IONIZATION CONSTANTS OF FLUORINATED ACIDS

DISSERTATION

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INTRODUCTION

The measurement of ionization constants and their use in interpreting the effect of substituents on the degree of dissociation of many carboxylic acids have been reviewed¹. The degree of dissociation and hence the ionization constant is enhanced by displacement of electrons from the carboxyl group. This displacement facilitates the loss of a proton which permits resonance stabilization of the anion:

The net result is a shift in the equilibrium to the dissociated form.

For saturated aliphatic acids this method has been used to evaluate the relative induction of electronegative elements and groups and to measure the distance from the carboxyl group through which the induction remains effective^{2,3}. For aromatic acids a second effect is called for in addition to induction. Although all halogenated benzoic acids are stronger than benzoic, the ionization constants increase with substituents in the order

$\text{F} < \text{Cl} < \text{Br}$, while induction alone would have called for the reverse order⁴. This may be pictured for p-halogenated benzoic acids as a series of electronic shifts

which oppose resonance stabilization of the anion,

and in which halogens are effective in the order $F > Cl > Br$. This is termed mesomerism and is a polarization effect for a system in equilibrium.

The subject of this thesis comprises two parts:

A. The investigation of the series of saturated aliphatic acids CF_3CO_2H , $CF_3CH_2CO_2H$, and $CF_3CH_2CH_2CO_2H$ is extended to include the synthesis and measurement of the ionization constant of $CF_3CH_2CH_2CH_2CO_2H$. This compound tests the idea that when intramolecular hydrogen bonding is possible, e.g.

the degree of dissociation is enhanced and that this effect should be more pronounced when the γ -hydrogens are activated by a strong electronegative group such as $-CF_3$.

B. A study of the methods of preparation for fluorinated acrylic acids and of the effect of vinyl fluorine on the degree of dissociation of the carboxyl group is originated.

This is an attempt to discover if the mesomeric effect in equilibrium systems is limited to substituents on the aromatic nucleus. For this purpose $\text{CF}_3=\text{CHCO}_2\text{H}$, $\text{CH}_2=\text{CFCO}_2\text{H}$, and $\text{CF}_3=\text{CFCO}_2\text{H}$ are prepared and their ionization constants are compared with existing data on chlorinated acrylic acids. New measurements are presented on fluorinated benzoic acids and phenols in water.

HISTORICAL

Pertinent information on saturated fluorinated acids is recorded in the literature^{3,5}. In contrast, there is no reference to any fluorinated acrylic acid. The patent literature mentions the preparation of $\text{CH}_2=\text{CF}-\text{CO}_2\text{CH}_3$ ⁶, $\text{CF}_2=\text{CF}-\text{CN}$ ⁸ and $\text{CF}_2=\text{CHCO}_2\text{CH}_3$ ⁹, the latter without documentation by reproducible evidence. Compounds like $\text{CH}_2=\text{C}(\text{CHF}_2)\text{CO}_2\text{CH}_3$ ⁷ are also mentioned, which do not have a vinylic type of fluorine and are therefore comparable only to $\text{CF}_3-\text{CH}=\text{CH}-\text{CO}_2\text{H}$.

With few exceptions, ionization constants of acrylic acids bearing halogens are unknown and very few such compounds have been prepared. Ionization constants for trichloroacrylic acid, cis and trans 3-chloroacrylic acid¹¹, 2- and 3-chlorocrotonic acid¹² and 2- and 3-chloroisocrotonic acid¹² are reported in the literature and will be discussed in the following section.

RESULTS OF THIS INVESTIGATION

Syntheses

Preparation of 5,5,5-Trifluorovaleric Acid, $\text{CF}_3(\text{CH}_2)_3\text{CO}_2\text{H}$.

The following sequence was used:

In the first step, complete fluorination of the $-\text{CCl}_3$ group with $\text{SbF}_3\text{-SbF}_3\text{Cl}_2$ is accompanied by partial fluorination and chlorination of the $-\text{CH}_2-$ groups¹³. Specifically, $\text{CCl}_3(\text{CH}_2)_3\text{CH}_2\text{Cl}$ (b. 210°C) gives rise to three fluorinated compounds with B.P. 100° , 121° and 151°C , respectively. The material with B.P. 121°C gives the correct sequence for synthesis of $\text{CF}_3(\text{CH}_2)_3\text{CO}_2\text{H}$, and material with B.P. 100°C gives rise to a secondary alcohol and is therefore considered an isomer of $\text{CF}_3(\text{CH}_2)_3\text{CH}_2\text{Cl}$.

An alternate sequence is attempted:

but fails when ethylene oxide does not condense properly with the Grignard reagent and only tar is obtained after hydrolysis.

Preparation of 4,4,4-Trifluorocrotonic Acid, $\text{CF}_3\text{CH}=\text{CHCO}_2\text{H}$.

Hydrolysis of $\text{CF}_3\text{CH}_2\text{CHBrCCl}_3$ in concentrated H_2SO_4 gives $\text{CF}_3\text{CH}=\text{CHCO}_2\text{H}$ and $\text{CF}_3\text{CH}_2\text{CHBrCO}_2\text{H}$. It is significant

that the CF_3 -group is not attacked under such rigorous conditions. This synthesis is presented as unrecorded work by Dr. Maxwell Nager.

Preparation of 2-Fluoroacrylic Acid, $\text{CH}_2=\text{FCO}_2\text{H}$

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The patent literature claims the preparation of methyl 2-fluoroacrylate by the sequence:

The entire sequence is not employed because saponification in the presence of the double bond is not desirable; the technique for fluorination in the α -position is however used successfully.

Working syntheses are developed as follows. Dehydrohalogenation of $\text{CH}_2\text{BrCHBrCO}_2\text{CH}_3$ with quinoline gives $\text{CH}_2=\text{CBrCO}_2\text{CH}_3$ ¹⁴ which is chlorinated in the presence of LiCl and/or intense illumination to $\text{CH}_2\text{ClCBrClCO}_2\text{CH}_3$ or brominated under intense illumination to $\text{CH}_2\text{BrCBr}_2\text{CO}_2\text{CH}_3$. $\text{CH}_2\text{BrCBr}_2\text{CO}_2\text{CH}_3$, $\text{CH}_2\text{ClCBrClCO}_2\text{CH}_3$ and $\text{CH}_2\text{BrCHBrCO}_2\text{CH}_3$ are subjected to monofluorination in the α -position with HgF_2 under reduced pressure at 110-130°C and under rigorously observed conditions; the products are $\text{CH}_2\text{BrCBrFCO}_2\text{CH}_3$, $\text{CH}_2\text{ClCBrFCO}_2\text{CH}_3$ and $\text{CH}_2\text{BrCHFCO}_2\text{CH}_3$, respectively.

The structure of $\text{CH}_2\text{BrCBrFCO}_2\text{CH}_3$ is demonstrated by a sequence ending in the desired $\text{CH}_2=\text{FCO}_2\text{H}$:

Although polymerization is extensive in the last step, no trace of Br is detected in the product.

The structure of $\text{CH}_2\text{BrHF}\text{CO}_2\text{CH}_3$ is demonstrated by dehydrohalogenation with $(\text{C}_2\text{H}_5)_3\text{N}$ and isolation of $\text{CHBr}=\text{CH}-\text{CO}_2\text{CH}_3$ an isomer of the known $\text{CH}_2=\text{CBrCO}_2\text{CH}_3$; polymerization is extensive and although $(\text{C}_2\text{H}_5)_3\text{N}\cdot\text{HBr}$ is present as one of the expected reaction products, $\text{CH}_2=\text{CF}-\text{CO}_2\text{CH}_3$ is not isolated.

The structure of $\text{CH}_2\text{ClCFClCO}_2\text{CH}_3$ is adopted by analogy; further work with this compound is abandoned in favor of the more practical $\text{CH}_2\text{BrCBrFCO}_2\text{CH}_3$.

Preparation of Perfluoroacrylic Acid, $\text{CF}_2=\text{FCO}_2\text{H}$

Attempts to prepare $\text{CF}_2=\text{FCO}_2\text{H}$ by (1) dehydrohalogenation of $\text{CHF}_2\text{CF}_2\text{CO}_2\text{H}$, (2) bromination of $\text{CHF}_2\text{CF}_2\text{CO}_2\text{H}$ for subsequent dehalogenation or (3) dehalogenation of $\text{CF}_3\text{CF}_2\text{CO}_2\text{H}$ with zinc proved unsuccessful.

Spontaneous decomposition of $\text{CF}_2=\text{FCO}_2\text{H}$ in water, extensive polymerization of $\text{CF}_2=\text{FCO}_2\text{CH}_3$ in alcohols and apparent solubility of $\text{CF}_2=\text{FCO}_2\text{CH}_3$ in water demonstrate the sensitivity of $\text{CF}_2=\text{FCO}_2\text{H}$ to nucleophilic agents and necessarily excludes a procedure which includes saponification of the ester or hydrolysis of the corresponding nitrile; and, in fact, failure to obtain $\text{CF}_2=\text{FCO}_2\text{H}$ from $\text{CF}_2=\text{FCN}$ has been reported ¹⁵.

Consideration of these facts indicates that the double

bond must necessarily be introduced as the last step of the sequence under conditions in which the double bond is stable, and that creation of the double bond by dehalogenation requires removal of halogen other than fluorine at least as a first step of the mechanism. These requirements are met by a sequence of the following type:

(1) oxidation of a fluorinated olefin of the type $\text{XCF}_2\text{-CF=CX}_2$ in the presence of a halogen to an acid chloride of the type $\text{XCF}_2\text{-CFX-COX}$, (2) hydrolysis to the free acid $\text{XCF}_2\text{CFX-CO}_2\text{H}$ and (3) dehalogenation with zinc in absolute ether to $\text{CF}_2\text{=CF-CO}_2\text{H}$.

The patent literature^{8,16,17} reports the oxidative-chlorination of $\text{CF}_2\text{ClCF=CCl}_2$ to $\text{CF}_2\text{ClCCFClCOCl}$ and of $\text{CF}_2\text{ClCCl=CCl}_2$ to $\text{CF}_2\text{ClCCl}_2\text{COCl}$. The former example gives a desired product, but the olefin $\text{CF}_2\text{ClCF=CCl}_2$ is not described in the literature or in the patent claims and hence presents the problem of synthesis as a new compound.

Synthesis of $\text{CF}_2\text{ClCF=CCl}_2$ is first achieved by the sequence:

The first step has the advantage that only one original adduct forms; the second step involves the separation of $\text{CF}_2\text{ClCF=CCl}_2$ from $\text{CF}_2\text{ClCF}_2\text{-CCl}_2\text{H}$ which is difficult because little change in boiling point accompanies the removal of HF.

An alternate synthesis is obtained by the sequence:

Elimination of HCl in the second step is accompanied by an appreciable drop in B.P. which facilitates separation of the olefin, $\text{CF}_2\text{ClCF}=\text{CCl}_2$. The first step, however, is a difficult condensation and with an 8% yield of the original adduct is not yet practical.

It is significant that both sequences give the same olefin; this fact necessitates formulation of the adduct in sequence (2) as $\text{CF}_2\text{ClCFClCHCl}_2$ and not as $\text{CFCl}_2\text{CF}_2\text{CHCl}_2$ as previously described¹⁸. This confirms reports from this laboratory that "Prins" reactions with $\text{CF}_2=\text{CFCl}$ give adducts with the $-\text{CFCl}-$ group in the middle as in:

For the oxidative-chlorination reaction the following sequence has been postulated^{16,17}:

When this sequence is carried out and the resulting acid halide is esterified with ethanol, only one well defined

product is obtained which proves to be $\text{CF}_2\text{ClCFClCO}_2\text{Et}$. Thus, reaction 2b is overshadowed or excluded by 2a.

Dehalogenation of the ester $\text{CF}_2\text{ClCFClCO}_2\text{Et}$ with zinc occurs readily in dioxane, ethanol, butanol or ethylene glycol, but polymerization occurs simultaneously in all cases. In contrast, when saponification to $\text{CF}_2\text{ClCFClCO}_2\text{H}$ is performed before dehalogenation by zinc in dry ether, polymerization is avoided; however, clean separation of liquid $\text{CF}_2\text{ClCFClCO}_2\text{H}$ from $\text{CF}_2=\text{CFCO}_2\text{H}$ (later found to be crystalline) is not achieved.

To facilitate both the last dehalogenation step and the purification of the final product, attempts are made to utilize brominated compounds instead of chlorinated compounds. The reaction:

is attempted, but forms only charred decomposition products.

To gain the advantage of at least a partly brominated compound, the oxidation of the olefin was tried in the presence of bromine instead of chlorine. Reasoning that, if the epoxide is an intermediate in the oxidative chlorination of $\text{CF}_2\text{ClCF}=\text{CCl}_2$ (reaction 1, page 10), the subsequent reaction may not be strictly an intramolecular rearrangement as postulated^{16,17} (shown as 2a and 2b, page 10), but might be an attack by a chlorine atom generated by the ultra-violet illumination such as:

It follows that an oxidative-bromination may proceed in like fashion:

In practice this reaction proceeds with formation of both $\text{CF}_2\text{ClCFBrCOCl}$ and $\text{CF}_2\text{ClCFClCOCl}$ in a molar ratio of 1/1.2.

Dehalogenation of $\text{CF}_2\text{Cl}-\text{CFBrCO}_2\text{H}$ with zinc occurs readily in dry ether. The product, $\text{CF}_2=\text{CF}-\text{CO}_2\text{H}$ is easily separated by distillation at room temperature under reduced pressure, and is not contaminated by either chlorine or bromine.

Breakdown of $\text{CF}_2=\text{CFCO}_2\text{H}$ in Water. In aqueous solution, $\text{CF}_2=\text{CFCO}_2\text{H}$ hydrolyzes with formation of fluorine ions, F^- . Over a period of 30 hours, the concentration of acid in a sample increases from an original 0.0331 mole/liter to 0.123 mole/liter, or roughly four times the original concentration before it levels off. This can represent the formation of 2 molecules of HF and one molecule of a dicarboxylic acid, by such sequences as:

Other sequences, which would involve an attack on the central carbon seem less probable, as they would result in the formation of three moles of HF; however, this is speculation.

The hydrolysis of $\text{CF}_2=\text{CF}-\text{CO}_2\text{H}$ is compatible with the apparent solubility of $\text{CF}_2=\text{CF}\text{CO}_2\text{CH}_3$ in water although the latter may occur by another mechanism such as acid catalyzed saponification.

Preparation of 3,3-Difluoroacrylic Acid, $\text{CF}_2=\text{CHCO}_2\text{H}$

The preparation of $\text{CF}_3\text{CH}_2\text{CO}_2\text{H}$ is achieved in 95% yield²⁰ by the Arndt-Eistert synthesis from CF_3COCl and CH_2N_2 ; however, distillation results in decomposition to HF and a polymer. Rearrangement of the intermediate diazoketone in methanol gives a mixture of $\text{CF}_3\text{CH}_2\text{CO}_2\text{CH}_3$ and $\text{CF}_2=\text{CHCO}_2\text{CH}_3$ ²⁰ which is not separated into its components by distillation and polymerizes on standing. Since $\text{CF}_3\text{CH}_2\text{CO}_2\text{H}$ is a fairly

stable compound^{5,13}, the above work demonstrates the unstable character of $\text{CF}_2=\text{CHCO}_2\text{H}$ and $\text{CF}_2=\text{CHCO}_2\text{CH}_3$, and the experimental details show that this is not an attractive way to make $\text{CF}_2=\text{CHCO}_2\text{H}$.

It is now observed that dehydrohalogenation of $\text{CF}_3\text{CH}_2\text{-CO}_2\text{H}$ proceeds slowly at room temperature in a dilute solution of aqueous sodium hydroxide. The crystalline material obtained from an ether extract appears to be a mixture of hydrates and of ether complexes of $\text{CF}_2=\text{CHCO}_2\text{H}$. Hydrates and ether complexes of highly fluorinated acids have been observed before²¹. This material in water does not give a positive test for fluorine ion until it is strongly heated showing that hydrolysis of $\text{CF}_2=\text{CHCO}_2\text{H}$ is not nearly as pronounced as that of $\text{CF}_2=\text{CFCO}_2\text{H}$. The amorphous solid which remains when the complex is dried contains 10.5%F and is a partly decomposed polymer which can no longer be dissolved in water. Similarly, the unsaturated material obtained by debromination of $\text{CF}_2\text{BrCHBrCO}_2\text{H}$ with zinc in absolute ether visibly decomposes when ether is completely removed and a protecting complex can no longer exist. Distillation of the mixture of crystalline complexes does give a small sample of material which on the basis of analysis and neutral equivalent is formulated as a dihydrate, $\text{CF}_2=\text{CHCO}_2\text{H}\cdot 2\text{H}_2\text{O}$. This material is used to obtain an ionization constant for $\text{CF}_2=\text{CHCO}_2\text{H}$ with the assumption that this formulation is correct.

Physical Measurements

Significant and readily measured differences in ionization constants are observed when comparisons are made for a series of aliphatic acids which are substituted with different halogens (e.g. $\text{CH}_2\text{ClCO}_2\text{H}$ and $\text{CH}_2\text{FCO}_2\text{H}$); in which varying degrees of halogenation are present (e.g. $\text{CH}_2\text{XCO}_2\text{H}$, $\text{CHX}_2\text{CO}_2\text{H}$, and $\text{CX}_3\text{CO}_2\text{H}$); or in which the substituent is displaced from the carboxyl group³.

This makes data which are semi-quantitative and give the order of magnitude to one or two decimal places acceptable and obviates measurements which are extremely precise. The measurements in this research are carried out with this limitation; comparisons are made whenever possible on measurements obtained using identical methods and apparatus so that any inherent error becomes a common factor. The reliability obtained in each series of data is denoted by specifying the average deviation of the mean.

Two methods are used to obtain values for the ionization constants:

A. Potentiometric Titrations. Ionization constants are calculated from measured values of pH at appropriate intervals during titration, correcting for concentration of acid, salt and hydrogen ion with the equation²²:

$$\text{pK} = \text{pH} - \log \left[\frac{((\text{salt}) + \text{C}_{\text{H}^+})}{((\text{acid}) - \text{C}_{\text{H}^+})} \right]$$

Within the limits of pH = 4 to 10, C_{H^+} may be neglected²² so:

$$pK = pH - \frac{\log[(\text{salt})]}{\log[(\text{acid})]}$$

and at the half-neutralization point (salt) = (acid) so:

$$pH = pK$$

The latter two equations are employed only where experimental conditions justify their use.

Values for p H are read directly to three significant figures so that when K is obtained from pK by the equation: $pK = \log 1/K$, only two significant figures are acceptable.

This method is used for the weak aliphatic acids, substituted benzoic acids, and substituted phenols. For the aliphatic acids the results are in accord with those obtained by conductance measurements.

B. Conductance Measurements. The equivalent conductances, (Λ) in mhos, of the solutions are obtained from the equation²³:

$$\Lambda = \frac{1000 \times \text{cell constant}}{C \times R}$$

where C is concentration in equivalents/liter and R is resistance in ohms of the solution obtained experimentally. The cell constant is evaluated from the measured resistance of a 0.1000 molal solution of KCl⁵.

So called classical ionization constants (K_{Cl}) are obtained by the equation²⁴:

$$K_{Cl} = \frac{Cx^2}{1-x}$$

where C is concentration and x is the conductance ratio

Λ/Λ_0 in which Λ_0 is the limiting equivalent conductance. Values for Λ_0 for weak acids are obtained by the equation⁵:

$$\Lambda_0(\text{acid}) = \Lambda_0(\text{Na salt}) + \lambda_0(\text{H}^+) - \lambda_0(\text{Na}^+)$$

Extrapolation of the straight line from a plot of $\Lambda(\text{salt})$ vs. $\frac{1}{C^2}$ gives $\Lambda_0(\text{salt})$ which is used with reported values of $\lambda_0(\text{H}^+)$ and $\lambda_0(\text{Na}^+)$.²⁵

The thermodynamic ionization constants (K_{Th}) are obtained by the equation²⁶:

$$\log K_{\text{Th}} = \log \frac{x^2 C}{1-x} - 2A\sqrt{x C}$$

where $A = 0.51$ at 25°C , and x is the ratio Λ/Λ' . The equivalent conductance corrected for interionic forces (Λ') is obtained by use of a form of the Onsager equation^{27,28}:

$$\Lambda' = \sqrt{\Lambda_0^2 - 2b(\Lambda_0 \Lambda C)^{\frac{1}{2}}}$$

where the value used for the Onsager slope (b) for aqueous solutions at 25°C is $(0.2271 \Lambda_0 + 59.78)$.²⁸

The resistances of the solutions are evaluated to four significant figures by comparison with a standard resistance box; the fourth digit being extrapolated from the potentiometer reading using ratio tables for bridge calculations.²⁹ The concentration is obtained to four significant figures by titration with standard base. Allowing for error introduced by the limited precision of the apparatus and apparent from the reproducibility of the measurements, the values of K are reported to three significant figures only.

The accuracy of the bridge is checked by measuring the resistances of solutions of $\text{CH}_2\text{ClCO}_2\text{H}$ which are previously reported³⁰. The results are recorded in the experimental section and are quite acceptable.

This method is used to obtain ionization constants for $\text{CH}_2=\text{CFCO}_2\text{H}$ and $\text{CF}_2=\text{CFCO}_2\text{H}$ to be quite certain that the right order of magnitude is obtained.

Both classical and thermodynamic ionization constants are calculated for $\text{CH}_2=\text{CFCO}_2\text{H}$ and $\text{CF}_2=\text{CFCO}_2\text{H}$. Thermodynamic ionization constants are also calculated from pre-existing data on $\text{CF}_3\text{CH}_2\text{CO}_2\text{H}$, $\text{CF}_3\text{CH}_2\text{CH}_2\text{CO}_2\text{H}$, $\text{CH}_2\text{FCO}_2\text{H}$ and $\text{CCl}_2=\text{CClCO}_2\text{H}$. This comparison is made to avoid overlapping data which might invalidate the interpretation and also with the understanding that thermodynamic ionization constants are more acceptable from a theoretical standpoint.

The results of these measurements are recorded in Tables I and II. An interpretation will be presented in the following section.

Table I
Ionization Constants of Halogenated Aliphatic Acids at
25°C in Water.

	$K \times 10^5$ from pH	$K_{Cl} \times 10^5$	$K_{Th} \times 10^5$
$CF_3CH_2CO_2H^5$		93.9 ± 0.9	84.8 ± 0.08
$CF_3CH_2CH_2CO_2H^5$	7.0 ± 0.1	6.98 ± 0.03	6.62 ± 0.05
$CF_3CH_2CH_2CH_2CO_2H$	3.2 ± 0.03		
$CF_3CH=CHCO_2H$	45 ± 0.6		
$CF_2=CHCO_2H$	68 ± 1		
$CH_2=CFCO_2H$	270 ± 3	306 ± 6	279 ± 3
$CF_2=CFCO_2H$		1570 ± 10	1610 ± 70
$CF_2HCO_2H^{21}$		218 ± 2	161 ± 2
$CCl_2=CClCO_2H^{10}$		7000 ± 100	5440 ± 50

Table II
Ionization Constants of Fluorinated Benzoic Acids and
Phenols at 25°C in Water.

	Benzoic Acids $K \times 10^5$	Phenols $K \times 10^{10}$
-H	6.2 ± 0.2	2.1 ± 0.02
o-F	29 ± 0.2	26 ± 0.2
m-F	15 ± 0.2	8.7 ± 0.08
p-F	30 ± 0.8	1.8 ± 0.04

Effect of Substituents on the Ionization Constants

Many workers have attempted to correlate ionization constants of acids with other physical properties; for acids containing halogen and similar substituents the dipole moment is an important factor. The efforts made in this direction to 1939 have been reviewed³¹.

Some of the notable contributions are as follows:
A. MacInnes³² obtained a straight line relationship by plotting $\log K$ vs. $1/d$ where $d = 1, 2$ and 3 for halogen (Cl, Br, I) in α , β and γ positions of saturated aliphatic acids respectively. The data fit the equation $\log K = C + S 1/d$ where C and S are constants peculiar to the substituent and in which C is a log function of the dissociation constant of an hypothetical acid obtained by moving the substituent an infinite distance along its chain. This hypothetical acid is not the same as the corresponding unsubstituted acid, for the substituent introduces energy changes in the molecule. MacInnes concludes that theoretically the formula applies if the substituent and the carboxyl group repel each other according to the inverse square of the distance between their polar bonds and if the free energy of ionization is increased in proportion to the mutual potential energy of the two groups.

This equation was elaborated upon³³ by replacing d by l^2 where l is the distance in $\text{\AA}$ between dipole center of

the group and the carboxyl center, assuming an extended chain. This follows as a consequence of the definition of the inductive effect, that the magnitude of K of an acid will be governed in a simple manner by the distance separating the carboxyl group and substituent. In aliphatic acids, this rule is observed, but in benzoic acids it is masked by additional factors, mesomerism and steric influences.

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B. Kirkwood and Westheimer further developed a hypothesis, that the ratio of the ionization constant of an acid with a polar substituent to that of the unsubstituted acid depends upon a statistical factor and upon the electrostatic influence of the substituent, on the assumption that the molecules are cavities of low dielectric constant in which the charges are inbedded. In place of the dielectric constant of the solvent they use the effective dielectric constant which is a function of the shape of the molecule, the position of the charges within the molecule, the dielectric constant of the solvent, and dielectric constant of the cavity. Their equation gives the interprotonic (for dibasic acids) or proton-dipole distance calculated on the basis of an extended chain model and a reasonable (but not rigid) lower limit based on the principle of free rotation, in order to substantiate the hypothesis. This concept is satisfactorily applied to dibasic, dipole-substituted, alkyl-substituted, and

amino-substituted aliphatic acids³⁵ and to p-substituted phenylacetic acids, benzoic acids, phenols and anilines³⁶, and is indicative of an electrostatic effect.

C. Ives and Sames³⁷ develop a relatively simple treatment based on accepted interatomic distances and bond angles which enables correlation of dipole moments of substituents and ionization constants for acids of similar type. Their equation permits an approximate calculation of the distance the carboxyl hydrogen must be from the molecule before it separates as a proton; this value is remarkably constant for halogenated (Cl, Br, I) acids with substituents in the α , β and γ positions and leads to a "tentative inference that the substitutional effects are predominantly electrostatic".

Since reasonable explanations for the effect of substituents on ionization constants are obtained when the selected parameters are similar but not identical, no definite conclusion is possible and the absolute significance of any one treatment is debatable. The inductive and steric effects both seem to play a part; yet when treated independently or in conjunction, the inductive effect predominates and offers the best explanation^{32,33,37}.

Using the data obtained on the fluorinated acids in one or more of these theoretical treatments, to show that any equation is more or less extendable, does not offer any advantage. It is possible that such treatment for the

fluorinated acrylic acids would show that vinylic fluorine is not exhibiting an inductive effect; this will be kept in mind for future publication.

The order of $F > Cl > Br > I$ for electronegative induction^{3,4} is well established. Since fluorine is the smallest of the halogens any steric effect is expected to be less pronounced. The following qualitative discussion on fluorinated acids is presented with consideration of these properties.

Ionization Constants of Saturated Aliphatic Acids

In the series of unsubstituted aliphatic acids, butyric is reported to be more ionized than propionic acid³⁸, the values for $K_A \times 10^5$ being 1.51 and 1.34, respectively. This small increase has been attributed³⁹ to intramolecular hydrogen bonding:

possible in butyric acid but not in propionic acid;

branching on the chain as in diethylacetic acid and isovaleric acid ($K \times 10^5 = 1.77$ and 1.67 , respectively)³⁹ permits greater frequency of hydrogen bonding and explains the increased acidity. The greater protonic character observed for hydrogen atoms adjacent to a $-CF_3$

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group, indicates they may be expected to enter more readily into hydrogen bonding if given an opportunity in space; which should result in an appreciable increase in ionization of the acid group.

Table III

Ionization Constants of Saturated Aliphatic Acids at
25°C

Acid	$K_{pH} \times 10^5$	$K_{Cl} \times 10^5$	$K_{Th} \times 10^5$
$CH_3CH_2CH_2H$	-	-	1.34*
$CH_3CH_2CH_2CO_2H$	1.6 ± 0.01	-	1.51**
$CH_3CH_2CH_2CH_2CO_2H$	-	-	1.38**
CF_3CO_2H	-	5×10^{-1} (strong electrolyte)	-
$CF_3CH_2CO_2H$	-	93.9 ± 0.9	84.8 ± 0.8
$CF_3CH_2CH_2CO_2H$	7.0 ± 0.1	6.98 ± 0.03	6.62 ± 0.05
$CF_3CH_2CH_2CH_2CO_2H$	3.2 ± 0.03	-	-

* Reference 38; ** Reference 39

The inductive effect of the $-CF_3$ group falls rapidly with increasing distance (Table III); the ratio of K for the fluorinated acid to the unfluorinated analog being: for CF_3CO_2H a factor of 10^4 ; for $CF_3CH_2CO_2H$ a factor of 10^2 ; and for $CF_3CH_2CH_2CO_2H$ less than a factor of 5. Roughly this decrease obeys the inverse square law expected for induction³³. By extrapolation $CF_3CH_2CH_2CH_2CO_2H$ could not be expected to differ measurably from valeric acid; however,

its ionization constant is more than twice as large. This is interpreted as an indication of intramolecular hydrogen bonding with a six-membered ring formation such as;

which is more pronounced than for the hydrocarbon acids despite the fact that it involves only two hydrogens instead of three in butyric acid or six in isovaleric and diethylacetic acids.

Ionization Constants of Unsaturated Aliphatic Acids

The mesomeric effect is explained by Remick as follows ⁴¹:

"If it is possible to write two or more different electronic structures for a given molecule without changing the arrangement of the atoms or exceeding the number of electrons which can exist in the valence shell of any one atom, then none of these structures represents the true state of the molecule, which is correctly represented by an intermediate mesomeric state. Thus these contributing structures will always undergo a mesomeric displacement in the direction of this intermediate state".

The overall result is a permanent polarization of the molecule, in contrast to polarizability, and as such is most readily observed for systems in equilibrium.

The ionization constants of substituted benzoic acids ⁴²

have been observed to portray this effect and in these studies the acidities of the meta and of the para halogenated acids are in the order $F < Cl < Br$; this order has also been observed for the halogenated phenols which serves to extend this concept.

New values of ionization constants for the fluorinated benzoic acids and phenols are tabulated, with selected existing data in Table IV.

The trend of the fluorinated phenols determined here agrees with results reported in the literature; the displacement to higher values is expected from the use of water instead of aqueous-alcohol as a solvent. The only discrepancy is that p-fluorophenol proves slightly less acid than phenol while the literature shows a small difference

Table IV

Ionization Constants of Halogenated Benzoic Acids

	Benzoic Acids		Phenols	
	$K \times 10^5$		$K \times 10^{10}$	
	(a)	(b)	(a)	(c)
-H	6.2 ± 0.2	6.27	2.1 ± 0.02	0.32
o-F	29 ± 0.2	54.1	26 ± 0.2	4.27
m-F	15 ± 0.2	13.6	8.7 ± 0.08	1.51
p-F	30 ± 0.8	7.22	1.8 ± 0.04	0.76

- (a) This research; at $25 \pm 1^\circ$ in H_2O solution; potentiometric titration
 (b) Ref. 2, p. 65; at 25° in H_2O solution; conductance measurement
 (c) Ref. 20; at 25° in 30% H_2O - C_2H_5OH solution; potentiometric titration

in the opposite direction; this does not alter the picture as a whole.

A large discrepancy appears in the series of fluoro-benzoic acids: results determined here show the ortho- and para-fluorobenzoic are equally dissociated. The measurements are checked on duplicates and the samples seem authentic and in good condition (see experimental p.63). These acids are found to be difficultly soluble in water, a fact which was previously reported for the brominated but not the fluorinated benzoic acids⁴² and which may have significance. However, additional work is necessary before further discussion is warranted, meanwhile the previously reported values are accepted.

Thus the mesomeric effect created by halogen gives the order $F > Cl > Br$ and in this case prevails over induction, also a polarization effect, which would increase the acidity in the same order. For the para-halogenated benzoic acids the contribution by mesomerism may be pictured as a series of electronic shifts culminating in c and in opposition to a and b which are required for resonance stabilization of the anion:

For the meta-halogenated benzoic acids it is necessary to picture a series of shifts relayed by an inductive mechanism⁴:

For the ortho-halogenated acids the mesomeric effects may again be pictured as a series of electronic shifts:

Although the order observed for the ionization constants remains $\text{o-F} < \text{o-Cl} < \text{o-Br}$ this has not been considered as reliable evidence of mesomerism since the ortho substituents are subject to steric hindrance and chelation.

However, in the case of fluorine, steric hindrance is ruled out because fluorine approaches hydrogen in size. Chelation may be pictured as:

with the carboxyl hydrogen labilized by the fluorine. Such an effect would also be possible in the aliphatic series (Table III, p. 23) where it would be magnified in $\text{CF}_3\text{CH}_2\text{CO}_2\text{H}$ with ring formation such as:

However, if this effect is very important, one would not expect the large decrease in ionization constant observed from $\text{CF}_3\text{CO}_2\text{H}$ ($K \times 10^5 = 50,000$) to $\text{CF}_3\text{CH}_2\text{CO}_2\text{H}$ ($K \times 10^5 = 85$) or the further decrease to $\text{CF}_3\text{CH}_2\text{CH}_2\text{CO}_2\text{H}$ ($K \times 10^5 = 6.6$) where chelation is still possible by seven membered ring formation. The order of this decrease does apply very well to the principle of induction⁵.

This is an important point since chelation in the β -fluorinated acrylic acids is also possible.

A comparison of propionic acid, $\text{CH}_3\text{CH}_2\text{CO}_2\text{H}$ ($K \times 10^5 = 1.33$) and acrylic acid $\text{CH}_2=\text{CHCO}_2\text{H}$ ($K \times 10^5 = 5.50$) indicates the vinyl group is electronegative; however, a comparison of the differences between ratios of ionization constants of the unsaturated acids to the saturated acids for acrylic acid and its homologs, $\text{CH}_2=\text{CHCH}_2\text{CO}_2\text{H}$ and $\text{CH}_2=\text{CHCH}_2\text{CH}_2\text{CO}_2\text{H}$, indicated that in the α, β -unsaturated acids the effect of the double bond is not proportional to that found for the β, γ and γ, δ unsaturated acids, and an opposing mesomeric disturbance such as:

is effective⁴⁴. This serves to reduce the dissociation constant.

By analogy with the halogenated benzoic acids the mesomeric effect in acrylic acids will be enhanced by halogen and in the order $\text{F} > \text{Cl} > \text{Br}$.

For the fluorinated acrylic acids the experimental results are tabulated in Table V.

Table V

Ionization Constants of Fluorinated Acrylic Acids at 25°C in Water.

	$K_{pH} \times 10^5$	$K_{Cl} \times 10^5$	$K_{Th} \times 10^5$
$CF_2=CHCO_2H$	68 ± 1	-	-
$CH_2=CFCO_2H$	270 ± 3	306 ± 6	279 ± 3
$CF_2=CFCO_2H$	-	1570 ± 10	1610 ± 70
$CF_3CH=CHCO_2H$	45 ± 0.6	-	-

The consequence of the inductive effect exerted by fluorine in alpha position is an increase in acidity. For $CH_2=CFCO_2H$ any mesomeric effect arising from the vinylic fluorine shifts electrons toward the beta carbon, away from the acid group and this would serve to further enhance the acidity. The ionization constant measured for $CH_2=CFCO_2H$ ($K_{Th} \times 10^5 = \text{ca. } 280$) is in fact greater than that recalculated for CH_2FCO_2H ²¹ ($K_{Th} \times 10^5 = 161$) and this is consistent with a shift of electrons such as:

which does not oppose resonance stabilization of the anion. This does not account for the inherent effect of introducing

unsaturation; however, from existing data on similar chlorinated acids this factor does not seem too important.

Thus going from 2-chlorobutyric acid³, $\text{CH}_3\text{CH}_2\text{CHClCO}_2\text{H}$
($K \times 10^5 = 139$) to 2-chlorocrotonic acid¹²,

or 2-chloroisocrotonic acid¹²,

there is no large change on introducing unsaturation and the vinylic chlorine does not seem to contribute a significant mesomeric effect. In view of the apparent cis-trans isomeric effect, measurements on α -chloroacrylic acid would appear much preferable for comparison.

In the beta position, fluorine can increase the acidity over the unsubstituted acid by an inductive mechanism or by a chelation effect; however, it has been pointed out that the inductive mechanism is acceptable and that chelation is not likely. If chelation becomes effective with fluorine in vinylic position the dissociation would be further enhanced:

but a mesomeric effect would shift electrons toward the carboxyl group and oppose resonance stabilization of the anion with an overall decrease in acidity:

For $\text{CF}_2=\text{CHCO}_2\text{H}$ ($K \times 10^5 = 68$) the decrease from $\text{CF}_3\text{CH}_2\text{CO}_2\text{H}$ ($K \times 10^5 = \text{ca. } 90$) is in line with a net mesomeric effect; however, the difference in degree of halogenation does not permit induction to be ruled out.

A comparison of similar chlorinated compounds shows that (1) a chelation effect is possible for vinylic chlorine in the β -position only when the chlorine and the carboxyl are in cis positions:

and (2) that here a mesomeric effect does not successfully oppose the electronegative induction, which however is enhanced by unsaturation. Thus cis-3-chloroacrylic acid¹¹,

is a stronger acid than either trans-3-chloroacrylic¹¹,

or its saturated analog 3-chloropropionic acid⁴⁵, $\text{CH}_2\text{ClCH}_2\text{CO}_2\text{H}$ ($K \times 10^5 = 8.4$); and 3-chlorocrotonic acid¹²,

is a stronger acid than either 3-chloroisocrotonic acid¹²,

or its saturated analog 3-chlorobutyric acid³, $\text{CH}_3\text{CHClCH}_2\text{CO}_2\text{H}$
 $K \times 10^5 = 8.9$).

A comparison of cis- and trans-3-fluoroacrylic acid with 3-fluoropropionic would be very helpful in confirming (1) that a single vinylic fluorine in β -position reverses the electronegative induction in spite of unsaturation and (2) that the chelation effect apparent for chlorine when cis- to the carboxyl group is insignificant when fluorine is substituted. However, these compounds have not yet been prepared.

The ionization constant of $\text{CF}_2=\text{CFCO}_2\text{H}$ ($K_{\text{Th}} \times 10^2 = 1.61 \pm 0.07$) approaches the value obtained for saturated per-fluoro acids⁵ ($K \times 10^{-2} = \text{ca. } 5$). This indicates a strong electronegative induction and if this effect alone is operative $\text{CF}_2=\text{CFCO}_2\text{H}$ should be a stronger acid than $\text{CCl}_2=\text{CClCO}_2\text{H}$; whereas, a significant mesomeric effect in which F is again more effective than Cl would reverse the direction. It is the latter which is observed and $\text{CCl}_2=\text{CClCO}_2\text{H}$ ($K_{\text{Th}} \times 10^2 = 5.44 \pm 0.05$) is appreciably stronger than $\text{CF}_2=\text{CFCO}_2\text{H}$. This does not take into account the chelation possible for vinylic chlorine in β -position which would serve to enhance the dissociation. A chelation effect involving fluorine is not likely for if it were at all important it would be magnified

by the greater electronegativity of fluorine and also oppose any mesomeric effect; the net result would be a reversal of the observed order.

The general picture observed for fluorinated and chlorinated acrylic acids is consistent: (1) in the alpha position both vinylic halogens exert an electronegative induction which is greater for fluorine and is even further enhanced by a mesomeric shift of electrons; (2) in the beta position the vinylic fluorine exhibits an inductive effect which is partially offset by a mesomeric shift of electrons with a net decrease in the ionization constant while the inherent inductive effect of the vinylic chlorine is further enhanced by what may be chelation involving the carboxyl hydrogen.

A significant observation is that $\text{CF}_3\text{CH}=\text{CHCO}_2\text{H}$ ($K \times 10^5 = 45$) is a weak acid and not a vinylog of $\text{CF}_3\text{CO}_2\text{H}$. Its ionization constant is slightly less than but of the same order of magnitude as that for $\text{CF}_2=\text{CHCO}_2\text{H}$. This is in accord with the concept that a fluorine molecule has a more effective electronegativity than a $-\text{CF}_3$ group as a whole. Thus $\text{FCH}_2\text{CO}_2\text{H}$ ($K_{\text{Th}} \times 10^5 = 161 \pm 2$) is a stronger acid than $\text{CF}_3\text{CH}_2\text{CO}_2\text{H}$ ($K_{\text{Th}} \times 10^5 = 84.8 \pm 0.8$). This comparison for $\text{CF}_3\text{CH}=\text{CHCO}_2\text{H}$ is not consistent with resonance of the type

which has been postulated to explain the increase in ionization constant going from m-trifluoromethylbenzoic acid to p-trifluoromethylbenzoic acid, and the physical properties of similar compounds⁴⁶ in which the trifluoromethyl group is conjugated with a functional group. Again a more valid comparison would be with cis and trans CHF=CHCO₂H which have not yet been prepared.

EXPERIMENTAL

A. SYNTHESIS

1.0 Preparation of 5,5,5-Trifluorovaleric Acid, $\text{CF}_3(\text{CH}_2)_3\text{CO}_2\text{H}$.

1.1 Fluorination of $\text{CCl}_3(\text{CH}_2)_3\text{CH}_2\text{Cl}$. $\text{CCl}_3(\text{CH}_2)_3\text{CH}_2\text{Cl}$ (210g, 1 mole) in $\text{CCl}_2=\text{CClCCl}=\text{CCl}_2$ (200 ml) is added by drops to a vigorously stirred slurry of SbF_3 (138g, 0.7 moles) and SbF_3Cl_2 (220g, 0.8 moles, total 50 mole % F excess) in $\text{CCl}_2=\text{CClCCl}=\text{CCl}_2$ (30 ml) cooled in an ice bath. When addition is complete SbF_3Cl_2 (80g, 0.3 moles) is added to promote fluorination of mono- and difluorinated products. After 2 hours the mixture is permitted to warm up and is stirred 4 hours at room temperature then hydrolyzed with HCl in ice and steam distilled. The distillate is washed with aqueous NaHCO_3 , H_2O , saturated NaCl and dried over MgSO_4 . Distillation gives material (19g) b. $97-98^\circ\text{C}$, n_D^{29} 1.3521, d_4^{29} 1.195; $\text{CF}_3(\text{CH}_2)_3\text{CH}_2\text{Cl}$ (11g, .07 mole, 7%) b. 121°C , n_D^{27} 1.3691, d_4^{27} 1.217, M.R. 29.6, AR_F 0.93, found 32.40%F, 25.07%Cl, ratio Cl:F = 1:2.4 (calcd. 35.6%F, 21.9%Cl, ratio Cl:F = 1:3.0); and material (27g) b. $150-152^\circ\text{C}$, n_D^{29} 1.4070, d_4^{29} 1.264. The solvent and starting material are not readily separated. Similar reactions give identical products in the same relative amounts.

1.2 Preparation of $\text{CF}_3(\text{CH}_2)_3\text{CH}_2\text{OH}$. $\text{CF}_3(\text{CH}_2)_3\text{CH}_2\text{Cl}$ (43g, 0.26 mole) in 150 ml of dry ether is added to Mg (8g, 0.3 mole) stirred in 150 ml of dry ether. Reaction starts when

several crystals of I_2 are added to the reaction, but not when $CF_3(CH_2)_3CH_2Cl$ (2g) is heated with Mg or when C_2H_5I (20 drops) is added to the reaction (although C_2H_5I reacts), and proceeds satisfactorily when heated slightly with formation of an orange precipitate. The suspension is siphoned into an addition funnel and added slowly to dry ether into which O_2 is bubbled while stirring and which is cooled in an acetone-dry ice bath. When addition is complete, O_2 is slowly bubbled into the mixture another 8 hours; precipitation is voluminous. The suspension is hydrolyzed with dilute HCl with formation of two clear layers. The ether layer and ether extract of the aqueous layer are washed with saturated NaCl, dried over $MgSO_4$ and the ether is distilled. The residue is mixed with Hg to remove I_2 , filtered, and C_6H_6 is added and distilled to remove H_2O . Distillation of the residue gives $CF_3(CH_2)_3CH_2OH$ (18g, 0.13 mole, 50% yield) b. $80-85^\circ C$ at 69mm which reacts slowly with Na but not with Lucas reagent. No further attempt at purification or identification is made.

1.3 Oxidation of $CF_3(CH_2)_3CH_2OH$. $CF_3(CH_2)_3CH_2OH$ (18g, 0.13 mole) is added by drops to a solution of $Na_2Cr_2O_7 \cdot 2H_2O$ (24g, 0.08 mole) and H_2SO_4 (15ml, .34 mole) in 250 ml H_2O stirred at $50^\circ C$ for 48 hours. Additional H_2SO_4 (50ml) is added to the cold mixture which is then continuously extracted with ether. C_6H_6 is added to the extract and distilled to remove H_2O . Distillation under reduced pressure gives crude

$\text{CF}_3(\text{CH}_2)_3\text{CO}_2\text{H}$ (11g, .066 mole, 51% yield) b. $93-100^\circ\text{C}$ at 16 mm, NE 163, which contains a small amount of H_2O insoluble material. Neutralization of an aqueous solution with NaOH and extraction with ether (3 times) gives ca. 0.5g oil in the extract. Aqueous solution is acidified with H_2SO_4 (50 ml), continuously extracted with ether and extract is dried over MgSO_4 , then C_6H_6 is added and distilled with ether to remove H_2O . Distillation under reduced pressure gives $\text{CF}_3(\text{CH}_2)_3\text{CO}_2\text{H}$ (9g), b. $93.8-95^\circ\text{C}$ at 15mm; cut b. $94.8-95.0^\circ\text{C}$ at 15mm has n_D^{25} 1.3632, d_4^{25} 1.293, MR 26.93, AR_F 1.10, NE 155.3 (calcd. 156), found 36.96%F (calcd. 36.54%F), qualitative test for Cl on fusion with Na is negative.

1.4 Attempted Preparation of $\text{CF}_3(\text{CH}_2)_3\text{CH}_2\text{OH}$ from $\text{CF}_3\text{CH}_2\text{CH}_2\text{Cl}$.

Reaction of $\text{CF}_3\text{CH}_2\text{CH}_2\text{MgCl}$ (1 mole) with ethylene oxide is carried out as described for the preparation of n-hexyl alcohol⁴⁸. The reaction proceeds normally and the rearrangement occurs smoothly. However after hydrolysis no material is isolated other than solid decomposition products. Direct oxidation with $\text{Na}_2\text{Cr}_2\text{O}_4$ and H_2SO_4 after hydrolysis also fails to give any product.

1.5 Attempted Preparation of $\text{CF}_3(\text{CH}_2)_3\text{CO}_2\text{C}_2\text{H}_5$ from $\text{CF}_3\text{CH}_2\text{CH}_2\text{Cl}$. Independently Mr. D. Krehbiel of this laboratory has found $\text{CF}_3\text{CH}_2\text{CH}_2\text{Cl}$ with $\text{NaCH}(\text{CO}_2\text{C}_2\text{H}_5)_2$ gives exclusive dehydrohalogenation to $\text{CF}_3\text{CH}=\text{CH}_2$.

2.0 Preparation of $\text{CF}_3\text{CH}=\text{CHCO}_2\text{H}$. Synthesis of $\text{CF}_3\text{CH}=\text{CHCO}_2\text{H}$ was carried out by Dr. Maxwell Nager and is heretofore des-

cribed only in notes. The following is a description of his work. Hydrolysis of $\text{CF}_3\text{CHBrCH}_2\text{CCl}_3$ is carried out in 95.5% H_2SO_4 at 125°C for 12 hours. Evolution of HCl , HBr and Br_2 is observed; no hydrolysis of the CF_3 -group occurs. Working up the product (presumably by ether extraction) and recrystallization from petroleum ether gives insoluble $\text{CF}_3\text{CHBrCH}_2\text{CO}_2\text{H}$ m. $132-134^\circ\text{C}$ and soluble $\text{CF}_3\text{CH}=\text{CHCO}_2\text{H}$ m. $49.5-50.5^\circ\text{C}$, NE 140.1 (calcd. 141), found 33.74%C, 2.30%H (calcd. 34.30%C, 2.16%H).

3.0 Preparation of 2-Fluoroacrylic acid, $\text{CH}_2=\text{FCO}_2\text{H}$.

3.1 Preparation of $\text{CH}_2\text{BrCHBrCO}_2\text{CH}_3$. Methyl acrylate containing hydroquinone (880g, 10.2 moles) in CH_3OH (500ml) is brominated with commercial Br_2 (1630g, 10.2 moles) as described in the literature¹⁴. Distillation gives $\text{CH}_2\text{BrCHBrCO}_2\text{CH}_3$ (2311g, 9.4 moles, 92% yield) b. $96-102^\circ\text{C}$ at 21mm.

3.2 Preparation of $\text{CH}_2\text{ClCBrClCO}_2\text{CH}_3$. Quinoline (125g, 1 mole) and $\text{CH}_2\text{BrCHBrCO}_2\text{CH}_3$ (246g, 1 mole) were mixed in an atmosphere of nitrogen under reduced pressure. Heat is evolved and when precipitation of quinoline hydrochloride is complete the mixture is dissolved in CHCl_3 . The CHCl_3 solution is washed with 5% HCl , H_2O , dried over anhydrous Na_2SO_4 and chlorinated while illuminating with a "sun lamp" until Cl_2 is no longer absorbed. Distillation gives $\text{CH}_2\text{ClCClBrCO}_2\text{CH}_3$ (120g, 0.51 mole, 51% yield) b. $67-69^\circ\text{C}$ at 4mm, n_D^{25} 1.5000.

3.3 Fluorination of $\text{CH}_2\text{ClCBrClCO}_2\text{CH}_3$. Anhydrous HgF_2 (Penn-

sylvania Salt Mfg. Co.) (37g, 0.15 mole) and $\text{CH}_2\text{ClCBrClCO}_2\text{CH}_3$ (70.8g, 0.3 mole) are mixed and heated to 120°C where reaction is evident. Strong fumes which may be COF_2 are evolved when pressure is reduced. The temperature is maintained at 110°C while stirring overnight. Distillation at 25mm results in extensive decomposition. Redistillation gives material (12g) b. $74-80^\circ\text{C}$ at 48mm, n_D^{25} 1.4370-1.4449, which on fusion with Na gives a positive qualitative test for F^- and Br^- ; and recovered $\text{CH}_2\text{ClCBrClCO}_2\text{CH}_3$ (17g). Preparation of $\text{CH}_2\text{ClCFClCO}_2\text{CH}_3$ was abandoned in favor of $\text{CH}_2\text{BrCFBrCO}_2\text{CH}_3$.

3.4 Preparation of $\text{CH}_2\text{BrCBr}_2\text{CO}_2\text{CH}_3$. The dehydrohalogenation of $\text{CH}_2\text{BrCHBrCO}_2\text{CH}_3$ was best carried out by the method of Marvel¹⁴. Quinoline (126g, 1 mole) and $\text{CH}_2\text{BrCHBrCO}_2\text{CH}_3$ (246g, 1 mole) are mixed in a nitrogen atmosphere and the pressure reduced to 10mm. When quinoline hydrochloride precipitates heat is applied and $\text{CH}_2=\text{CBrCO}_2\text{CH}_3$ distilled. The ester is dissolved in CHCl_3 (300 ml) containing LiCl (0.5g) and hydroquinone, and Br_2 (160g, 1 mole) is added slowly while stirring. The bromination reaction is initiated by illuminating with a "sun lamp" but this is not essential. The CHCl_3 solution is treated with aqueous $\text{Na}_2\text{S}_2\text{O}_3$ to remove excess Br_2 , washed with H_2O , saturated NaCl , and dried over anhydrous MgSO_4 . Distillation gives $\text{CH}_2\text{BrCBr}_2\text{CO}_2\text{CH}_3$ (174g, 0.535 mole, 56% overall yield on 96% conversion) b. $93-95^\circ\text{C}$ at 5mm.

3.5 Fluorination of $\text{CH}_2\text{BrCBr}_2\text{CO}_2\text{CH}_3$ with HgF_2 . Mercuric

fluoride (91g, 0.37 mole) and $\text{CH}_2\text{BrCBr}_2\text{CO}_2\text{CH}_3$ (278g, 0.86 mole) are stirred at 5mm and heated slowly to 140°C and the crude product distilled with no attempt to fractionate. The distillate (205g) is diluted with ether (100ml), washed with dilute HCl, H_2O and saturated NaCl, and dried over anhydrous MgSO_4 . Distillation gives $\text{CH}_2\text{BrCBrFCO}_2\text{CH}_3$ (64g, 0.25 mole 44% yield on 66% conversion) b. $76-78^\circ\text{C}$ at 9mm, n_D^{27} 1.4885, d_4^{27} 1.99, MR 38.2, AR_F 1.44, and $\text{CH}_2\text{BrCBr}_2\text{CO}_2\text{CH}_3$ (186g, 0.57 mole).

3.6 Saponification of $\text{CH}_2\text{BrCBrFCO}_2\text{CH}_3$. Sodium bicarbonate (21.6g, 0.21 mole) in H_2O (600ml) and $\text{CH}_2\text{BrCBrFCO}_2\text{CH}_3$ (64g, 0.21 mole) are stirred at room temperature until one phase is present (10 days). The aqueous solution is acidified with dilute H_2SO_4 and continuously extracted with ether. Ether is removed, and H_2O is removed from the residue by azeotropic distillation with benzene. Distillation of the dark residue gives $\text{CH}_2\text{BrCBrFCO}_2\text{H}$ (45g, 0.18 mole, 90% yield) b. 105°C . at 5mm, sublimes under reduced pressure at ca. 70°C , m. $70.5-72.5^\circ\text{C}$, NE 247 (calcd. 249.8).

3.7 Dehalogenation of $\text{CH}_2\text{BrCBrFCO}_2\text{H}$. A solution of $\text{CH}_2\text{BrCBrFCO}_2\text{H}$ (10g, 0.04 mole) in ether (300ml) is stirred with powdered Zn (3g, 0.06 mole) and refluxed (8 hours). Appreciable precipitate is evident and the solution is filtered. Ether is removed under reduced pressure (H_2O aspirator) and carries some unsaturated product. The residue is placed in a sublimation apparatus and the product sublimed. Reduced

pressure facilitates removal of the product from the viscous residue. $\text{CH}_2=\text{CFCO}_2\text{H}$ (2g, 0.022 mole, 55% yield), resublimed three times, m. $51-52^\circ\text{C}$, found 20.65%F (calcd. 21.10%F) NE 91.5 (calcd. 90.05) is obtained as colorless crystals which on fusion with Na give a negative test for Br^- . The yield is lowered by each sublimation. The residue after sublimation is quite viscous and after standing (7 days) at room temperature the sublimed product is an amorphous powder which softens and darkens at $130-140^\circ\text{C}$.

3.8 Fluorination of $\text{CH}_2\text{BrCHBrCO}_2\text{CH}_3$ with HgF_2 . Mercuric fluoride (150g, 0.6 mole) and $\text{CH}_2\text{BrCHBrCO}_2\text{CH}_3$ (150g, 0.6 mole) are stirred at 150mm and the temperature raised slowly. Reaction starts vigorously at 130°C and reducing pressure to 120mm causes evolution of fumes and solidification of the mixture. Distillation is interrupted, additional $\text{CH}_2\text{BrCHBrCO}_2\text{CH}_3$ (100g, 0.4 moles) added and the crude product (156g) b. 100°C at 120 mm is distilled. The distillate is washed with dilute HCl, H_2O , saturated NaCl, and dried over anhydrous MgSO_4 . Distillation gives a monofluorinated product (92g, 0.5 mole, 55% yield on 88% conversion) b. $92-94^\circ\text{C}$ at 80mm, n_D^{30} 1.4389, d_4^{30} 1.624, MR 30.0, AR_F 1.01 which is assumed to be $\text{CH}_2\text{BrCHF}\text{CO}_2\text{CH}_3$ and $\text{CH}_2\text{BrCHBrCO}_2\text{CH}_3$ (30g, 0.12 mole).

3.9 Attempted Dehydrohalogenation of $\text{CH}_2\text{BrCHF}\text{CO}_2\text{CH}_3$ to form $\text{CH}_2=\text{CFCO}_2\text{CH}_3$. Treating $\text{CH}_2\text{BrCHF}\text{CO}_2\text{CH}_3$ with inorganic or organic bases (eg. NaHCO_3 , aqueous NaOH, $\text{CH}_3\text{CO}_2\text{K}$ in $\text{CH}_3\text{CO}_2\text{H}$,

quinoline, and triethyl amine) resulted in positive tests for F^- and Br^- in the mixture. On a larger scale, treating $CH_2BrCHFCO_2CH_3$ (0.13 mole) with quinoline (0.13 mole) at $80^\circ C$ under 50mm gives a product which redistilled b. $58-60^\circ C$ at 17mm and although positive for unsaturation to aqueous $KMnO_4$ and Br_2 in CCl_4 gave on fusion with sodium tests for F^- and Br^- . Reaction of $CH_2BrCHFCO_2CH_3$ (0.2 mole) and $(CH_3CH_2)_3N$ (0.1 mole) in an ice bath, the mixture washed (H_2O , saturated $NaCl$), dried over $MgSO_4$, filtered and distilled gives material b. $48^\circ C$ at 19mm, n_D^{25} 1.4725, 6g ($CH_2=CHBrCO_2CH_3$ ¹⁴ b. $72-79^\circ C$ at 78mm, n_D^{20} 1.4840) which is unsaturated to Br_2 in CCl_4 and on fusion with sodium gives a test positive for Br^- but negative for F^- . A great deal of polymer is present as the residue and the distillate also polymerizes on standing in the refrigerator to form a hard, strong, transparent plastic which does not distort vision.

4.0 Preparation of Perfluoroacrylic acid, $CF_2=CFCO_2H$.

4.1 Preparation of $CHCl_2CF_2CF_2Cl$. Acid catalyzed addition of $CHCl_3$ to $CF_2=CF_2$ ¹⁸ is carried out in a 3 liter steel cylinder fitted with a suitable gauge and needle valve in a T arrangement. Aluminum chloride and $CHCl_3$ are introduced in an atmosphere of air or nitrogen, then the cylinder is sealed and the contents frozen in a mixture of dry-ice and acetone. The system is evacuated and C_2F_4 is bled into the system using a soft copper coupling. The cylinder is placed in a jacketed shaking device with electronic temperature

control. A temperature of 50°C is generally satisfactory for the reaction after an initiation period of 6-8 hours. Only when a pressure drop is not realized after 12 hours was the temperature raised slowly to 75°C at which point the reaction occurred. The results are recorded in Table VI. No correlation of conditions and yield is possible; serious deviations in conditions resulted in an abnormally low yield. The product is worked up by washing with HCl and extracting with CHCl₃ or more satisfactorily by steam distillation.

Table VI

C ₂ F ₄		CHCl ₃		AlCl ₃	T _{max}	psig.		Yield on C ₂ F ₄		C ₂ F ₄
g	m	g	m	g	°C	max.	min.	g	m	Conv.
							25°C			%
190	1.9	1194	10	50	50	230	39	248	1.13	84
215	2.15	1194	10	50	45	230	30	299	1.43	96
250	2.5	1194	10	75	45	230	20	267	1.68	90
300	3	1074	9	75	50	270	80	280	1.28	58
200	2	472	4	50	50	200	fume off thru 600 psi gauge; no explosion; no liquid residue; carbon only			
110	1.1	597	6	50	50	---	--	254	1.16	98
130	1.3	597	6	50	50	---	--	combined		
210	2.1	1194	10	50	50	---	--	186	.85	95
210	2.1	1194	10	60	75	---	--	347	1.59	95
reaction heated 50° 8 hrs. then 75° 2 hrs. before pressure drops										
210	2.1	910	7.6	50	50	---	--	255	1.17	95
235	2.35	1004	8.4	50	50	---	--	271	1.24	91
last 6 runs combined mat. b. > 92°C = 196g; not investigated										

4.2 Dehydrohalogenation of CHCl₂CF₂CF₂Cl. Best results are obtained by addition of NaOC₂H₅ (136g, 2 moles) in C₂H₅OH (900ml) to CHCl₂CF₂CF₂Cl heated at 110°C and stirred; product is removed rapidly at 72-73°C as an azeotrope with C₂H₅OH and CHCl₂CF₂CF₂Cl through a column 3" long packed

with glass helices. The azeotrope and residue are washed with water and insoluble material dried over MgSO_4 . Separation of the olefin from $\text{CHCl}_2\text{CF}_2\text{CF}_2\text{Cl}$ is difficult. Using a 2' column packed with Podbielnak 0.2mm nichrome helices a good fraction is obtained b. 86.2°C at 745.2mm, n_D^{25} 1.3950, d_4^{25} 1.576, MR 30.2, AR_F 1.12, found 28.71%F (calcd. 28.59%F); material b. $86-89^\circ\text{C}$ (281g, 70% as $\text{CCl}_2=\text{CFCF}_2\text{Cl}$ on 100% conversion). Less efficient separations gave material with unsatisfactory AR_F and analysis, eg. material b. $85.5-85.6^\circ\text{C}$ has n_D^{25} 1.4010, d_4^{25} 1.585, MR 30.6, AR_F 1.23, found 24.66%F, 51.88%Cl. Attempts to increase $\text{CCl}_2=\text{CFCF}_2\text{Cl}$ yield by decreasing the rate of take-off resulted in the formation of substantial amounts of substitution products. $\text{CHCl}_2\text{CF}_2\text{CF}_2\text{Cl}$ (502g, 2.3 moles) with NaOC_2H_5 (136g, 2ml) in $\text{C}_2\text{H}_5\text{OH}$ (900ml) gave $\text{CCl}_2=\text{CFCF}_2\text{Cl}$ (260g, 1.3 moles, 62.5% on 91% conversion); material b. 154°C (68g) n_D^{28} 1.4209, d_4^{28} 1.425, calcd. as $\text{C}_2\text{H}_5\text{OCCl}=\text{CFCF}_2\text{Cl}$ or $\text{CCl}_2=\text{CFCF}_2\text{OC}_2\text{H}_5$, MR 37.28, AR_F 1.46; and material b. 55°C at 20mm (41g) which was not investigated. Dehydrohalogenation with alcoholic KOH gave 56% $\text{CCl}_2=\text{CFCF}_2\text{Cl}$ on 55% conversion; manipulation of rates during addition and distillation was difficult. An insignificant amount of olefin was obtained by distillation with alcohol from the H_2O wash solution.

4.3 Dehydrohalogenation of $\text{CHCl}_2\text{CFClCF}_2\text{Cl}$. $\text{CHCl}_2\text{CFClCF}_2\text{Cl}^{18}$, b. $125-130^\circ\text{C}$, n_D^{29} 1.4141 (36g, 0.15 mole, 8.5%) obtained by addition of CHCl_3 (1194g, 10 moles) to $\text{CF}_2=\text{CFCl}$ (232g,

2 moles) with AlCl_3 (30g) is treated with NaOC_2H_5 (10.4g, 0.15 mole) in $\text{C}_2\text{H}_5\text{OH}$ (65ml). The azeotrope b. $69-72^\circ\text{C}$ is washed and dried; distillation gives $\text{CCl}_2=\text{CFCF}_2\text{Cl}$ b. $84.5-85.5^\circ\text{C}$ (12g, 0.06 mole, 55% yield on 73% conversion) n_D^{22} 1.4046, d_4^{22} 1.590, MR 30.75, AR_F 1.29, found 23.64%F, 52.75%Cl.

4.4 Oxidative-Chlorination of $\text{CCl}_2=\text{CFCF}_2\text{Cl}$; Esterification of $\text{CF}_2\text{ClCFClCOCl}$. A mixture of O_2 and Cl_2 in a 5:1 ratio is passed as steady bubbles into $\text{CF}_2\text{ClCF}=\text{CCl}_2$ (223g, 1.12 moles, containing some $\text{CF}_2\text{ClCF}_2\text{CCl}_2\text{H}$) maintained at $35-40^\circ\text{C}$ by a water bath and illuminated by an ultra violet flood lamp for 24 hours. The reaction is protected by a finger type condenser with external jacket, an ice-water trap, and an EtOH bubbler. Material in the ice-water trap is periodically returned to the reaction. EtOH (46g, 1 mole) is added slowly to material from the reaction (179g); reaction is exothermic. The mixture is refluxed (4 hours) and washed with H_2O ; insoluble material is dried with MgSO_4 and filtered. Similarly insoluble material (21g) is recovered from the EtOH bubbler. Distillation gives a mixture b. $85-92^\circ\text{C}$ of $\text{CHCl}_2\text{CF}_2\text{CF}_2\text{Cl}$ and $\text{CCl}_2=\text{CFCF}_2\text{Cl}$ (45g) and $\text{CF}_2\text{ClCFClCO}_2\text{Et}$ (88g, 0.39 mole, 50% overall yield on 69% conversion) b. $138-140^\circ\text{C}$, material b. 139.5°C has n_D^{29} 1.3795; literature¹⁷ reports b. 142°C , n_D^{23} 1.3830, d_4^{23} 1.405. Distillation of the alcohol solution affords the product as an azeotrope b. ca. 80°C accompanied by entrained HCl. The intermediate

acid chloride does not react readily with H_2O . Additional products are not encountered; any water soluble material is lost in washing. Similar results are obtained in other runs.

4.5 Attempted Dehalogenation of $CF_2ClCFC1CO_2C_2H_5$. Treating $CF_2ClCFC1CO_2C_2H_5$ with NaI in acetone inconsistently liberates small amounts of I_2 .

No reaction occurs with Zn in $(C_2H_5)_2O$.

With Zn in 1,4-dioxane reaction is evident but with excessive foaming. No method is found for working up the product. Washing with H_2O leaves only saturated ester.

With Zn in C_2H_5OH reaction is evident at $80^\circ C$; no product azeotropes with C_2H_5OH ; distillation of water insoluble material from the residue does not give a clean fraction; all fractions are acidic and contain solid which predominates on standing and gives a negative Cl^- test on fusion.

With Zn in $n-C_4H_9OH$ reaction is evident at $110^\circ C$; unsaturated material (20g) b. $55-130^\circ C$ distills from the reaction as an azeotrope. The residue is washed to remove $ZnCl_2$; distillation gives some unsaturated material as an azeotrope and high boiling saturated products.

Reaction with Zn in CH_2OHCH_2OH is vigorous at $110^\circ C$; Zn becomes coagulated in very hard pellets as the reaction proceeds. Some unsaturated but poorly defined material is obtained by distillation under reduced pressure; a variety of methods prove unsuccessful in working up the product. There is indication that $CF_2=CFCO_2C_2H_5$ b. ca. $72-78^\circ C$; however, no

material is obtained free of Cl^- . Also there is evidence that $\text{CF}_2=\text{CFCO}_2\text{C}_2\text{H}_5$ is soluble in H_2O producing an acid solution. In one experiment ca. 2g of material is distilled through a condenser at 30mm with pot temperature 120°C and collected in a dry ice trap. This material is strongly lachrymatory, is unsaturated to Br_2 in CCl_4 and dissolves slowly but noticeably in H_2O .

In all preceding dehalogenations, material which tests positive for unsaturation becomes solid on standing and liberates acidic fumes; frequently during fractional distillation polymerization occurs in the still head even when prevented in the pot and column.

4.6 Saponification of $\text{CF}_2\text{ClCFClCO}_2\text{C}_2\text{H}_5$. Saponification of $\text{CF}_2\text{ClCFClCO}_2\text{C}_2\text{H}_5$ (30g, 0.13 mole) does not occur on stirring with NaHCO_3 (11g, 0.13 mole) in H_2O (100ml) for 4 days at room temperature; addition of NaOH (5.2g, 0.13 mole) in H_2O (25ml) and continued stirring for 2 days is required. The solution is acidified with H_2SO_4 (50ml), and continuously extracted with ether. Distillation after removing H_2O with ether and benzene gives $\text{CF}_2\text{ClCFClCO}_2\text{H}$ (16g, 0.08 mole, 80% yield on 77% conversion) b. $83-85^\circ\text{C}$ at 30mm, n_D^{25} 1.3868, d_4^{25} 1.591, MR 29.08, AR_F 1.68, NE 197.5 (calcd. 197).

4.7 Dehalogenation of $\text{CF}_2\text{ClCFClCO}_2\text{H}$. Refluxing $\text{CF}_2\text{ClCFClCO}_2\text{H}$ (5g) with Zn (1.5g) in ether (300ml) for 8 hours results in reaction as indicated by ZnCl_2 formed and tests for unsaturation in the ether solution. Separation of $\text{CF}_2=\text{CFCO}_2\text{H}$

from $\text{CF}_2\text{ClCFClCO}_2\text{H}$ by distillation is unsuccessful although some crystals separate on standing.

4.8 Attempted preparation of $\text{CHBr}_2\text{CF}_2\text{CF}_2\text{Br}$. C_2F_4 (110g, 1.1 moles) does not react with CHBr_3 (1265g, 5 moles) in the presence of AlBr_3 (52g) at 60°C with pressure 160 psig. during 48 hours. At 150°C pressure drops slowly from 180 psig. to 40 psig. at 30°C during 48 hours. Considerable carbon is in the residue from the steam distillation; after drying and distillation of CHBr_3 (1199g) only 13g remains as high boiling residue. The reaction is considered impractical.

4.9 Oxidative-Bromination of $\text{CF}_2\text{ClCF}=\text{CCl}_2$. Oxygen is bubbled through $\text{CF}_2\text{ClCF}=\text{CCl}_2$ (100g, 0.5 mole containing $\text{CF}_2\text{ClCF}_2\text{CF}_2\text{Cl}$) while stirring and adding Br_2 (40g, 0.25 mole) very slowly. The reaction is protected by a condenser followed by an ice and a dry-ice trap; material collecting in the traps is recycled over a period of 96 hours at which point unreacted Br_2 returned to reaction is not decolorized. The mixture does not react with H_2O ; added slowly to NaOH (20g, 0.5 mole) in 100 ml H_2O while refluxing, reaction is vigorous. Insoluble material remains which, separated, washed, dried over MgSO_4 and distilled, is $\text{CF}_2\text{ClCF}_2\text{CHCl}_2$ and/or $\text{CF}_2\text{ClCF}=\text{CCl}_2$ (29g, 0.14 mole). The basic solution is acidified with H_2SO_4 (50ml) and continuously extracted with ether for 12 hours. Water is removed by distillation with ether and benzene; distillation under reduced pressure gives $\text{CF}_2\text{ClCFClCO}_2\text{H}$ (23g, 0.117 mole) b. 65°C at 8mm, NE 196 (cal-

culated 197) and $\text{CF}_2\text{ClCFBrCO}_2\text{H}$ (23g, 0.095 mole) b. 75°C at 7mm or $85-86^\circ\text{C}$ at 15mm, m. 23.9°C (cooling curve), n_D^{25} 1.4156, d_4^{25} 1.948, MR 31.09, AR_F 1.39, NE 240.5 (calcd. 241.5), found 24.45%F (calcd. 23.65%F). Combined amount of Cl and Br weighed as AgCl and AgBr is 98.5% of the theoretical amount. Correcting for entrainment of Cl and/or Br in F analysis gives 23.25%F found. Separation is clean using a 2' column with "Podbielnak" nichrome packing; however, decomposition of $\text{CF}_2\text{ClCFBrCO}_2\text{H}$ occurs.

5.0 Dehalogenation of $\text{CF}_2\text{ClCFBrCO}_2\text{H}$; Preparation of $\text{CF}_2=\text{FCO}_2\text{H}$.

$\text{CF}_2\text{ClCFBrCO}_2\text{H}$ (5g, 0.02 moles) is heated at 40°C with Zn (2g) in dry ether (300ml) for 3 hours while stirring; reflux is rapid for a short period and reaction is evident. The cool mixture is filtered and ether is removed under reduced pressure through a water cooled condenser. Very little residue is obtained from the ether distillate on redistillation at 1 atmosphere. The residue is placed in a 5ml flask and $\text{CF}_2=\text{FCO}_2\text{H}$ (ca. 1.0g) sublimed under reduced pressure through an inverted U tube into an ice- H_2O cooled receiver as a colorless crystalline solid m. $35.5-36.5^\circ\text{C}$ (sealed tube), NE 126.7, found 45.16%F (calcd. 45.25%F), qualitative analysis for fluorine after Na fusion is negative. The residue is very viscous and polymerizes to a solid on standing.

$\text{CF}_2=\text{FCO}_2\text{H}$ is extremely hygroscopic and great care must be observed to obtain a high m.p.; all weighings are made by difference in a ground weighing bottle; neutral equivalents

must be made immediately after solution since the F hydrolyzes. $\text{CF}_2=\text{CFCO}_2\text{H}$ polymerizes at room temperature (3 days) coating the vessel with a viscous film and liberating acidic fumes. Identical experiments in which heating at 40°C was continued for 2 hours and 45 minutes gives respectively 0.7g and 0.3g and in the latter case is complicated by contamination with $\text{CF}_2\text{ClCFBrCO}_2\text{H}$. $\text{CF}_2\text{ClCFBrCO}_2\text{H}$ (3g) and Zn (1g) in ether (300ml) heated 1 hour at 40°C gives 0.4g $\text{CF}_2=\text{CFCO}_2\text{H}$.

6.0 Preparation of $\text{CF}_2\text{HCF}_2\text{CO}_2\text{H}$. $\text{CF}_2\text{HCF}_2\text{CH}_2\text{OH}$ (660g, 5 moles) (E.I. DuPont de Nemours Co.) is added as drops to $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ (1020g, 3.33 moles + 0.1 mole excess) and H_2SO_4 (1290g, 13.3 moles + 0.4 mole excess) in 1050ml H_2O with temperature maintained below 55°C with an ice bath. When the reaction is no longer spontaneous, heat is applied to incipient reflux and continued for 120 hours. Continuous extraction of the cold solution for 48 hours and distillation gives acidic material b. $126-131^\circ\text{C}$ (58g) and $\text{CF}_2\text{HCF}_2\text{CO}_2\text{H} \cdot \frac{1}{2}\text{H}_2\text{O}$ (543g, 3.32 moles, 67% yield b. $131.5-132.5^\circ\text{C}$, NE 152 (caled. 155). Another reaction gives material (59%) b. $136-137^\circ\text{C}$, n_D^{25} 1.3250, NE 160, 158 (caled. as $\text{CF}_2\text{HCF}_2\text{CO}_2\text{H} \cdot \text{H}_2\text{O}$ 164).

6.1 Dehydration of $\text{CF}_2\text{HCF}_2\text{CO}_2\text{H} \cdot \frac{1}{2}\text{H}_2\text{O}$. Adding $\text{CF}_2\text{HCF}_2\text{CO}_2\text{H} \cdot \frac{1}{2}\text{H}_2\text{O}$ (437g, 2.81 moles) to P_2O_5 (166g, 1.17 moles) while stirring forms a slurry then a viscous mass. Distillation gives $(\text{CF}_2\text{HCF}_2\text{CO})_2\text{O}$ (375g, 1.37 moles, 98% yield) b. $122.5-123.5^\circ\text{C}$ at 744.1mm, NE 276, 275, 272.4 (caled. 274). Reflux-

ing the mixture for 12 hours fails to give lower boiling material. Using sufficient P_2O_5 to obtain $CF_2HCF_2CO_2H$ does not give clean results and some material b. $117-118^\circ C$ is obtained.

6.2 Esterification of $CF_2HCF_2CO_2H \cdot \frac{1}{2}H_2O$. $CF_2HCF_2CO_2H \cdot \frac{1}{2}H_2O$ (36g, 0.23 moles) and 95.5% H_2SO_4 (52g, 0.50 mole) are mixed (slightly exothermic) and added to CH_3OH (16g, 0.5 mole) while stirring (strongly exothermic); two layers separate. Distillation of the upper layer over P_2O_5 gives $CF_2HCF_2CO_2CH_3$ (28g, 0.175 moles, 76%) b. $93-94^\circ C$ at 753.8mm, n_D^{29} 1.3152, found 46.55%F (calcd. for 47.5%F); no ester is recovered by attempted distillation of the H_2SO_4 layer.

6.3 Amidification of $CF_2HCF_2CO_2CH_3$. Dry NH_3 is slowly bubbled into $CF_2HCF_2CO_2CH_3$ (2.5g, 0.0156 mole) in 25 ml dry ether for 2 hours at 0° . Ether is removed under reduced pressure and $CF_2HCF_2CONH_2$ is recrystallized from $CHCl_3$ as colorless flaky crystals (2g, 0.0138 mole, 88%) m. $58.4-59.4^\circ C$ which sublimates at room temperature.

6.4 Attempted Dehydrohalogenation of $CF_2HCF_2CO_2CH_3$. A mixture of $CF_2HCF_2CO_2CH_3$ (16g, 0.1 mole), CH_3ONa (5.4g, 0.1 mole) and CH_3OH (16g, 0.5 mole) is sealed in a cylinder and heated at $150^\circ C$ for 8 hours. No trace of F^- is detected in the solution. Identical results are obtained on refluxing at 1 atmosphere.

6.5 Attempted Bromination of $CF_2HCF_2CO_2H \cdot \frac{1}{2}H_2O$. Reaction of $CF_2HCF_2CO_2H$ with Br_2 in the presence of $((CH_3)_3CO)_2$ or of

$(\text{CF}_2\text{HCF}_2\text{CO})_2\text{O}$ with N-bromsuccinimide appears to give $\text{CF}_2\text{HCF}_2\text{COBr}$ or decomposition products thereof (i.e. $\text{CF}_2\text{HCF}_2\text{H}$). There is no indication of the formation of $\text{CF}_2\text{BrCF}_2\text{CO}_2\text{H}$.

7.0 Preparation of $\text{CF}_2=\text{CHCO}_2\text{H} \cdot 2\text{H}_2\text{O}$.

7.1 Dehydrohalogenation of $\text{CF}_3\text{CH}_2\text{CO}_2\text{H}$. $\text{CF}_3\text{CH}_2\text{CO}_2\text{H}$ (11g, 0.086 mole) in 150 ml H_2O is stirred and NaOH (6.9g, 17 moles) in 200 ml H_2O is added intermittently at room temperature over a period of 10 days keeping the solution slightly basic. The neutral solution is made acid with cold 10% H_2SO_4 and continuously extracted with ether. Ether is removed under reduced pressure and well defined crystals separate. Recrystallization from ether or filtration gives an amorphous solid. Analysis of the original crystals after removing excess ether in a stream of dry air gives 25.08%F (calcd. for $\text{CF}_2=\text{CHCO}_2\text{H} \cdot 2\text{H}_2\text{O}$ 26.4%F); drying under reduced pressure causes a loss of 83.6% of the original weight in 5 hours and leaves an amorphous residue containing 10.52%F. Titration of the air dried crystals gives NE 115, 118, 129, 132, 112, 147, ave. = 125 (calcd. for $\text{CF}_2=\text{CHCO}_2\text{H} \cdot \text{H}_2\text{O}$ 126). The crystals give a positive test for unsaturation with aqueous KMnO_4 and appear to react with Br_2 in CCl_4 . Distillation at 5mm gives saturated material with NE 127, 129 (calcd. for $\text{CF}_3\text{CH}_2\text{CO}_2\text{H}$ 126) and ca. 0.5g of unsaturated material with NE 146 (calcd. for $\text{CF}_2=\text{CHCO}_2\text{H} \cdot \text{H}_2\text{O}$ 144); analysis gives 27.05%F. Material unsaturated to aqueous KMnO_4 failed to react appreciably with Br_2 in CCl_4 when illuminated.

7.2 Dehalogenation of $\text{CF}_2\text{BrCHBrCO}_2\text{H}$. $\text{CF}_2\text{BrCHBrCONHBr}$ ¹³ (ml 51-153°C) (1.5g) is hydrolyzed with 50% H_2SO_4 at 60-70°C for 10 minutes after which solution is complete. The cool solution is continuously extracted with ether and ether is removed leaving an acidic, water soluble yellow oil (1g), which distilled, b. 60°C at 5 mm (estimated), m 15-20°C, qualitative analysis after fusion with Na is positive for F^- and Br^- . $\text{CF}_2\text{BrCHBrCO}_2\text{H}$ (0.9g) is refluxed with Zn in 100ml ether for 30 minutes while stirring; the solution is positive for Br^- but not F^- . After filtration ether is removed under reduced pressure and the residue is positive for unsaturation. Distillation of the residue at 1mm results in darkening when the entrained ether is gone and the residue becomes viscous in a water bath at 30°C; a small amount of $\text{CF}_2\text{BrCHBrCO}_2\text{H}$ is distilled by heating with an open flame. A water extract of the decomposed residue gives a positive test for unsaturation with KMnO_4 .

7.3 Attempted Preparation of $\text{CF}_2\text{ClCHClCH}_2\text{OH}$. $\text{CF}_2\text{ClCHClCH}_2\text{Br}$ fails to react with acetic AgNO_3 .

$\text{CF}_2\text{ClCHClCH}_2\text{Br}$ (23g, 0.1 mole) refluxed with $\text{CH}_3\text{CO}_2\text{K}$ (20g, 0.2 mole) in 50ml AcOH for 2 days gives H_2O insoluble material which proves to be recovered $\text{CF}_2\text{ClCHClCH}_2\text{Br}$ (12g, 52%) and an olefin (7g), positive test for unsaturation with aqueous KMnO_4 and Br_2 in CCl_4 on illumination, positive test for Br^- and F^- on fusion with Na, b. 76.5-77.5°C, n_D^{27} 1.4100, d_4^{27} 1.655, MR as $\text{CF}_2=\text{CClCH}_2\text{Br}$ 28.59, AR_F 1.28.

$\text{CF}_2\text{ClCHClCH}_2\text{Br}$ (114g, 0.5 mole) refluxed with $\text{CH}_3\text{-CO}_2\text{K}$ (75g, 0.75 mole) in CH_3OH (120ml) gives recovered $\text{CF}_2\text{Cl-CHClCH}_2\text{Br}$ (15g, 0.066 mole) and what is probably $\text{CF}_2=\text{CClCH}_2\text{Br}$ (42g, 2.4 moles) (48%) b. $76-77^\circ\text{C}$, n_D^{27} 1.4100; however, the loss of material is high from solution in H_2O with CH_3OH .

B. PHYSICAL MEASUREMENTS.

1.0 Conductance Measurements; Apparatus. The Wheatstone bridge used is previously described⁵ with the exception of use of an oscilloscope as a null-point indicator; a Leeds and Northrup four dial resistance box with a capacity of 9,999 ohms is used. The resistance of triple distilled water consistently exceeds the capacity of the standard resistance box in use, so no correction is made.

A constant temperature of $25.01^{\circ} \pm .05^{\circ}$ is maintained in the bath with a thyatron on-off circuit in conjunction with a mercury expansion thermoregulator controlling a knife blade heater and a fan.

The cell constant is evaluated from the resistance of a standard 0.1000 molal solution of KCl⁵.

The accuracy of the apparatus is checked by measuring the resistance of solutions of $\text{CH}_2\text{ClCO}_2\text{H}$; the results are in excellent agreement with those reported in the literature³⁰, and are included in Table VII.

A key to the tables in this section is as follows:
C is concentration in g. equivalents/liter; R is the resistance measured in ohms, Λ is the equivalent conductance in mhos, Λ_0 is the limiting conductance, Λ' is the equivalent conductance corrected for interionic forces, K is the ionization constant from pH measurements, K_{Cl} is the classical ionization constant and K_{Th} is the thermodynamic ionization constant.

Table VII

This research (cell constant = .4061)				Reference 30 $K_{Th} \times 10^{-3} = 1.396$		
CHCl ₃ CO ₂ H						
C	R	$K_{Cl} \times 10^3$		C	$K_{Cl} \times 10^3$	
0.02220	203.4	89.80	1.54	0.03019	78.95	1.56
0.01110	304.4	120.2	1.53	0.02444	86.51	1.47
0.005550	471.1	155.6	1.47	0.009464	127.9	1.52
0.002220	858.1	213.1	1.47	0.005222	159.6	1.49
Mean=1.50				1.51		
Meandeviation=0.032				0.030		
Ave. $K \times 10^3 = 1.50 \pm 0.016$				1.51 ± 0.015		
$\Lambda_o(\text{acid}) = 389.5$ from				$\Lambda_o(\text{salt}) = 89.80$ by extrapolation ³⁰		

2.0 Potentiometric Titrations; Apparatus. A Beckman (Model H-2) direct reading pH meter is used to measure the pH of water solutions of weighed amounts of the acids at appropriate intervals during titration with standard base. The instrument is adjusted by calibration with standard buffer solutions²⁹ of pH 4 and/or 10 before individual titrations. The equivalent points are determined graphically by plotting pH vs. ml. of standard base added.

The solutions are immersed in a temperature bath regulated manually to $25 \pm 1^\circ$ and stirred automatically during titration.

The results are tabulated in the following sections.

3.0 Ionization Constants of CF₃(CH₂)₃CO₂H. Solutions of CF₃(CH₂)₃CO₂H in 60 ml H₂O are titrated with 0.05088 N NaOH. The average equivalence point falls at pH 8.1. CF₃(CH₂)₂CO₂H and CH₃(CH₂)₃CO₂H are similarly titrated with 0.04985 N NaOH to enable comparisons of K obtained under identical circumstances.

Table VIII

grams/ml	ml NaOH	pH	pK	$K \times 10^5$	NE (156)
.1158/60	5.00	4.20	4.50	3.2	
"	7.00	4.46	4.50	3.2	
"	7.32	4.49	4.49	3.1	
"	8.00	4.58	4.50	3.2	
"	10.00	4.80	4.47	3.0	
"	14.70				155.3
.1617/60	7.00	4.21	4.49	3.1	
"	10.00	4.49	4.50	3.2	
"	10.25	4.50	4.50	3.2	
"	11.00	4.56	4.50	3.2	
"	14.	4.82	4.49	3.1	
"	20.50				155.1

Mean=3.2

Mean deviation = 0.1

Ave. $K = 3.2 \pm 0.03$

grams/ml	ml NaOH	pH	pK	$K \times 10^5$	NE (142)
.1012/60	6.00	4.02	4.15	7.1	
"	7.00	4.16	4.16	7.0	
"	8.00	4.27	4.15	7.1	
"	9.00	4.38	4.13	7.4	
"	10.00	4.50	4.10	7.7	
"	14.00				144.0
.1159/60	7.00	4.06	4.18	6.6	
"	8.00	4.17	4.18	6.6	
"	8.09	4.18	4.18	6.6	
"	9.00	4.27	4.17	6.8	
"	10.00	4.39	4.18	6.6	
"	16.18				143.1

Mean=7.0

Mean deviation=0.3

Ave. $K = 7.0 \pm .1$

Table VIII contd.

ml	pH	pK	K x 10 ⁵
9	4.60	4.80	1.6
10	4.69	4.81	1.6
11	4.77	4.82	1.5
12	4.82	4.80	1.6
13	4.91	4.81	1.6
23.40	8.20		
8	4.66	4.82	1.5
9	4.74	4.81	1.6
10	4.83	4.81	1.6
11	4.92	4.81	1.6
12	5.02	4.82	1.5
19.48	8.00		

Mean=1.6

Mean deviation = .03

Ave. K = $1.6 \pm .01 \times 10^{-5}$

4.0 Ionization Constants of $\text{CF}_3\text{CH}=\text{CH}-\text{CO}_2\text{H}$. Solutions of $\text{CF}_3\text{CH}=\text{CHCO}_2\text{H}$ in 60 ml H_2O are titrated with 0.04985 N NaOH. Equivalence points are determined graphically and the ionization constants are calculated at appropriate intervals accounting for the H^+ concentration.

Table IX

grams	ml NaOH	pH	pK	K x 10 ⁴	NE (140)
0.1231	7.00	3.26	3.38	4.2	140.1
"	8.00	3.30	3.38	4.2	
"	9.00	3.38	3.36	4.4	
"	10.00	3.47	3.35	4.5	
"	11.00	3.58	3.36	4.4	
"	17.60				140.1
0.1522	8.00	3.13	3.36	4.46	
"	9.00	3.21	3.36	4.4	
"	10.00	3.26	3.33	4.7	
"	11.00	3.33	3.32	4.8	
"	12.00	3.40	3.31	4.9	
"	21.80				139.9

Mean = 4.9

Mean deviation=0.2

Ave. K = $4.5 \pm 0.06 \times 10^{-4}$

5.0 Ionization Constant of $\text{CH}_2=\text{CFCO}_2\text{H}$. Measurements are made on samples of $\text{CH}_2=\text{CFCO}_2\text{H}$ which are negative for Br^- after fusion with Na. A solution of $\text{CH}_2=\text{CFCO}_2\text{Na}$ is prepared by titration to a predetermined end-point ($\text{pH} = 7.25$) with 0.1006 N NaOH using a Beckman pH meter. Values of K obtained from the pH during titration and conductance measurements made on solutions of $\text{CH}_2=\text{CFCO}_2\text{Na}$ and $\text{CH}_2=\text{CFCO}_2\text{H}$ are recorded in Table X and values for K_{Cl} and K_{Th} are calculated.

Table X					
grams/ml	ml NaOH	$\text{CH}_2=\text{CFCO}_2\text{H}$		$K \times 10^3$	NE (90.05)
		pH	pK		
.9694/25	16	2.42	2.60	2.5	
"	18	2.49	2.59	2.6	
"	20	2.55	2.56	2.7	
"	22	2.61	2.59	2.6	
"	24	2.69	2.54	2.9	
"	41.41	7.25			91.2
Mean = 2.7					
Mean deviation = 0.1					
Ave. $K = 2.7 \pm 0.03 \times 10^{-3}$					

$\text{CH}_2=\text{CFCO}_2\text{Na}$
(cell constant = .4061)

C	$C^{\frac{1}{2}}$	R	Λ
.02985	.1728	174.6	77.93
.01492	.1222	336.7	80.83
.00597	.07727	815.3	83.40
.002985	.05462	1580	86.10
.001492	.03863	3129	86.97

$$\Lambda_o(\text{salt}) = 87.25$$

$$\Lambda_o(\text{acid}) = 87.25 + 349.82 - 50.11 = 387.0$$

Table X contd.

$\text{CH}_2=\text{CFCO}_2\text{H}$
(*cell constant = .4061; others = .4040)

C	R	Λ	Λ'	$K_{Cl} \times 10^3$	$K_{Th} \times 10^3$
.04220	101.2*	95.10	379.9	3.38	2.77
.02110	153.0*	128.8	382.6	3.30	2.79
.01040	241.4*	161.9	382.6	3.13	2.76
.008440	274.0*	175.6	382.9	3.18	2.77
.005200	382.4	203.1	383.6	3.01	2.74
.004220	438.7*	219.3	383.9	3.13	2.86
.002110	721.0*	266.9	384.7	3.24	3.03
.002080	747.3	259.9	385.4	2.85	2.68
.00104	1308	297.1	386.7	2.65	2.52
.000844	1528	315.7	385.6	3.05	2.93
Mean =				3.06	2.79
Mean deviation =				0.19	0.095
Ave. $K=3.06 \pm 0.06$					$2.79 \pm 0.03 \times 10^{-3}$

6.0 Ionization Constants of $\text{CF}_2=\text{CFCO}_2\text{H}$. Measurements are made on samples of $\text{CF}_2=\text{CFCO}_2\text{H}$ which give a negative test for Br^- after fusion with Na. Attempts to obtain values of K by titration led to low neutral equivalents or what amounted to higher than theoretical concentrations of acid. Results of titrations over a period of time are as follows:

Table XI

Time hours	Concentration of acid m/l	NE
0	.0331 (calcd.)	126
1	.0444	94
2	----	66
16	.111	38
30	.123	34

The solution gives a strong positive test for F^- . The resistance of solutions of $\text{CF}_2=\text{CFCO}_2\text{H}$ measured over a period of 1-4 hours give values of Λ which plotted vs. $C^{\frac{1}{2}}$ forms a smooth curve typical of a weak electrolyte but displaced to

higher values of Λ . Calculation of K from these measurements indicate an order of magnitude of $1-3 \times 10^{-2}$.

To avoid solvolysis of F as a factor, solutions of $\text{CF}_2=\text{CFCO}_2\text{Na}$, prepared by rapid titration to a predetermined end point with a pH meter, and of $\text{CF}_2=\text{CFCO}_2\text{H}$ are made up and the resistances measured rapidly so the entire procedure did not exceed a total of 30 minutes. This rapid measurement undoubtedly introduced a small error of temperature coefficient which cannot be avoided. The results are recorded in Table XII.

Table XII

$\text{CF}_2=\text{CFCO}_2\text{Na}$
(cell constant = .4061)

C	$C^{\frac{1}{2}}$	R	Λ
.008740	.09348	571	81.37
.0004370	.06610	1100	84.47
.0001748	.04180	2700	86.03

$$\Lambda_0(\text{salt}) = 90.5$$

$$\Lambda_0(\text{acid}) = 90.5 + 349.8 - 50.1 = 390.2$$

$\text{CF}_2=\text{CFCO}_2\text{H}$
(cell constant = .4061)

C	R	Λ	Λ'	$K_{Cl} \times 10^2$	$K_{Th} \times 10^2$
.01535	110.0	240.5	375.5	1.152	1.39
.007675	184.0	287.5	378.9	1.58	1.53
.003070	394.0	335.8	382.6	1.63	1.71
.001535	739.0	359.0	384.7	1.56	1.83
				Mean=1.57	1.61
				Mean deviation=0.03	0.15
				Ave. $K \times 10^2 = 1.57 \pm 0.01, 1.61 \pm 0.07$	

7.0 Ionization Constant of $\text{CF}_2=\text{CHCO}_2\text{H}$. Titration of a distillate material isolated from dehydrohalogenation of

$\text{CF}_3\text{CH}_2\text{CO}_2\text{H}$ gives evidence that the dihydrate of $\text{CF}_2=\text{CHCO}_2\text{H}$ is present. Values of K are computed from the pH measured during titration with .05088 N NaOH.

Table XIII

grams/ml	ml NaOH	pH	pK	K x 10 ⁴	NE (144)
.1355/60	6	2.89	3.21	6.2	
"	7	2.96	3.17	6.8	
"	8	3.03	3.15	7.1	
"	9	3.12	3.14	7.2	
"	10	3.20	3.17	6.8	
"	11	3.30	3.14	7.2	
"	18.52	7.40			146

Mean=6.8

Mean deviation=0.3

Ave. K = $6.8 \pm 0.1 \times 10^{-4}$

8.0 Ionization Constants of Miscellaneous Halogenated

Aliphatic Acids. Values of K obtained from pH measurements during titration with .05088 N NaOH are recorded for some acids obtained as intermediates in this research.

Table XIV

grams/ml	ml NaOH	pH	pK	K x 10 ³	NE (249.8)
.2287/80	8	2.37	2.47	3.4	
"	9	2.42	2.42	3.8	
"	10	2.48	2.40	4.0	
"	18.2	6.9			247

Mean=3.7

Mean deviation=0.2

Ave. K = $3.7 \pm 0.1 \times 10^{-3}$

Table XIV contd.

CF ₂ ClCBrFCO ₂ H					
grams/ml	ml NaOH	pH	pK	K x 10 ³	NE (241.5)
.1226/60	4.00	2.30	2.49	3.2	
"	5.00	2.38	2.40	4.0	
"	6.00	2.47	2.32	4.8	
"	10.35	6.9			240.5
				Mean=4.0	
				Mean deviation=0.5	
				Ave. K = 4.0 ± 0.3 x 10 ⁻³	

CF ₂ ClCFClCO ₂ H					
grams/ml	ml NaOH	pH	pK	K x 10 ³	NE (197)
.0804/60	3.00	2.39	2.50	3.2	
"	4.00	2.49	2.49	3.2	
"	5.00	2.63	2.40	4.0	
"	8.00	7.00			197.5
				Mean=3.4	
				Mean deviation=0.3	
				Ave. K = 3.4 ± 0.2 x 10 ⁻³	

9.0 Ionization Constants of o, m, and p-Fluorophenol and o, m, and p-Fluorobenzoic Acids. Samples of o, m, and p-fluorophenols and o, m, and p-fluorobenzoic acids are supplied by Dr. G.C. Finger of Illinois State Geological Survey Division. Solutions of these compounds in H₂O are titrated with .05088 N NaOH and values of K are calculated from pH measured at intervals to obtain results compatible with those heretofore described. The benzoic acids dissolve in warm water and remain in solution at 25°C.

Table XV

o-FC₆H₄OH

grams/ml	ml NaOH	pH	pK	K x 10 ⁹	NE (112)
.1040/60	7.00	8.37	8.57	2.7	
"	9.10	8.57	8.57	2.7	
"	11.00	8.75	8.57	2.7	
"	18.21	10.2			112.3
.1395/60	10.00	8.41	8.58	2.6	
"	12.42	8.59	8.59	2.6	
"	15.00	8.79	8.61	2.5	
"	24.85	10.25			110.5

Mean 2.6

Mean deviation 0.06

Ave. K = 2.6 ± .02 x 10⁻⁹m-FC₆H₄OH

grams/ml	ml NaOH	pH	pK	K x 10 ¹⁰	NE (112)
.1215/60	9.00	9.93	9.07	8.5	
"	10.75	9.06	9.06	8.7	
"	13.00	9.26	9.08	8.3	
"	21.50	10.45			111.1
.1506/60	11.00	8.90	9.04	9.1	
"	13.13	9.05	9.05	8.9	
"	15.00	9.17	9.05	8.9	
"	26.25	10.40			112.9

Mean 8.7

Mean deviation 0.2

Ave. K = 8.7 ± 0.08 x 10⁻¹⁰p-FC₆H₄OH
(sublimed m. 47-48°C)

grams/ml	ml NaOH	pH	pK	K x 10 ¹⁰	NE (112)
.1118/60	8.00	9.58	9.75	1.8	
"	9.87	9.72	9.72	1.9	
"	12.00	9.90	9.71	1.9	
"	19.75	10.78			111.1
.0973/60	6.00	9.50	9.77	1.7	
"	8.58	9.73	9.73	1.9	
"	11.00	9.98	9.73	1.9	
"	17.17	10.78			111.7

Mean 1.9

Mean deviation 0.1

Ave. K = 1.8 ± 0.04 x 10⁻¹⁰

Table XV contd.

grams/ml	ml NaOH	pH	pK	K x 10 ¹⁰	NE (94)
.1372/60	11.00	9.48	9.71	2.0	
"	14.80	9.69	9.69	2.0	
"	17.00	9.80	9.67	2.1	
"	29.60	10.67			93
.1103/60	9.00	9.47	9.68	2.1	
"	11.90	9.67	9.67	2.1	
"	14.00	9.80	9.65	2.2	
"	23.80	10.72			92.9

Mean 2.1

Mean deviation 0.06

Ave. K = 2.1 ± .02 x 10⁻¹⁰

grams/ml	ml NaOH (.04985N)	pH	pK	K x 10 ⁴	NE (140)
.0702/65	4.00	3.39	3.56	2.8	
"	5.00	3.54	3.54	2.9	
"	6.00	3.69	3.53	2.9	
"	10.06	7.80			140.2
.0684/65	4.00	3.40	3.56	2.8	
"	5.00	3.56	3.54	2.9	
"	6.00	3.71	3.51	3.1	
"	9.85	7.81			139.0

Mean 2.9

Mean deviation 0.06

Ave. K = 2.9 ± .02 x 10⁻⁴

grams/ml	ml NaOH	pH	pK	K x 10 ⁴	NE (140)
.0872/75	5.00	3.70	3.86	1.4	
"	6.00	3.82	3.84	1.4	
"	7.00	3.98	3.86	1.4	
"	12.35	7.95			141.3
.1312/75	7.00	3.61	3.83	1.5 x 10	
"	9.00	3.79	3.82	1.5	
"	11.00	3.98	3.82	1.5	
"	18.72	7.87			140.5

Mean 1.5

Mean deviation 0.05

Ave. K = 1.5 ± .02 x 10⁻⁴

p-FC₆H₄CO₂H
m. 182-4

grams/ml	ml NaOH	pH	pK	K x 10 ⁴	NE (140)
.0780/65	4.00	3.31	3.56	2.8	
"	5.60	3.56	3.56	2.8	
"	7.00	3.81	3.57	2.7	
"	11.20	7.70			139.5
.0922/65	5.00	3.31	3.51	3.1	
"	6.55	3.48	3.49	3.2	
"	8.00	3.67	3.47	3.4	
"	13.10	7.70			141.0
				Mean 3.0	
				Mean deviation 0.2	
				Ave. K = 3.0 ± 0.08 x 10 ⁻⁴	

C₆H₅CO₂H
m. 122 (sealed tube)

grams/ml	ml NaOH	pH	pK	K x 10 ⁵	NE (122)
.1106/65	7.00	4.00	4.23	5.9	
"	9.47	4.22	4.22	6.0	
"	11.00	4.39	4.25	5.6	
"	18.95	8.15			117
.1194/65	7.00	3.90	4.16	6.9	
"	9.85	4.16	4.16	6.9	
"	12.00	4.35	4.16	6.9	
"	19.70	8.10			121.5
				Mean 6.2	
				Mean deviation 0.5	
				Ave. K = 6.2 ± 0.2 x 10 ⁻⁵	

10.0 Thermodynamic Ionization Constants for CF₃CH₂CO₂H⁵, CF₃(CH₂)₂CO₂H⁵, CH₂FCO₂H⁴⁷, CCl₂=CClCO₂H¹⁰. Conductance data are available from the literature for calculation of thermodynamic ionization constants which is carried out for purposes of comparison; the results are in Table XVI.

Table XVI
CF₃CH₂CO₂H

C	Δ	Δ'	$K_{Cl} \times 10^4$	$K_{Th} \times 10^4$
.1009	35.9	373.3	9.54	8.21
.05045	50.1	375.8	9.64	8.33
.02522	68.6	377.9	9.56	8.67
.02018	75.71	378.6	9.53	8.69
.01009	101.6	380.3	9.35	8.69
.005045	132	381.7	8.77	8.30
			Mean 9.39	8.48
			Mean deviation 0.22	0.20
			Ave. $K \times 10^4 = 9.39 \pm .09$	$8.48 \pm .08$

CF₃(CH₂)₂CO₂H

C	Δ	Δ'	$K_{Cl} \times 10^5$	$K_{Th} \times 10^5$
.09970	10.0	373.6	6.93	6.54
.04985	13.9	374.8	8.91	6.44
.02492	19.6	375.9	6.95	6.56
.01246	27.7	376.6	7.10	6.76
.009970	30.9	377.0	7.14	6.81
.004985	42.2	377.8	6.88	6.61
			Mean 6.98	6.62
			Mean deviation 0.08	0.11
			Ave. $K \times 10^5 = 6.98 \pm 0.03$	6.62 ± 0.05

CCl₂=CClCO₂H

C	Δ	Δ'	$K_{Cl} \times 10^2$	$K_{Th} \times 10^2$
.03122	279.6	365.2	7.4	5.49
.01561	312.5	371.2	7.0	5.45
.007805	337.4	375.6	6.8	5.23
.003902	353.2	379.2	6.8	5.58
0	388.1 (from $\Delta_{osalt} = 88.4$)			
			Mean 7.0*	5.44
			Mean deviation 0.2	0.10
			Ave. $K \times 10^2 = 7.0 \pm 0.1$	5.44 ± 0.55
*Author's Calculations ¹⁰				

Table XVI contd.

C	Λ	Λ'	$K_{Cl} \times 10^3$	$K_{Th} \times 10^3$
.25000	33.0	366.0	2.29	1.57
.1250	44.8	385.0	2.15	1.45
.06250	61.8	373.3	2.18	1.62
.03125	82.5	375.9	2.17	1.60
.01562	112.4	378.1	2.17	1.67
.007810	147.0	380.1	2.17	1.67
.003905	187.6	381.7	2.15	1.67
.001952	232.1	383.2	2.18	1.68
0	388.2 (from $\Lambda_{\text{osalt}} = 88.5$)			
		Mean	2.18	1.61
		Mean deviation	0.02	0.06
		Ave. $K \times 10^3 =$	2.18 ± 0.017	1.61 ± 0.02

Table XVII
NEW COMPOUNDS

Compound	B.P. °C/mm	M.P.	n_D^t	d_4^t	t °C	MR
$\text{CF}_2\text{ClCF}=\text{CCl}_2$	86.2	-	1.3950	1.576	25	30.2
$\text{CF}_2=\text{CFCO}_2\text{H}$	-	35.5-6.5	-	-	-	-
$\text{CF}_2\text{ClCFBrCO}_2\text{H}$	75/7 or 85/15	23.9	1.4156	1.948	25	31.09
$\text{CH}_2\text{BrCBrFCO}_2\text{H}$	105/5	70.5-2.5	-	-	-	-
$\text{CF}_2\text{ClCFClCO}_2\text{H}$	83-5/30	-	1.3868	1.591	25	29.08
$\text{CH}_2=\text{CFCO}_2\text{H}$	-	51-2	-	-	-	-
$\text{CF}_2=\text{CHCO}_2\text{H} \cdot 2\text{H}_2\text{O}$	-	-	-	-	-	-
$\text{CHF}_2\text{CF}_2\text{CO}_2\text{H} \cdot \text{Y}_2\text{H}_2\text{O}$	131.5-2.5	-	-	-	-	-
$\text{CHF}_2\text{CF}_2\text{CO}_2\text{H} \cdot \text{H}_2\text{O}$	136-7	-	1.3250	-	25	-
$\text{CHF}_2\text{CF}_2\text{CONH}_2$	-	58.5-9.4	-	-	-	-
$\text{CF}_3\text{CH}=\text{CHCO}_2\text{H}^*$	-	49.5-50.5	-	-	-	-
$\text{CHF}_2\text{CF}_2\text{CO}_2\text{CH}_3$	93-4	-	1.3152	-	29	-
$\text{CH}_2\text{BrCBrFCO}_2\text{CH}_3$	76-8/9	-	1.4885	1.990	27	38.2
$\text{CH}_2\text{ClCFClCO}_2\text{CH}_3$	74-80/48	-	1.4370 to 1.4449	-	-	-
$\text{CH}_2\text{BrCHFCO}_2\text{CH}_3$	92-4/80	-	1.4390	1.624	30	30.0
$\text{CF}_3(\text{CH}_2)_3\text{CO}_2\text{H}$	94.8-5/15	-	1.3632	1.293	25	26.83
$\text{CF}_3(\text{CH}_2)_3\text{CH}_2\text{OH}$	90-5/69	-	-	-	-	-
$\text{CF}_3(\text{CH}_2)_3\text{CH}_2\text{Cl}$	121	-	1.3691	1.217	27	29.6

* Prepared by and reported for Dr. Maxwell Nager, Shell

XVII

COMPOUNDS

C	MR	AR _F	%F (calcd)	NE (calcd)	K _A
	30.2	1.12	28.71(28.59)	-	-
	-	-	45.16(45.25)	126.7(126)	1.61±0.07x10 ⁻²
	31.09	1.39	23.25(23.65)	240.5(241.5)	4.0 ±0.3 x10 ⁻³
	-	-	-	247(249.8)	3.7 ±0.1 x10 ⁻³
	29.08	1.68	-	197.5(197)	3.4 ±0.2 x10 ⁻³
	-	-	20.65(21.10)	91.5(90.5)	2.79±0.03x10 ⁻³
	-	-	27.05(26.40)	146(144)	6.8 ±0.1 x10 ⁻⁴
	-	-	-	152(155)	-
	-	-	-	160(164)	-
	-	-	-	-	-
	-	-	-	140.1(141)	4.5 ±0.06x10 ⁻⁴
	-	-	46.55(47.5)	-	-
	38.2	1.44	-	-	-
	-	-	-	-	-
	30.0	1.01	-	-	-
	26.83	1.10	36.96(36.54)	155.3(156)	3.2 ±0.03x10 ⁻⁵
	-	-	-	-	-
	29.6	0.93	32.40(35.6)	-	-

Shell Oil Co., Houston, Texas.

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AUTOBIOGRAPHY

I, Charles Junius Fox, was born in Detroit, Michigan, November 22, 1926. I received by secondary school education in the public schools of the cities of East Tawas, Michigan; Detroit, Michigan; and Bexley, Ohio. My undergraduate training was obtained at The Ohio State University from which I received the Degree Bachelor of Science in 1947. While employed as Research Associate at the Kettering Laboratory of Applied Physiology, Cincinnati, Ohio, during the years 1947-1949, I attended the Graduate School of the University of Cincinnati. From The Ohio State University, I received the degree Master of Science in 1950.

While in residence at The Ohio State University, I served as Research Assistant in the Department of Chemistry under the Research Foundation during the year 1950-1951, as Socony-Vacuum Oil Company Fellow in the Department of Chemistry during the year 1951-1952 and as Teaching Assistant in the Department of Chemistry while completing the requirements for the degree Doctor of Philosophy.