These bonds are weak, being of the order of 5 kcal. per mole.<sup>16</sup> Thermal agitation, *i.e.*, increased temperature, disrupts them leading to the disappearance of metachromasy. Conversely, lowering the temperature to near  $0^{\circ}$  induces metachromasy in solutions which are orthochromatic at room temperature.

In order for the dye "non-polar" residues to polymerize, it is necessary to secure the correct ratio of dye to substrate concentration. In the presence of a large excess of substrate, a small number of dye molecules may form the usual polar link at random, but, being widely separated, the aromatic rings of the dye cannot polymerize to yield metachromasy. In view of the findings of Rabinowitch and Sheppard<sup>15,14</sup> with regard to the spacing requirement for aggregation of thiazine dyes, it should be noted that nucleic acids have been reported to have a spatial unit of 3.5 Å.<sup>17</sup>

(16) L. Pauling in K. Landsteiner, "The Specificity of Serological Reactions," Harvard University Press, Cambridge, Mass., 1945, p. 275.
(17) W. T. Astbury, "Symposia of the Society for Experimental

Biology," Vol. I, Cambridge, 1947, p. 66.

The effect of solvents on the van der Waals binding also has been shown. Alcohol abolished metachromasy of toluidine blue induced by gum arabic.<sup>5</sup> We have found that alcohol also abolishes metachromasy induced by nucleic acids.<sup>9</sup> These findings supplement the observations of Sheppard that aggregation of thiazine dyes may involve the bonding of a molecule of water between neighboring resonating dye ions<sup>18</sup> and those of Rabinowitch and Epstein<sup>15</sup> that alcohol prevents the dimerization of the thiazine dyes methylene blue and thionine.

Acknowledgment.—This work was aided by a grant from the American Cancer Society to the Department of Preventive Medicine, the Johns Hopkins University School of Medicine, recommended by the Committee on Growth of the National Research Council.

(18) S. E. Sheppard and A. L. Geddes, This Journal, 66, 2003 (1944).

BALTIMORE, MARYLAND RECEIVED MAY 26, 1951

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE OHIO STATE UNIVERSITY]

## Acidity of Trifluorinated Alcohols and Saponification Rates of their Acetates

BY ALBERT L. HENNE AND RALPH L. PELLEY<sup>1</sup>

Measured by an electrometric procedure, the ionization constants for CF<sub>3</sub>CH<sub>2</sub>OH, CF<sub>3</sub>CH(CH<sub>3</sub>)OH and CF<sub>3</sub>C(CH<sub>2</sub>)<sub>2</sub>OH were found to be not more than  $10^{-12}$ . In 50% aqueous acetone 0.1 N in NaOH at 25°, the saponification of CF<sub>3</sub>CH<sub>2</sub>OAc and CF<sub>3</sub>CH(CH<sub>3</sub>)OAc showed second order kinetics with K 0.6 and 0.15 l. mole<sup>-1</sup> sec.<sup>-1</sup>. The rate constants for 0.1 N acid-catalyzed reactions expressed as  $K \times 10^6$  sec.<sup>-1</sup> were found to be: CHF<sub>2</sub>CH<sub>2</sub>OAc 2.0, CF<sub>3</sub>CH<sub>2</sub>OAc 1.4, CF<sub>3</sub>CH-(CH<sub>3</sub>)OAc 1.2, CF<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>OAc 2.6 and C<sub>6</sub>H<sub>5</sub>OAc 4.0. These values are discussed.

Fluorinated alcohols are known to be acidic. They are reported to form alcoholates on standing with alkali carbonates, alkaline-earth carbonates, but not bicarbonates,<sup>2</sup> not to form complexes with calcium chloride,<sup>3</sup> tenaciously to resist dehydration,<sup>4</sup> and one of them, CF<sub>3</sub>CHOHCH<sub>3</sub>, is reported to have an ionization constant of  $K = 10^{-7}$ , intermediate between phenol and acetic acid.<sup>5</sup>

The following alcohols were synthesized:  $CF_3$ -CH<sub>2</sub>OH,<sup>6</sup> CHF<sub>2</sub>CH<sub>2</sub>OH by reduction of difluoroacetic acid obtained in much improved yield, CF<sub>3</sub>CHOHCH<sub>3</sub> by reduction of CF<sub>3</sub>COCH<sub>3</sub> obtained in improved yield, CF<sub>3</sub>C(CH<sub>3</sub>)<sub>2</sub>OH<sup>7</sup> and CF<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>OH.<sup>8</sup>

Ionization constants were determined by measuring the pH at the half-equivalence point, which is equal to the pK between the limits of 10 and  $4^9$ and, for acids with  $K_s$  in the range of  $10^{-3}$  to  $10^{-5}$ , a good approximation of it slightly beyond these limits.<sup>10</sup> The observed results at 25° were: CF<sub>3</sub>CH<sub>2</sub>OH 4.0, CF<sub>3</sub>CH(CH<sub>3</sub>)OH 6.3 and CF<sub>3</sub>C-

(3) F. Swarts, Bull. soc. chim. Belg., 43, 471 (1934).

(5) F. Swarts, *ibid.*, **38**, 99 (1929).

- (6) A. L. Henne, R. M. Alm and M. A. Smook, THIS JOURNAL, 70, 1968 (1948).
  - (7) E. Gryszkiewicz-Trochimowski, Rec. trav. chim., 66, 427 (1947).

(9) G. M. Bennett, G. L. Brooks and S. Glasstone, J. Chem. Soc., 1821 (1935).

(10) A. L. Henne and C. J. Fox, THIS JOURNAL, 73, 2323 (1951).

 $(CH_2)_2OH 2.5 \times 10^{-12}$ . The order of magnitude contradicts that given by Swarts,  $5 10^{-7}$ , but agrees with those obtained by Richter<sup>11</sup> for HOCH<sub>2</sub>CF<sub>2</sub>-CF<sub>2</sub>CH<sub>2</sub>OH,  $10^{-11}$  and  $10^{-12}$  and by McBee<sup>12</sup> for HOCH<sub>2</sub>CF<sub>2</sub>CF<sub>2</sub>CH<sub>2</sub>OH and HOCH<sub>2</sub>(CF<sub>2</sub>)<sub>4</sub>CH<sub>2</sub>OH,  $10^{-12}$ . To test the results, U.S.P. phenol was measured in like fashion, and found to have K = $1 \times 10^{-9}$ , while the accepted value<sup>18</sup> for specially repurified phenol is  $1 \times 10^{-10}$ . Since glass electrode measurements tend to give values which are too low in solutions of pH > 10, and since the actual difference of pH before and after adding the alcohols to the sodium hydroxide was very small, it may be said that the ionization constants of these alcohols has been shown to be not more than  $10^{-12}$ , and that a plausible value might be taken as 4  $\times 10^{-12}$ . This shows that the fluorinated alcohols are at least 10<sup>4</sup> times more acid than ethanol.<sup>14</sup>

The hydrolysis of esters by hydroxide ions in aqueous solvents is known to show second order kinetics. The accepted explanation is

$$\begin{array}{c} O & O^{-} \\ R'C - OR + OH^{-} \rightleftharpoons R'C - OH, \text{ slow} \\ OR \end{array}$$

(14) J. H. Hildebrand and P. S. Denner, THIS JOURNAL, 44, 2824 (1922).

<sup>(1)</sup> Socony Vacuum Fellow, 1949-1950.

<sup>(2)</sup> F. Swarts, Bull. Classe sci., Acad. Roy. Belg., 731-760 (1902).

<sup>(4)</sup> F. Swarts, *ibid.*, **36**, 191 (1927), and J. V. Schmitz, Ph.D. dissertation, The Ohio State University, 1949.

<sup>(8)</sup> E. T. McBee and A. Truchan, THIS JOURNAL, 70, 2910 (1948).

<sup>(11)</sup> S. B. Richter, PhD. dissertation, The Ohio State University, 1951.

<sup>(12)</sup> E. T. McBee, W. F. Marzluff and O. R. Pierce, Verbal, 118th A.C.S. Meeting, Chicago, Ill., September, 1950.

<sup>(13)</sup> M. Mizutani, Z. phys. Chem., 118, 318 (1925).

а

$$\begin{array}{ccc} O^{-} & O \\ R'C & OH \rightleftharpoons R'C & OH + OR^{-}, \text{ fast} \\ OR \\ nd R'CO_{2}H + RO^{-} \swarrow RCO_{2}^{-} + ROH, \text{ fast} \end{array}$$

The slow step is facilitated by recession of electrons from the seat of reaction. Since in alkaline solution the probability factor PZ in the Arrhenius equation  $K = PZ^{\circ}e^{-E/RT}$  remains fairly constant with changes in the activation energy E, the mechanism is largely independent of steric influences and consequently, since there is only one main parameter, the effect of an electronegative group in the ester can be easily measured. In good agreement with expectations, it was found that the base hydrolysis rate of CF<sub>3</sub>CH<sub>2</sub>OAc (K = 0.6 1. mole<sup>-1</sup> sec.<sup>-1</sup>) was six times faster than that of CH<sub>3</sub>CH<sub>2</sub>OAc (0.108<sup>15</sup>), and that of CF<sub>3</sub>CH(CH<sub>3</sub>)OAc (0.155) six times faster than that of CH<sub>3</sub>CH(CH<sub>3</sub>)OAc (0.026<sup>15</sup>).

For acid-catalyzed hydrolysis, the assumed<sup>16</sup> mechanism is a bimolecular, pseudo-first order one

$$\begin{array}{c} O & O \\ R'C - OR + H^{+} \rightleftharpoons R'C - OHR, \text{ fast} \\ O & O \\ H_{2}O + R'C - OHR \rightleftharpoons H_{2}O - C - R' + ROH, \text{ slow} \\ O \\ C - OHR \rightleftharpoons R'C - OHR \rightleftharpoons R'CO_{2}H + H^{+}, \text{ fast} \end{array}$$

It has been shown<sup>17</sup> that the energy of activation decreases as substituents on the acid side of the ester become more strongly electron attracting. Since the slow step is the nucleophilic acceptance of a molecule of water, it might be expected that electropositive groups on the alcohol side of the ester would slow down the reaction, and it is generally accepted that isopropyl acetate is saponified at half the rate of ethyl or normal propyl acetate. Tertiary butyl acetate is, however, saponified just as fast as ethyl acetate, and this reversed trend is explained by calling for an additional mechanism.<sup>18</sup> Furthermore, Hinshelwood<sup>17</sup> points out that, in acid hydrolysis, changes in electronic (E) and steric (PZ) factors with change in structure are roughly equal and opposed, and that this causes close grouping of the rates.

In the present study, the rates were determined in a homogeneous solvent of 50% aqueous acetone by weight and in the presence of an unvarying 0.1 N acid concentration, by following the change of ester concentration with time. First order kinetics were observed, from which the hydrolysis constant was obtained as 2.303 times the slope of a log (a - x) versus t plot,<sup>19</sup> where a is the initial ester concentration, and x the hydrolyzed amount at time t; the customary check on accuracy was made by plotting ester concentrations at time t and obtaining a smooth curve. The rates measured, expressed as

- (17) E. W. Tim and C. N. Hinshelwood, J. Chem. Soc., 862 (1938).
- (18) S. Cohen and A. Schneider, THIS JOURNAL, 63, 3382 (1941).
- (19) W. E. Roseveare, ibid., 53, 1651 (1931).

 $K \times 10^6$  · sec.<sup>-1</sup> were: CF<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>OAc 2.6, CHF<sub>2</sub>CH<sub>2</sub>OAc 2.0, CF<sub>2</sub>CH<sub>2</sub>OAc 1.4, CF<sub>3</sub>(CH<sub>3</sub>)-CHOAc 1.2 and C<sub>6</sub>H<sub>5</sub>OAc 4.0.

Among the measured rates, phenylacetate agrees with the value 3.9 reported for a homogeneous system<sup>20</sup> and considered more reliable than the values 7.7 and 6.6 observed in heterogeneous systems<sup>15,21</sup>; the value for CHF<sub>2</sub>CH<sub>2</sub>OAc also agrees with the value of 1.7 reported by Swarts<sup>2</sup> in an heterogeneous system. It can also be said that our experimental results are consistent. CF3-CH2OAc and CF3(CH3)CHOAc have rates which differ only slightly; in the other two compounds, where the fluorine content is smaller (CHF<sub>2</sub>CH<sub>2</sub>-OAc) or more remote (CF<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>OAc), the rates are faster. However, all rates are slower than those of unfluorinated esters, while they should have been faster if nucleophilic acceptance of  $H_2O$ is the dominant factor. Patently, induction is not the main factor influencing the rates of acid hydrolysis, or else the accepted mechanism is inadequate.

All rates appear in Table I, with the literature values recalculated for  $K \times 10^6 \cdot \sec 7^1$ , log *e*, in 0.1 N acid where needed.

TABLE I								
Hydrolysis Rates of Acetates at 25.0°22								
Ester	K(acid) sec. <sup>-1</sup> •10 <sup>6</sup>	K(base) 1. mole <sup>-1</sup> sec. <sup>-1</sup>						
CH3CH2OAc	11.315	0.10815						
	$11.0^{23}$							
(CH <sub>3</sub> ) <sub>2</sub> CHOAc	$5.8^{19}$	.02615						
	6.224							
(CH <sub>3</sub> ) <sub>3</sub> COAc	13.319	$.0015^{15}$						
	$13.2^{19}$							
n-C <sub>3</sub> H <sub>7</sub> OAc	$11.2^{10}$							
	11.324							
$C_6H_5CH_2OAc$	10.819	. 19715						
C <sub>6</sub> H <sub>5</sub> OAc	$7.7^{19}$	$1.27^{15}$						
	6.620							
	4.0							
	3.918							
CF3CH2OAc	1.4	0.6						
CF <sub>3</sub> CH(CH <sub>3</sub> )OAc	1.2	. 15						
CF <sub>8</sub> CH <sub>2</sub> CH <sub>2</sub> OAc	2.6							
CHF <sub>2</sub> CH <sub>2</sub> OAc	2.0							
	1.7							

## Experimental

 $CHF_2CO_2H$ .—At Dry Ice temperature, anhydrous ammonia (130 g. or 7.7 moles) was liquefied into a 500-ml. steel vessel equipped with the customary gage and needle valve, and containing a few grams of cupric acetate; tetrafluoroethylene (65 g. or 0.65 mole) was sucked in. The reaction mixture was allowed to warm up to room temperature. An exothermic addition took place which was kept under control by intermittent immersion in a Dry Ice-bath to prevent the pressure from exceeding 500 p.s.i. The cupric salt moderates the reaction, which must nevertheless be treated with adequate precaution.<sup>26</sup> In 20 minutes, the reaction was over and the pressure fell to 220 p.s.i. The excess of ammonia (110 g. or 6.3 moles) was vented off.

(23) Average of twelve literature values.

(25) G. W. Rigby, U. S. Patent 2,484,528 to du Pont.

<sup>(15)</sup> A. Skrabal and A. M. Hugetz, Monaish., 47, 17 (1926).

<sup>(16)</sup> J. N. E. Day and C. K. Ingold, Trans. Faraday Soc., 37, 686 (1941).

<sup>(20)</sup> W. A. Waters, J. Chem. Soc., 1014 (1936).

<sup>(21)</sup> R. Lowenherz, Z. physik. Chem., 15, 389 (1894).

<sup>(22)</sup> A. Hemptinne, ibid., 13, 561 (1894).

<sup>(24)</sup> M. H. Palomaa, Ann. Acad. Sci. Fenn. Ser. A. Tome, 4, No. 2 (1913).

The reaction product could be steamed out, but it was found simpler to saw the vessel open and to scrape the bright red crystalline mixture of ammonium fluoride and fluorinated triazine (100 g. or 100% yield):  $3C_2F_4+9NH_3 \rightarrow$ 

 $6NH_4F + N = C(CHF_2) - N = C(CHF_2)_- N = C(CHF_2).$ This mixture was refluxed with aqueous sodium hydroxide until the ammonia evolution ceased to be perceptible (about six hours), acidified and continuously extracted with ether. Rectification of the extract gave 61 g. of wet CHF\_2CO\_2H which was dried by distilling from P\_2O\_6 to yield 49.7 g. (0.52 mole or 80% over-all) of good acid, b.p. 134°,  $n^{20}$  D 1.3428.

which was dried by distilling from  $P_2O_6$  to yield 49.7 g. (0.52 mole or 80% over-all) of good acid, b.p. 134°,  $n^{20}$ D 1.3428. CHF<sub>2</sub>CO<sub>2</sub>H (alternate).—In a 500-ml. steel vessel, absolute ethanol (46 g. or 1 mole) was treated with sodium (2 g.); after cooling in Dry Ice, tetrafluoroethylene (67 g. or 0.67 mole) was added. The vessel was sealed and shaken at 55° for four hours. The pressure rose to 350 p.s.i. then fell to zero. Working up gave 78 g. (77%) of CHF<sub>2</sub>CH<sub>2</sub>-OEt, b.p. 54°. Fuming nitric acid (42 ml.) was added dropwise to this fluorinated ether (42 g. or 0.3 mole) and refluxed for 8 hours. Much etching occurred. Pouring into water permitted decantation of 23 g. (0.16 mole) of recovered fluorinated ether. Continuous extraction of the aqueous layer with ether, desiccation of P<sub>3</sub>O<sub>5</sub> and distillation gave 15 g. (0.15 mole) of ethyl difluoroacetate, b.p. 100°. This is 50% conversion and almost quantitative net yield.

CHF<sub>2</sub>CH<sub>2</sub>OH.—Difluoroacetic acid (85.5 g. or 0.89 mole) was slowly dropped into stirred benzoyl chloride (140 ml. or 1.2 moles); progressive heating to 170° caused the distillation of CHF<sub>2</sub>COCl (75 g., 0.65 mole or 74%) and CHF<sub>2</sub>-CO<sub>2</sub>H (10 g., 0.1 mole or 11%). The acyl chloride was dripped into a solution of LiAlH<sub>4</sub> (15 g. or 0.4 mole) in anhydrous ether (700 ml.) at the rate permitted by the capacity of the reflux condenser. Rapid stirring was required to keep the heavy slurry formed from setting. After refluxing for one hour, water (75 ml.) was cautiously added, the ether was decanted and the residue poured over a mixture of 500 ml. of 6 N H<sub>2</sub>SO<sub>4</sub> and ice. This was continuously extracted with the decanted ether. The extract gave 34 g. of wet CHF<sub>2</sub>CH<sub>2</sub>OH (about 69% yield); it is estimated that about 10% of product was accidentally lost during extraction.

CF<sub>3</sub>COCH<sub>3</sub> (improved).—The condensation of CF<sub>3</sub>CO<sub>2</sub>Et (780 g. or 5.5 moles) with CH<sub>3</sub>CO<sub>2</sub>Et (526 g. or 6 moles) was performed as usual.<sup>26</sup> After 6 hours of reflux instead of the 60 hours used before, ether and ethanol were removed by heating on a steam-bath. Complete removal of ethanol was then insured by heating under reduced pressure until a solid cake was formed. Sulfuric acid of 25% concentration (1500 ml.) was added and allowed to stand until the cake was dissolved. Concentrated sulfuric acid (400 g.) was then added to bring the solution back to 25% acid concentration. The mixture was heated under reflux with continued stirring until the organic layer had completely disappeared. The vapors passing through the reflux condenser were directed to a Dry Ice trap which collected 511 g. (83%) of CF<sub>3</sub>CO-CH<sub>3</sub>.

CH<sub>3</sub>, b.p.  $20-21^{\circ}$ CF<sub>3</sub>CHOHCH<sub>3</sub>.—Trifluoroacetone (40 g. or 0.36 mole) was bubbled into a solution of LiAlH<sub>4</sub> (4 g. or 0.1 mole) in dry ether (200 ml.) under a Dry-Ice reflux condenser. After two hours of refluxing, water (50 ml.) was added with stirring, and additional ether was supplied when the mixture became too viscous. Working up as before gave 34 g. of CI-2CHOHCH<sub>2</sub>, b.p. 77°, an 85% yield.

stirring, and additional ether was supplied when the initial end was supplied when the initial ether was supplied when the initial end of Cl<sup>3</sup><sub>3</sub>CHOHCH<sub>3</sub>, b.p. 77°, an 85% yield. Acetylation.—All alcohols were conventionally acetylated with acetyl chloride: CF<sub>3</sub>CH<sub>2</sub>OAc, b.p. 78°,  $n^{20}$ D 1.3202; CHF<sub>2</sub>CH<sub>2</sub>OAc, b.p. 106–106.5°; CF<sub>3</sub>CH<sub>4</sub>CH<sub>2</sub>OAc, b.p. 112.8–113°,  $n^{20}$ D 1.3410,  $d^{20}$ , 1.219,  $AR_{\rm F}$  1.09; F% 34.5, caled. 36.5; CF<sub>3</sub>CH(CH<sub>3</sub>)OAc, b.p. 85.6°; CF<sub>3</sub>C-(CH<sub>3</sub>)<sub>2</sub>OAc, b.p. 94–95°,  $n^{25}$ D 1.3424,  $d^{25}$ , 1.14, AR 1.05.

(26) A. L. Henne, M. S. Newman, L. L. Quill and R. A. Staniforth, THIS JOURNAL, 69, 1819 (1947). Ionization Constants.—Ten ml. of 0.0446 N CF<sub>3</sub>CH<sub>2</sub>OH mixed with 7.40 ml. of 0.0303 N NaOH (half neutralization point) showed pH 11.4; hence  $K = 4 \times 10^{-12}$ . Ten ml. of 0.039 N CF<sub>3</sub>CH(CH<sub>3</sub>)OH mixed with 6.40 ml. of 0.0303 N NaOH showed pH 11.2; hence  $K = 6 \times 10^{-12}$ . Ten ml. of 0.440 N CF<sub>3</sub>C(CH<sub>3</sub>)<sub>2</sub>OH mixed with 7.30 ml. of 0.0303 N NaOH showed pH 11.60; hence  $K = 2.5 \times 10^{-12}$ . Ten ml. of 0.040 N NaOH showed pH 10.05.P.) and 10.50 ml. of 0.0303 N NaOH showed pH 8.90; hence  $K = 1 \times 10^{-9}$ . The precision of the pH reading was  $\pm 0.05$  unit.

Claim of the pri reading was  $\pm 0.00$  mint. Base-catalyzed Hydrolysis.—Known amounts of ester were sealed in thin wall bulbs placed in 50% aqueous acetone by weight, 0.01 N in NaOH. After holding 20 minutes in a thermostat held at  $25.00 \pm 0.05^\circ$ , the bulb was crushed at time zero; at time t, 1 ml. of 0.1 N HCl was added, and the excess of acid was back-titrated with 0.01 N NaOH to a phenolphthalein end-point. Separate bulbs were used for  $t_1, t_2, t_3$ , etc. The rate constant  $K = [2.303/t(a - b) \log [b(b - x)/a(a - x)]$ , where a and b are the concentration of base and ester, and x the hydrolyzed ester, is reduced to K = [1/t][x/a(a - x)] when a and b are approximately equal.

Hydrolysis of CF<sub>3</sub>CH(CH<sub>3</sub>)OAc at 25.0°.—a = 0.00907; b = 0.00875; stopped with 1 ml. 0.1013 N HCl and back titrated with 0.00907 N NaOH. Time in sec.: 0, 30, 60, 120, 180, 240, 360, 480; corresponding x: 0, 0.00045, 0.00089, 0.00187, 0.00205, 0.00245, 0.00301 and 0.00350; K = 0.155 1. mole<sup>-1</sup> read from the 1/(a - x) vs. t slope.

CF<sub>3</sub>CH<sub>2</sub>OAc measured under comparable conditions gave, for two sets of measurements, K = 0.61. mole<sup>-1</sup> sec.<sup>-1</sup>.

Acid-catalyzed Hydrolysis.—Aqueous acetone 50% by weight and 0.1 N in HCl was brought to  $25.00 \pm 0.05^{\circ}$ . A weighed amount of ester was diluted in this solvent to give 25.0 ml. of solution about 0.1 N in ester. A 2-ml. aliquot was withdrawn at noted intervals and titrated with 0.03 N NaOH to phenolphthalein end-point. Notations are: t, time in minutes; [H]<sup>+</sup>, acid concentration at t min.; x, amount of acetic acid formed and a the ester concentration at time zero. The rate constant was determined by taking 2.303 times the slope of log (a - x) versus t plot, a procedure which is regarded<sup>19</sup> as more accurate than the averaging of constants determined from the equation K = $[1/t] 2.303 \log [a/(a - x)]$ ; however, when the rates were calculated from this equation (Table II, last column) the results were practically identical.

TABLE II

ACID-CATALYZED HYDROLYSES AT 25.00 :	$\pm 0.05^{\circ}$	
--------------------------------------	--------------------	--

TICED-CATAGOLISES AT 20.00 12 0.00							
CHF2CH2OAc <i>t</i> , min.	[H]+	x	(a – x)	(a - x)	$\log a/(a-x)$	104K min1	
0	0.0960		0,1263	0.1014			
245	.0998	0.0037	.1226	.0885	0.0129	1.21	
725	.1070	.0110	.1153	.0618	.0396	1.25	
1295	.1144	.0184	.1079	.0331	.0683	1.22	
1700	.1277	.0317	.0976	,0099	.0915	1,24	
					Mean	1.23	
0	0.09815		0.03241	0.5106		••	
176	.09897	0.00082	.03158	.49 <b>9</b> 4	0.0112	1.46	
365	.09959	.00144	.03097	,4910	.0196	1.23	
620	.10049	.00234	.03007	.4771	.0324	1.21	
					Mean	1.30	

 $CF_3CH_2OAc$ ,  $CF_3CH(CH_2)OAc$  and  $CF_3CH_2CH_2OAc$ were subjected to similar measurements and computations.

Expressed in  $K \times 10^6$  sec.<sup>-1</sup> the experimental values, from slope reading and from averaging, respectively, were found to be: CHF<sub>2</sub>CH<sub>2</sub>OAc, 2.05 and 2.10; CF<sub>3</sub>CH<sub>2</sub>OAc, 1.45 and 1.56; CF<sub>3</sub>CH(CH<sub>3</sub>)OAc, 1.25 and 1.36, and CF<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>-OAc, 2.6 and 3.3.

Columbus, Ohio

RECEIVED SEPTEMBER 14, 1951