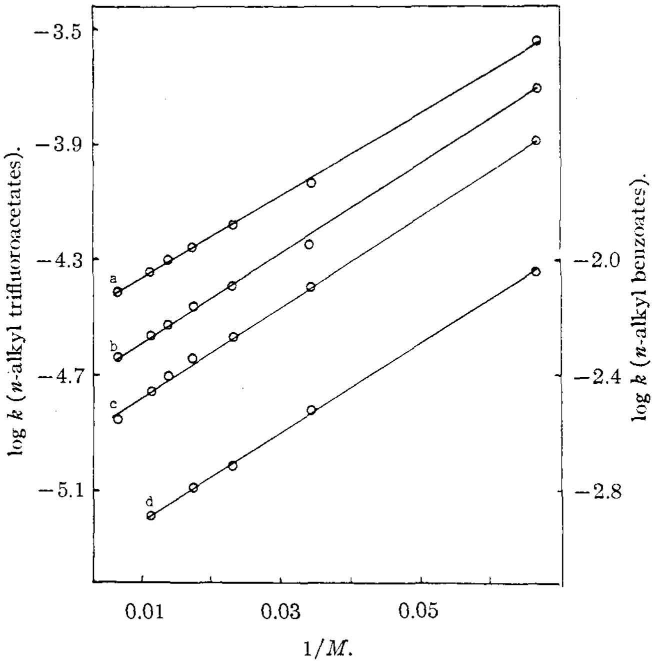

Fig. 1.—(a) CF_3CO_2R at 44.9°; (b) CF_3CO_2R at 34.9°; (c) CF_3CO_2R at 24.9°; (d) $C_6H_5CO_2R$ at 25°[4] (R = n-alkyl group).

Activation energies and frequency factors were determined in the usual way. Average values for k with mean deviations, activation energies and ln PZ factors are listed in Table II.

It is evident that some error will be introduced into calculations by use of eq. 1 due to the curvature of the plot of specific conductance *versus* acid concentration. Corrections for this curvature were found to be unnecessary probably because the concentration of the liberated acid was small and also because the inherent errors in such a correction are fairly large.

With an ester, $RCO_2C_2H_5$, the rate of hydrolysis is very dependent upon the part played by R in decreasing the availability of electrons at the "seat of the reaction."[2] If the hydrogen atoms in R are replaced with fluorine atoms, R becomes a very good electron withdrawing group. Electron withdrawing substituents decrease the ability of an ester to accept protons and increase the tendency for a water molecule to combine with the carbonyl carbon atom.[3] The reaction between most carboxylic esters and water is considerably less important than the acid or base-catalyzed hydrolysis. In the case of the esters of stronger acids, the reaction with water becomes more important and the acid catalyzed reaction becomes negligible.[3] Most of the reactions studied were followed to approximately 60% completion without significant change in the rate constants.

The hydrolysis rate constants for the *n*-alkyl trifluoroacetates level off rapidly with increasing chain length. These results are in agreement with the results of Tommila[4] on the alkaline hydrolysis of *n*-alkyl benzoates.

The hydrolysis rate constants for the *n*-alkyl trifluoroacetates can be quantitatively related to the structure of the *n*-alkyl group by

$$\ln k = a/M + b \qquad (2)$$

where a and b are constants and M is the molecular weight of R in CF_3CO_2R. The physical significance of the constants is as yet unknown.

The second-order rate constants for the alkaline hydrolysis of *n*-alkyl benzoates[4] can also be related to the molecular weight of the *n*-alkyl group by eq. 2. It is interesting to note that a for this ester series is almost identical to a for the *n*-alkyl trifluoroacetates (Fig. 1).

Equation 3

$$\log k/k_0 = a(M_0 - M)/2.303M_0M \qquad (3)$$

which is derived from eq. 2 is very closely related to eq. 4[5]

$$\log k/k_0 = fA \qquad (4)$$

where M_0 is molecular weight of CH_3–; M is the molecular weight of R for the compound in question; k_0 is the rate constant for the standard member of the series (methyl ester); k is the rate constant for the compound in question; f is a constant dependent upon the nature of the reaction series; and A is a substituent constant, dependent upon the nature of the substituent which makes the compound in question differ from the standard compound of its series and upon the set of reaction series to which the series in question belongs.[5] For each set of reaction series one series is defined as the standard, and the f value is defined as unity for this series. If eq. 3 and 4 are identical, then eq. 3 can be used to calculate absolute values for f and A whereas only relative values are given by eq. 4.

If $f = 1$ for the *n*-alkyl benzoates[4] then

$$A = a(M_0 - M)/2.303M_0M \qquad (5)$$

It is interesting to note that the A's calculated by eq. 5 are in agreement with the A's calculated by Taft.[5] The A's for the *n*-alkyl trifluoroacetates at 24.9° are listed in Table III under neutral hydrolysis.

TABLE III

SUBSTITUENT CONSTANTS, A

R	Base-cat. (Taft)[5]	Base-cat. (eq. 5)[4]	Neutral hydrolysis (eq. 5)
CH_3–	0.00	0.00	0.00
C_2H_5–	− .49	− .50	− .51
n-C_3H_7–	− .67	− .67	− .68
n-C_4H_9–	− .73	− .76	− .77
n-C_5H_{11}–	....	....	− .82
n-C_6H_{13}–	....	− .85	− .86
n-$C_{10}H_{21}$	....	....	− .93

Equation 2 is not limited to the *n*-alkyl trifluoroacetates and *n*-alkyl benzoates. Straight line plots can be obtained for many other reaction series. A few of these series are listed below,

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(2) C. N. Hinshelwood, *et al.*, *J. Chem. Soc.*, 857 (1938).

(3) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1940, p. 358.

(4) E. Tommila, *Ann. Acad. Sci. Fennicae*, **A59**, No. 3, 3 (1942).

(5) R. W. Taft, Jr., THIS JOURNAL, **74**, 2729 (1952).

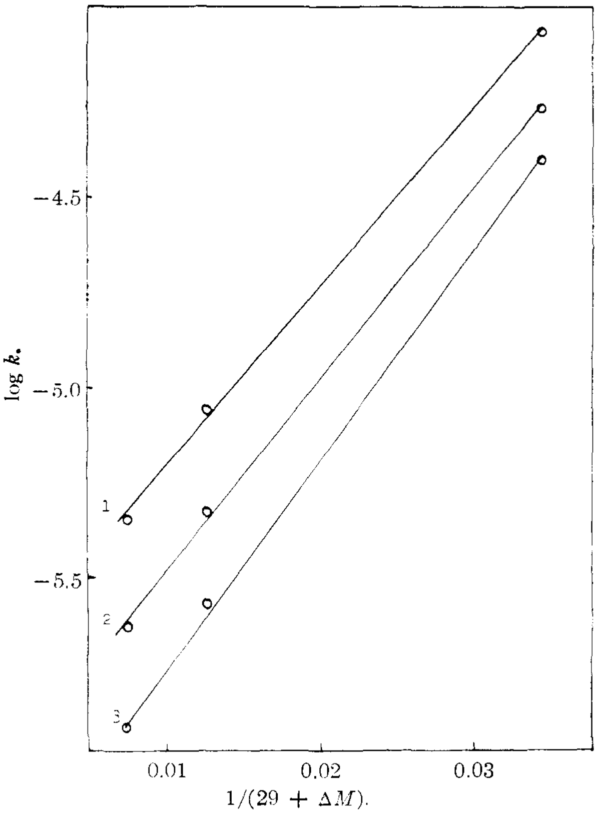

Fig. 2.—(1) $RCO_2C_2H_5$ at 44.9°; (2) $RCO_2C_2H_5$ at 34.9°; (3) $RCO_2C_2H_5$ at 24.9°; (R = CF_3–, C_2F_5– or C_3F_7–).

1. Alkaline hydrolysis[6] of $C_2H_5CO_2R$ where R is CH_3–, C_2H_5–, n-C_3H_7– or n-C_4H_9–.
2. $RI + C_6H_5CH_2O^- \rightarrow C_6H_5CH_2OR + I^-$ where R is CH_3–, C_2H_5–, n-C_3H_7– or n-C_4H_9–.[7]
3. $CH_3CO_2R + HBr \rightarrow RBr - CH_3CO_2H$ where R is CH_3–, C_2H_5–, n-C_3H_7– or n-C_4H_9–.[7]

It was found that increasing the chain length of the perfluorinated acid component of an ester beyond three carbon atoms has only a slight effect upon the rate constants. There is a large decrease in k in going from ethyl trifluoroacetate to ethyl pentafluoropropionate.

Henne and Fox[8] reported that the ionization constants for trifluoroacetic and heptafluorobutyric acids are approximately the same. Thus, the electron withdrawing effects of CF_3– and C_3F_7– groups should be approximately the same. If these two groups have approximately the same electron withdrawing power, then some other explanation must be found for the observed differences in the k's for this series.

According to Newman[9] an ester such as ethyl heptafluorobutyrate (3 atoms in 6-position) should be more sterically hindered than ethyl pentafluoropropionate (zero atoms in 6-position) and ethyl trifluoroacetate (zero atoms in 6-position). Ethyl trifluoroacetate and ethyl pentafluoropropionate should be approximately the same as far as steric hindrance is concerned. Thus, the Newman steric hindrance theory does not explain the large change in k occurring with the pentafluoropropionate.

There is a definite relationship between the k's and the change in molecular weight for the $RCO_2C_2H_5$ series (R = CF_3–, C_2F_5– and C_3F_7–). This relationship (Fig. 2) can be represented by

$$\ln k = a'/(M + \Delta M) + b' \qquad (6)$$

where a' and b' are constants; M is the molecular weight of C_2H_5– and ΔM is the difference between the molecular weight of the ester in question and the molecular weight of $CF_3CO_2C_2H_5$. It is significant that the k's for this ester series can be related quantitatively to molecular weight differences.

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[6] E. J. Salmi and R. Leimu, *Suomen Kemistilehti*, **20B**, 43 (1947).

[7] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1940, p. 154.

[8] A. L. Henne and C. J. Fox, THIS JOURNAL, **73**, 2323 (1951).

[9] M. S. Newman, *ibid.*, **72**, 4783 (1950).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WASHINGTON UNIVERSITY]

The Exchange of Oxygen between Sulfuric Acid and Water[1]

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The kinetics of the exchange of isotopic oxygen between sulfuric acid and water has been studied. The rate of the exchange was found to be first order with respect to hydrogen ion and first order with respect to bisulfate ion concentration. The rate of the exchange was found to vary as the 0.72 power of the sulfuric acid activity in 1.0 to 4.0 f H_2SO_4 at 100° and as the 0.80 power of the activity in 3.0 to 10 f H_2SO_4 at 25°. The activity coefficient of undissociated sulfuric acid in sulfuric acid solutions was approximated by solubility measurements on dimethyl sulfate. From this estimate, the exchange rate appears to vary as the concentration of the undissociated sulfuric acid. The dissociation of sulfuric acid into its anhydride and water is proposed as the rate-determining step.

There exist relatively few quantitative data on the exchange of isotopic oxygen between oxy-anions and water.[2] A reaction of this type is the exchange between sulfuric acid and water.

$$H_2SO_4 + H_2O^* = H_2SO_3O^* + H_2O \qquad (1)$$

This reaction has been studied qualitatively by several workers who found that an exchange occurs only in acid solutions.[3] This paper describes a de-

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[1] Taken in part from the thesis submitted by T. C. Hoering in partial fulfillment of the requirements of the Ph. D. degree, 1952; supported in part by U. S. A. E. C. contract AT(11-1)-259.

[2] J. O. Edwards, *Chem. Revs.*, **50**, 455 (1952); M. Dole, *ibid.*, **51**, 275 (1952).

[3] S. C. Data, J. N. E. Day and C. K. Ingold, *J. Chem. Soc.*, 1968 (1937); N. F. Hall and O. R. Alexander, THIS JOURNAL, **62**, 3455 (1940); G. A. Mills, *ibid.*, **62**, 2837 (1940); T. Titani and K. Goto, *Bull. Chem. Soc., Japan*, **14**, 77 (1939); J. L. Hyde, THIS JOURNAL, **62**, 873 (1940).