

MASS SPECTROMETRIC INVESTIGATION
OF SOME FLUORINATED ALCOHOLS

by

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INTRODUCTION

Recent reviews by Patrick and by Majer (32) reveal comparatively little thermodynamic information for organic compounds containing carbon, hydrogen, oxygen, and fluorine. Furthermore, a survey of recent literature failed to provide significant information of this type for fluorine-substituted hydrocarbons containing another functional group.

Several fluorinated alcohols are available commercially. The 2 and 3-carbon fluoro-alcohols are low boiling, colorless liquids with sufficient vapor pressures at room temperatures to be conveniently studied mass spectrometrically. The data obtained may provide interesting insights into the general structure of the compound, the bond dissociation processes, and heats of formation of ionic and molecular species.

An electron impact study of some primary and secondary aliphatic fluorinated alcohols was undertaken in an attempt to obtain basic information concerning mass spectral cracking patterns, ionization and appearance potentials, heats of formation of ions, and ionization and dissociation processes. The results of this study are compared to corresponding studies of other investigators wherever possible. Since no previous studies of fluorinated alcohols have been made, comparisons are restricted to species containing only carbon, hydrogen and fluorine. In addition, calculated heats of formation of ions, based on the reported process and experimentally determined appearance potentials, are given for ions containing carbon, hydrogen, fluorine and oxygen.

Experimentally determined ionization potentials are compared to values calculated using the group orbital method of Hall (14). No literature values for molecular ionization potentials or heats of formation in the gaseous phase were available for the compounds investigated.

Ionization potentials could not be determined experimentally for 2,2,3,3-tetrafluoro-1-propanol, 2,2,3,3,3-pentafluoro-1-propanol, 1,3-difluoro-2-propanol and 1,1,1-trifluoro-2-propanol due to the immeasurably low parent molecule-ion intensities. Neither was it possible to calculate suitable values for these compounds; this was mainly due to a lack of intermediate ionization potentials and group interaction parametric values necessary for the calculations.

Rearrangements were observed in several ion formation processes. In all but a few isolated cases, it was impossible to fit suitable processes consistent with the energetics; consequently, no detailed discussion of this aspect was considered.

THEORETICAL CALCULATIONS

The minimum energy that an impinging electron must possess before it can dislodge an electron by collision with a gaseous atom or molecule without increasing the kinetic energy of the displaced electron is defined as the ionization potential. This concept may also be considered as the energy corresponding to the passage from the most stable state of the particle to the most stable state of the ion. The ionization potential is commonly expressed in electron volts and is numerically equal to the work done during the ionization process. The ionization potential of a molecule can provide significant information regarding molecular structure, electron affinities and bond energies (7).

The experimental determination of ionization potentials requires mastery of varied instrumentation, plus a large amount of data reduction. The complexity of purely theoretical calculations of ionization potentials for even the simplest of particles makes this approach undesirable. Therefore, a suitable semi-empirical method for the calculation of ionization potentials is

desirable in attempting to circumvent these difficulties.

Methods for the determination of molecular orbitals, initially reported by Lennard-Jones (25, 26) based on the molecular orbital theory of chemical valency, prepared the way for formulation of semi-empirical methods for calculating ionization potentials. Two equally valid methods for establishing the electrostatic energy of an electron are given (28); the molecular and the equivalent orbital theories. In the molecular orbital approach, the electrons are assumed to be assigned to the entire molecule. For certain symmetrical molecules, orbitals containing paired electrons are considered identical in regard to distribution and differ only in spatial orientation. Molecules of this type may be described equally well by either theory. The molecular orbital approach satisfactorily applies to discussions of molecular energy levels or changes in energy levels. The directed orbital method is suitable for electron distribution studies of chemical bonds (25).

When an electron is excited through absorption of quantized energy, it is impossible to establish the directed bond involved. Any one of a set of equivalent orbitals within a symmetrical molecule may be affected, which is another way of stating that the electron has been removed from a molecular orbital.

The proposals of Lennard-Jones are extended and supplemented by a series of papers by G. G. Hall et al. (13, 15-18) starting in 1950. The molecular orbital theory of chemical valency states that each electron in a molecule must be regarded as distributed throughout the whole structure and not confined to any singular area. G. G. Hall and Lennard-Jones observed that a common relation existed between the ionization potential of a molecule and an energy parameter associated with a molecular orbital (17). The authors have shown that ionization occurs when an electron distributed over the entire molecule is removed without changing the remaining orbitals.

Two semi-empirical methods for calculation of ionization potentials are the equivalent orbital method and the group orbital method. Both are founded on experimentally determined ionization potentials, a small number of interaction parameters and a set of theoretically derived equations rather than on total energies of molecules (13).

A method for calculating the ionization potentials of normal paraffins applied by Hall (13) and Lennard-Jones and Hall (27) involves the solution of secular equation,

$$\left| e_{mn} - \delta E_{mn} \right| = 0, \quad (1)$$

where m and n are related to various bonds in the molecule. The lowest root of the secular equation is the negative of the ionization potential of the molecule.

The number of terms and the solution of the secular equation become inconveniently involved when large molecules are considered on the basis of equivalent orbitals. Hall has shown that a greatly simplified approach to the calculation of ionization potentials results when planar molecules having an orbital antisymmetrical to the plane of the molecule are separated into groups identified by characteristic orbitals (14). The determination of the ionization potentials of methyl substituted ethenes using the group orbital approach gives satisfactory results (15).

Franklin expanded the group orbital approach for calculation of ionization potentials to include cycloparaffins, alkyl halides, olefins, substituted aromatics, aldehydes, ketones, esters, carboxylic acids, aliphatic amines, ethers and alcohols (9). The calculated results are generally in quite good agreement with experimental values, even for non-planar molecules.

Application of the modified group orbital theory is illustrated in the

calculation of the ionization potentials of methanol and ethanol. Recent ionization potential values (23) in conjunction with group interaction parameters listed by Franklin (9) are used in the following discussions.

The minimum root of the determinantal equation resulting from the expansion of the expression,

$$\begin{vmatrix} (m - I) & x \\ x & (h - I) \end{vmatrix} = 0, \quad (2)$$

where:

m = the methyl group interaction parameter (taken as equal to the ionization potential of methane, $I(\text{CH}_4) = 12.98$ ev. (23));

h = the hydroxyl group parameter (taken as equal to the ionization potential of water, $I(\text{H}_2\text{O}) = 12.59$ ev. (23));

x = the C - O interaction taken as 2.06 ev. (9);

yields the ionization potential of methanol. The two roots of the equation are obtained from the equation,

$$I^2 - (m + h) I + (mh - x^2) = 0. \quad (3)$$

These values are 14.77 ev. and 10.80 ev., with 10.80 ev. being taken as the ionization potential of methanol. This value is in good agreement with the value of 10.85 ev. obtained by photoionization methods (23).

In a similar manner, the determinantal equation,

$$\begin{vmatrix} (m - I) & b & 0 \\ b & (m - I) & x \\ 0 & x & (h - I) \end{vmatrix} = 0, \quad (4)$$

where:

b = the C - C interaction, taken as 1.55 ev. (9);

m , x and h = the same values as used in Eq. (2), may be solved to yield the ionization potential of ethanol. This equation factors into,

$$I^3 - (h + 2m)I^2 + (2hm + m^2 - x^2 - b^2)I - (hm^2 - x^2m - b^2h) = 0, \quad (5)$$

and may be solved easily by the method of successive approximations. The calculated ionization potential is 10.83 ev. Ionization potential values obtained by electron impact are in fair agreement. However, this value is rather poor when compared to $I(\text{C}_2\text{H}_5\text{OH}) = 10.48$ ev. obtained by photoionization methods (23).

EXPERIMENTAL

Mass Spectrometry

A comprehensive review of published information on mass spectrometry and related topics through 1954 has been compiled by Dibeler (5). The Bendix model 12-100 time-of-flight (TOF) mass spectrometer has received detailed consideration as demonstrated in the number of papers published on various phases of the instrumentation by a number of investigators (2, 12, 21, 43, 44). Among the topics considered are the improvements within the ion source, resolution, ion flight time, advantages and disadvantages of (TOF), and gas chromatograph-mass spectrometer coupling.

The instrument used to obtain the mass spectra and appearance potentials reported here has been described previously (10); however, a brief review of important features will be included. A schematic diagram of the instrument and related equipment is given in Figure 1.

The Bendix model 12-100 instrument produces 10,000 mass spectra per second

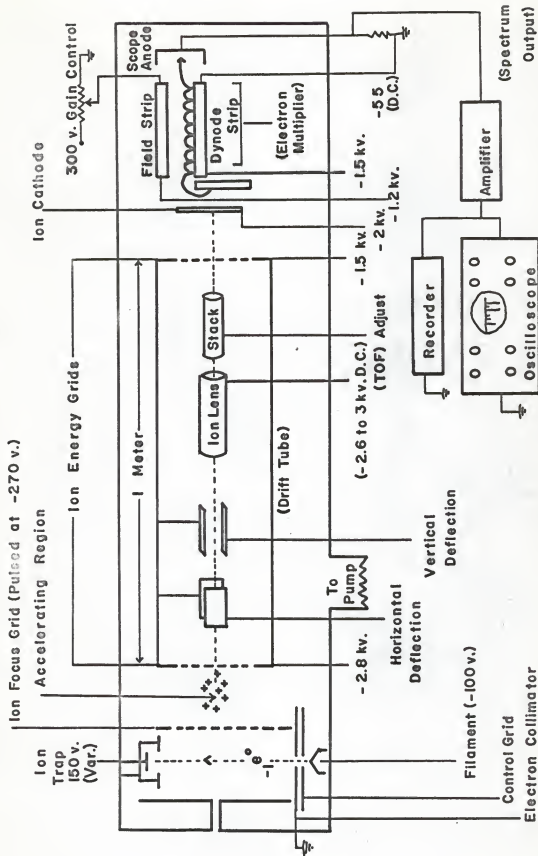


FIGURE 1. SCHEMATIC DIAGRAM OF THE BENDIX (TOF) MASS SPECTROMETER

of the gaseous sample introduced into the ion source. The positively charged particles are pulsed out of the ion source at a frequency of 10 kc. and are drawn into an accelerating electric field of approximately 2800 volts. The ions, on exit from this region, emerge into a field free drift tube which has a linear flight path of one meter. The time-of-flight principle, in which equal amounts of kinetic energy are imparted to each charged particle during the accelerating period, separates the ions into groups. The velocities vary inversely as the square root of the masses, with the smaller ions possessing the greater velocities. In essence, all ions formed leave the accelerating area at the same time. Those ions with the same mass-to-charge ratio tend to cluster and separate from other groups of unlike mass. If no doubly charged ions are involved, the lightest group reaches the detector first. As each group of ions strikes the ion collector cathode, secondary electrons are released. These electrons are multiplied in mutually perpendicular magnetic and electric fields and are focused onto the scope anode. The resulting electronic signal is amplified and displayed on the oscilloscope screen. A Sanborn model 152 dual channel recording system traces a permanent record of the data on heat sensitive permapaper.

Mass spectra for each of the compounds investigated were obtained at nominal electron energies of 70 ev. The instrument resolution is excellent up to mass 150 and is within $\Delta H \cdot H^{-1} = 0.5$ up to mass 250, where H equals the peak height and ΔH represents the overlap of two consecutive peaks of equal magnitude (1). Storage bulbs containing samples of the compounds were attached to a glass manifold inlet system suitably designed to allow homogeneous mixing of xenon-sample gases prior to admission into the ion source. The flow rate of the admixed gases into the ionizing region was controlled by a stainless steel needle valve assembly.

To study the variation of the relative abundances of the major ions with changing electron energy, spectra of each compound were taken as the ionizing energy was decreased. The fractional current of the i th ion was plotted as a function of the electron energy.

Appearance potential determinations were made at pressures ranging from 2×10^{-6} to 5×10^{-6} mm Hg. These pressures were obtained by the joint action of a forepump and the mercury diffusion pump. The optically-baffled cold trap of the diffusion pump was cooled with liquid nitrogen.

A tungsten wire filament of the ion source was heated at 2.5 amperes; nominal trap currents of 125 nanoamperes were used. The technique used in collecting data for the appearance potential values involved positioning one electronic gate of the electron multiplier on the peak being investigated and the other electronic gate on one of the major isotopic peaks of the calibrating gas. The initial 50 ev. electron energy was decreased at recorded intervals. The intensities of the ion currents as a function of decreasing electron energy for the species being investigated were permanently recorded with the Sanborn recording system.

Ionization and appearance potentials were obtained from experimentally determined ionization efficiency curves such as those shown in Figures 2 and 3. Ionization efficiency curves in which the ion current was plotted as a function of the electron energy were prepared for each determination and the linear portion made parallel.

The methods used for determining appearance potentials were the extrapolated voltage difference method proposed by Warren (42), the semi-log plot developed by Lossing et al. (30), and the energy compensation technique (22).

In the Warren method, ΔE , the voltage difference between the two parallel curves at selected ion currents, was plotted as a function of the ion

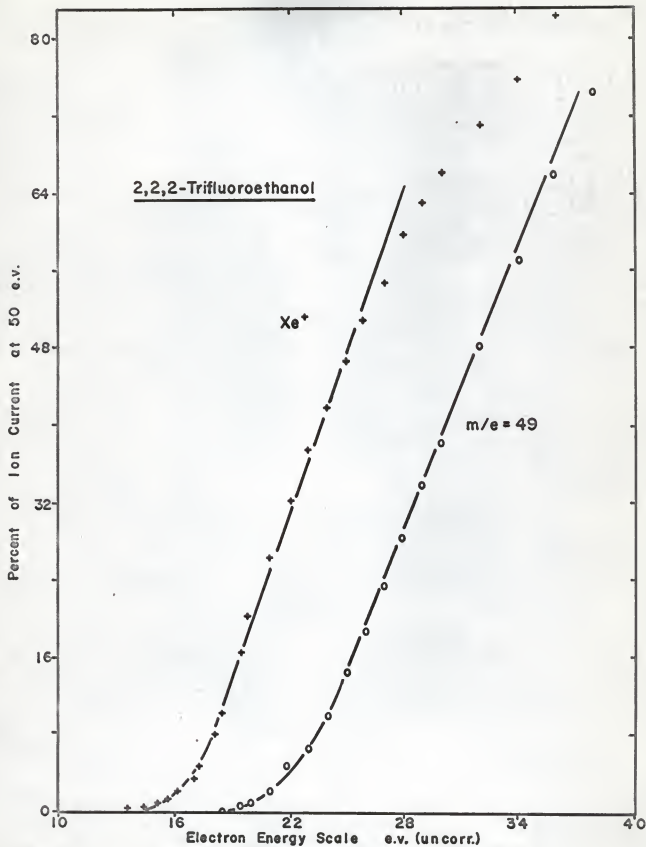


FIGURE 2. TYPICAL IONIZATION EFFICIENCY CURVE

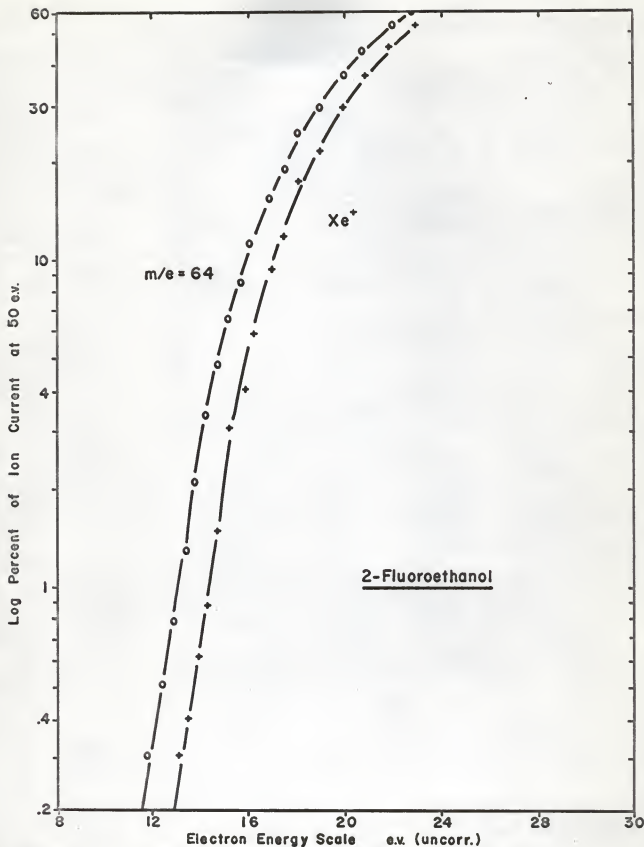


FIGURE 3. TYPICAL IONIZATION EFFICIENCY CURVE

current. The ΔE value obtained through extrapolation of the ion current to zero was added algebraically to the ionization potential of xenon (35). In the semi-log plot the difference in voltages in the region of 1% of the 50 ev. current is taken as the difference between the ionization potential of xenon and the appearance potential of the ion.

The energy compensation technique developed by R. W. Kiser and E. J. Gallegos (22) represents a method for determining the difference between the ionization potential of the calibrating gas and the ion being studied at 1% of 50 ev. ion current region through appropriate electrometer sensitivity changes that are quickly and easily performed. Appearance potentials obtained by this method were found in this study to be quite consistent and reproducible within the limits of experimental accuracy for all ions selected for investigation.

Chemicals Used

The sample of 2,2,2-trifluoroethanol used in this study was purchased from the Matheson Company, Inc. A boiling point of 73.9 to 74.1 °C is reported for this compound (3). No significant impurities were noted in the mass spectrum. A gas chromatographic analysis made with a Fisher-Gulf model 160 Partitioner, using a 4.25 meter column of tri-n-tolyl phosphate on Celite, confirmed the purity of the sample. (Chromatographic separations were satisfactory at 120-125 °C.)

The 2-fluoroethanol, 2,2,3,3-tetrafluoro-1-propanol and 1,3-difluoro-2-propanol were obtained from K and K Laboratories. Gas chromatographic analyses and the mass spectra showed negligible amounts of impurities in the mass ranges investigated. Boiling points of these compounds are 102-4 °C (24), 106-7 °C (19), and 105 °C (4), respectively.

The compounds, 1,1,1-trifluoro-2-propanol and 2,2,3,3,3-pentafluoro-1-

propanol were obtained from the Aldrich Chemical Co., Inc. The results of both gas chromatographic analysis and preliminary mass spectra indicated that these compounds were not pure. Samples of pure 1,1,1-trifluoro-2-propanol were obtained by determining the peak due to 1,1,1-trifluoro-2-propanol and then freezing out the desired fraction at liquid nitrogen temperatures as it was exhausted from the column. A similar approach was used in collecting the fractions of 2,2,3,3,3-pentafluoro-1-propanol. The boiling points of pure 1,1,1-trifluoro-2-propanol is 76 °C (31); that of 2,2,3,3,3-pentafluoro-1-propanol is reported as 80-81 °C (20).

RESULTS

The results of the mass spectrometric investigation of 2-fluoro- and 2,2,2-trifluoroethanol, 2,2,3,3-tetrafluoro- and 2,2,3,3,3-pentafluoro-1-propanol and 1,3-difluoro- and 1,1,1-trifluoro-2-propanol are summarized in Tables 1-6. The 70 ev. mass spectra and the relative abundances of the positive ions are given in columns 1 and 2. The appearance potentials of the ions investigated, along with the probable ionization process are shown in columns 3 and 4. The calculated heats of formation of the ions based on the experimentally determined appearance potentials and the listed process are recorded in the last column.

Values for the heats of formation of these compounds in the gaseous phase are not available in the literature. The following estimated heats of formation determined after the Franklin method (8) and other values from the literature were used: (a) $\Delta H_f(\text{CH}_2\text{FCH}_2\text{OH}) = -101$ kcal/mole; (b) $\Delta H_f(\text{CF}_3\text{CH}_2\text{OH}) = -205$ kcal/mole; (c) $\Delta H_f(\text{CHF}_2\text{CF}_2\text{CH}_2\text{OH}) = -250$ kcal/mole; (d) $\Delta H_f(\text{CF}_3\text{CF}_2\text{CH}_2\text{OH}) = -310$ kcal/mole; (e) $\Delta H_f(\text{CH}_2\text{F})_2\text{CHOH} = -155$ kcal/mole; and $\Delta H_f(\text{CF}_3\text{CHOHCH}_3) = -215$ kcal/mole.

Table 1. Mass Spectrum and Appearance Potentials of the Positive Ions of 2-Fluoroethanol ($\Delta H_f(\text{molecule}) = -101 \text{ kcal/mole}$).

m/e	Relative Abundance	Appearance Potential (ev.)	Process	ΔH_f^+ (kcal/mole)
15	16.2	15.8±0.4	$\text{C}_2\text{H}_5\text{FO} \rightarrow \text{CH}_3^+ + \text{CH}_2\text{O} + \text{F}$	273
17	5.2			
19	1.9			
26	3.8			
27	11.9	16.2±0.4	$\rightarrow \text{C}_2\text{H}_3^+ + \text{F} + \text{H}_2\text{O}$	312
29	19.2	15.5±0.3	$\rightarrow \text{CHO}^+ + \text{HF} + \text{H} + \text{CH}_2$	201
30	3.3			
31	100.0	12.6±0.2	$\rightarrow \text{CH}_3\text{O}^+ + \text{CH}_2\text{F}$	(17) ^a
33	4.5	15.3±0.3	$\rightarrow \text{CH}_2\text{F}^+ + \text{CH}_2\text{O} + \text{H}$	228
42	1.9			
43	11.8	13.9±0.2	$\rightarrow \text{C}_2\text{H}_3\text{O}^+ + \text{H}_2 + \text{F}$	201
45	2.9			
46	1.9			
64	14.6	11.0±0.15	$\rightarrow \text{C}_2\text{H}_5\text{FO}^+$	153

^aHeat of formation of radical.

Table 2. Mass Spectrum and Appearance Potentials of the Positive Ions of 2,2,2-Trifluoroethanol ($\Delta H_f(\text{molecule}) = -205 \text{ kcal/mole}$).

m/e	Relative Abundance	Appearance Potential (ev.)	Process	ΔH_f^+ (kcal/mole)
29	21.3	17.7±0.5	$\text{C}_2\text{H}_3\text{F}_3\text{O} \longrightarrow \text{CHO}^+ + \text{CF}_3 + 2\text{H}$	214
30	3.0			
31	100.0	13.3±0.3	$\longrightarrow \text{CH}_3\text{O}^+ + \text{CF}_3$	(-71) ^a
33	13.6	18.0±0.3	$\longrightarrow \text{CH}_2\text{F}^+ + \text{CF}_2 + \text{OH}$	235
49	2.5			
50	2.7			
51	7.3	16.6±0.3	$\longrightarrow \text{CHF}_2^+ + \text{???}$	
61	7.9	16.0±0.5	$\longrightarrow \text{C}_2\text{H}_2\text{FO}^+ + \text{HF} + \text{F}$	210
62	1.2			
69	3.6	18.4±0.3	$\longrightarrow \text{CF}_3^+ + \text{CHO} + 2\text{H}$	118
80	1.0			
81	3.0	15.4±0.3	$\longrightarrow \text{C}_2\text{H}_3\text{F}_2\text{O}^+ + \text{F}$	132
82	1.0			
83	1.1			
100	1.1	12.7±0.3	$\longrightarrow \text{C}_2\text{H}_3\text{F}_3\text{O}^+$	88

^a Heat of formation of radical.

Table 3. Mass Spectrum and Appearance Potentials of the Positive Ions of 2,2,3,3-Tetrafluoro-1-propanol ($\Delta H_f(\text{molecule}) = -250 \text{ kcal/mole}$).

m/e	Relative Abundance	Appearance Potential (ev.)	Process	ΔH_f^+ (kcal/mole)
15	1.7			
29	21.9	16.9±0.2	$\text{C}_3\text{H}_4\text{F}_4\text{O} \longrightarrow \text{CHO}^+ + \text{???}$	
30	1.9			
31	100.0	13.2±0.3	$\longrightarrow \text{CH}_3\text{O}^+ + \text{C}_2\text{F}_4 + \text{H}$	154
33	8.7	15.6±0.3	$\longrightarrow \text{CH}_2\text{F}^+ + \text{???}$	
43	1.7			
45	2.9			
49	6.3	16.3±0.4	$\longrightarrow \text{CH}_2\text{FO}^+ + \text{???}$	
51	18.8	17.2±0.3	$\longrightarrow \text{CHF}_2^+ + \text{???}$	
61	2.6			
63	2.4			
64	2.2			
65	6.7	15.5±0.3	$\longrightarrow \text{C}_2\text{H}_3\text{F}_2^+ + \text{HF} + \text{F} + \text{CO}$	180
81	1.2			
82	21.4	13.3±0.3	$\longrightarrow \text{C}_2\text{HF}_3^+ + \text{HF} + \text{CH}_2\text{O}$	149
83	1.6			
112	10.0	11.5±0.2	$\longrightarrow \text{C}_3\text{H}_3\text{F}_3\text{O}^+ + \text{HF}$	80
118	1.5			
120	1.6			
132				

Table 4. Mass Spectrum and Appearance Potentials of the Positive Ions of 2,2,3,3,3-Pentafluoro-1-propanol ($\Delta H_f(\text{molecule}) = -310$ kcal/mole).

m/e	Relative Abundance	Appearance Potential (ev.)	Process	ΔH_f^+ (kcal/mole)
29	24.1	17.2±0.2	$C_3H_3F_5O \rightarrow CHO^+ + C_2F_4 + F + H_2$	221
30	2.9			
31	100.0	12.7±0.2	$\rightarrow CH_3O^+ + C_2F_5$	(-190) ^a
33	4.8			
42	1.2			
43	1.9			
45	2.2			
49	13.2	16.6±0.3	$\rightarrow CH_2FO^+ + ???$	
50	3.1			
51	6.6	18.0±0.3	$\rightarrow CHF_2^+ + ???$	
61	2.8			
62	1.2			
63	1.6			
64	2.0			
67	1.4			
69	12.0	19.1±0.2	$\rightarrow CF_3^+ + ???$	
80	1.6			
81	1.3			
82	1.5			
83	5.6	16.5±0.2	$\rightarrow C_2H_2F_3^+ + FCO + HF (?)$	(158)(?)
100	6.0	14.6±0.3	$\rightarrow C_2H_3F_3O^+ + CF_2$	62
150				

^aHeat of formation of radical.

Table 5. Mass Spectrum and Appearance Potentials of the Positive Ions of 1,3-Difluoro-2-propanol ($\Delta H_f(\text{molecule}) = -155 \text{ kcal/mole}$).

m/e	Relative Abundance	Appearance Potential (ev.)	Process	ΔH_f^+ (kcal/mole)
15	61.0	15.5±0.2	$\text{C}_3\text{H}_6\text{F}_2\text{O} \longrightarrow \text{CH}_3^+ + \text{???}$	
26	4.1	16.9±0.6	$\longrightarrow \text{C}_2\text{H}_2^+ + \text{???}$	
27	14.1	16.7±0.2	$\longrightarrow \text{C}_2\text{H}_3^+ + \text{???}$	
29	19.7	15.8±0.1	$\longrightarrow \text{CHO}^+ + \text{CH}_3\text{F} + \text{CH}_2\text{F}$	251
			$\longrightarrow \text{CHO}^+ + \text{C}_2\text{H}_4\text{F}_2 + \text{H}$	223
30	1.8			
31	15.1	14.4±0.5	$\longrightarrow \text{CH}_3\text{O}^+ + \text{???}$	
33	21.2	18.4±0.3	$\longrightarrow \text{CH}_2\text{F}^+ + \text{???}$	
36	3.4			
37	2.3			
38	2.7			
39	3.1			
41	1.9			
42	7.3	15.9±0.4	$\longrightarrow \text{C}_2\text{H}_2\text{O}^+ + \text{???}$	
43	51.2	13.5±0.2	$\longrightarrow \text{C}_2\text{H}_3\text{O}^+ + \text{CH}_2\text{F} + \text{HF} (?)$	207
			$\longrightarrow \text{C}_2\text{H}_3\text{O}^+ + \text{CH}_3\text{F} + \text{F} (?)$	193
			$\longrightarrow \text{C}_2\text{H}_3\text{O}^+ + \text{CH}_2\text{F}_2 + \text{H} (?)$	210
45	3.9			
46	1.9			
47	2.8			
49	4.0			
51	2.5			
57	1.8			
59	2.2			

Table 5. (concl.)

m/e	Relative Abundance	Appearance Potential (ev.)	Process	ΔH_f^+ (kcal/mole)
61	2.2			
62	3.9			
63	100.0	11.7±0.1	→ C ₂ H ₄ FO ⁺ + ???	
64	4.9			
75	1.3			
76	2.3			
77	2.1			
79	1.4			
96				

Table 6. Mass Spectrum and Appearance Potentials of the Positive Ions of 1,1,1-Trifluoro-2-propanol ($\Delta H_f(\text{molecule}) = -215 \text{ kcal/mole}$).

m/e	Relative Abundance	Appearance Potential (ev.)	Process	ΔH_f^+ (kcal/mole)
15	6.3	20.4 \pm 1.0	$\text{C}_3\text{H}_5\text{F}_3\text{O} \longrightarrow \text{CH}_3^+ + \text{CHO} + \text{H} + \text{CF}_3(?)$	321
19	8.2	15.4 \pm 0.2	$\longrightarrow \text{F}^+ + ???$	
26	1.8			
27	19.3	16.4 \pm 0.4	$\longrightarrow \text{C}_2\text{H}_3^+ + \text{OH} + \text{CHF}_3(?)$	316
29	28.8	16.2 \pm 0.2	$\longrightarrow \text{CHO}^+ + \text{H} + \text{CH}_3 + \text{CF}_3(?)$	190
31	57.4	13.3 \pm 0.3	$\longrightarrow \text{CH}_3\text{O}^+ + ???$	
33	8.6	17.2 \pm 0.5	$\longrightarrow \text{CH}_2\text{F}^+ + ???$	
42	2.6			
43	18.7	15.2 \pm 0.5	$\longrightarrow \text{C}_2\text{H}_3\text{O}^+ + \text{CF}_2 + \text{HF} + \text{H}$	183
45	100.0	12.5 \pm 0.2	$\longrightarrow \text{C}_2\text{H}_3\text{O}^+ + \text{CF}_3$	188
46	5.8			
47	13.6	16.4 \pm 0.3	$\longrightarrow \text{C}_2\text{H}_4\text{F}^+ + \text{CF}_2 + \text{OH}$	188
49	4.7			
50	2.3			
51	13.8	16.9 \pm 0.4	$\longrightarrow \text{CHF}_2^+ + ???$	
61	4.4			
67	2.3			
69	8.0	20.0 \pm 0.5	$\longrightarrow \text{CF}_3^+ + \text{C}_2\text{H}_3 + \text{H} + \text{OH}$	120
75	3.0			
77	2.0			
79	5.6	15.0 \pm 0.5	$\longrightarrow \text{C}_2\text{HF}_2\text{O}^+ + \text{CH}_3 + \text{HF}$	163
81	1.5			
96	1.5			
99	6.3	14.1 \pm 0.4	$\longrightarrow \text{C}_2\text{H}_2\text{F}_3\text{O}^+ + \text{CH}_3$	78

Other heats of formation used in conjunction with the measured appearance potentials are: $\Delta H_f(\text{H}) = 52.089$ kcal/mole (38); $\Delta H_f(\text{CH}_3) = 32.0$ kcal/mole (38); $\Delta H_f(\text{C}_2\text{H}_2) = 64$ kcal/mole (40); $\Delta H_f(\text{CHF}_3) = -162.6$ kcal/mole (36); $\Delta H_f(\text{CH}_2\text{F}_2) = -105.5$ kcal/mole (36); $\Delta H_f(\text{C}_2\text{F}_4) = -152$ kcal/mole (6); $\Delta H_f(\text{CH}_2) = 68$ kcal/mole (11); $\Delta H_f(\text{F}) = 18.3$ kcal/mole (38); $\Delta H_f(\text{HF}) = -64.2$ kcal/mole (38); $\Delta H_f(\text{H}_2\text{O}) = -57.7979$ kcal/mole (38); $\Delta H_f(\text{OH}) = 10.06$ kcal/mole (38); $\Delta H_f(\text{CH}_2\text{O}) = -27.7$ kcal/mole (38); $\Delta H_f(\text{CHO}) = -2.8$ kcal/mole (38); $\Delta H_f(\text{CF}_2) = -35$ kcal/mole (34); $\Delta H_f(\text{CF}_3) = -115$ kcal/mole (33); and $\Delta H_f(\text{CO}) = -26.4$ kcal/mole (38). A calculated value of 10 kcal/mole was used as the heat of formation of the CH_3O radical.

The following heats of formation for neutral radicals were obtained by interpolations based on known heats of formation of related compounds:

$\Delta H_f(\text{FCO}) = -23$ kcal/mole, $\Delta H_f(\text{CH}_3\text{F}) = -55$ kcal/mole, $\Delta H_f(\text{C}_2\text{H}_4\text{F}_2) = -66$ kcal/mole and $\Delta H_f(\text{C}_2\text{H}_2\text{F}) = 14$ kcal/mole.

The value, 173 kcal/mole, for the heat of formation of CH_3O^+ was used to determine the $\Delta H_f(\text{CH}_2\text{F})$, $\Delta H_f(\text{CF}_3)$ and $\Delta H_f(\text{C}_2\text{H}_5)$ (7).

Mass Spectra

Shown in Figures 4 and 5 are graphical representations of the fragments occurring at impacting electron energies of 70 ev. The mass spectrum of 2,2,2-trifluoroethanol is in reasonable agreement with that reported in the MCA Mass Spectral Data Catalog, Serial 142 (45). Spectra of the other compounds are new.

Clastograms

Clastograms, in which the fraction of ion current over total ion current is plotted as a function of the electron energy, for the compounds investigated

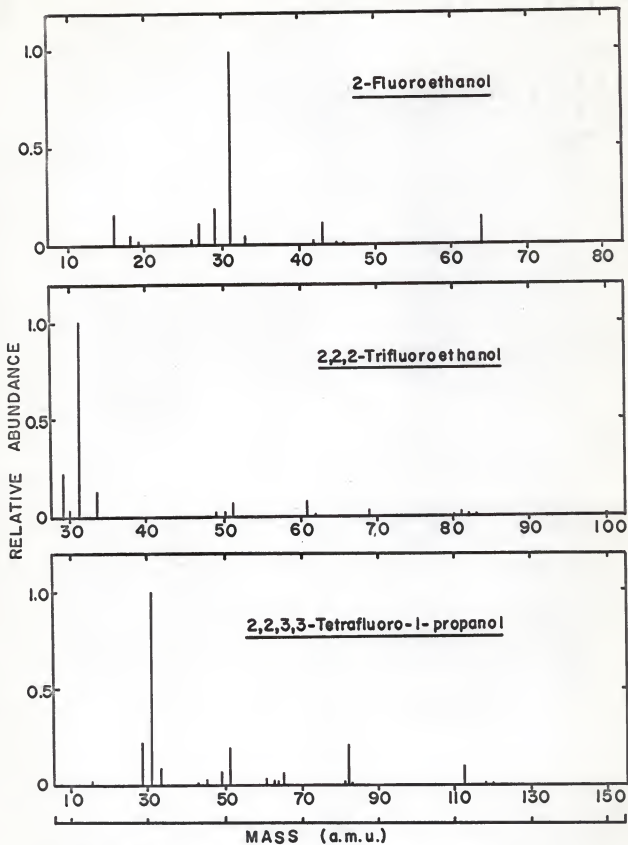


FIGURE 4. POSITIVE ION MASS SPECTRA

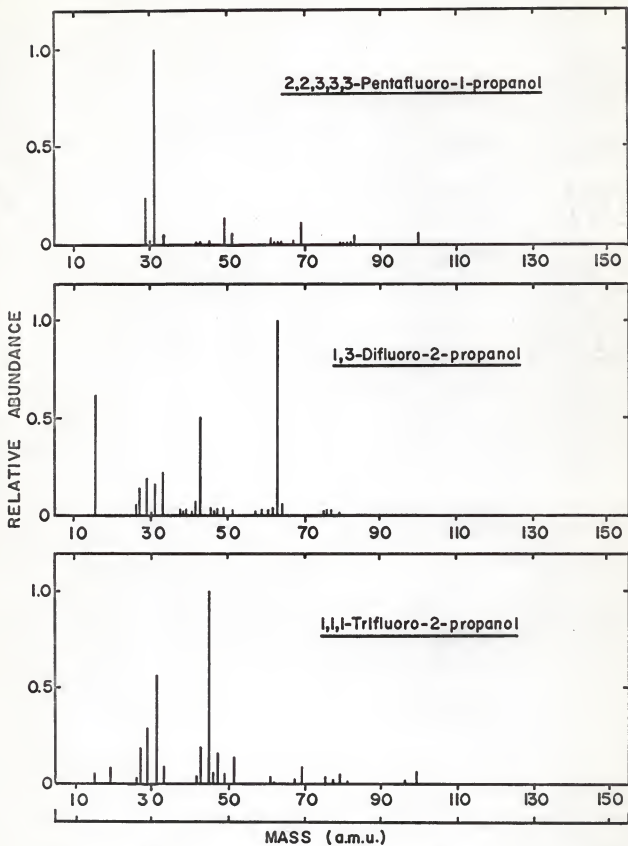


FIGURE 5. POSITIVE ION MASS SPECTRA

are shown in Figures 6 and 7. These diagrams indicate the general appearance of the mass spectra at electron energies other than 70 ev.

Ionization Potentials

The group orbital approach useful in the calculation of ionization potentials as extended by Franklin (9) to include substituted hydrocarbons was used to calculate an ionization potential value for 2-fluoroethanol and 2,2,2-trifluoroethanol. The results obtained were in rather poor agreement with the experimentally determined ionization potentials.

In the calculation of an ionization potential value for 2-fluoroethanol, the following determinantal equation was used:

$$\begin{vmatrix} (g - I) & b & 0 \\ b & (m - I) & x \\ 0 & x & (h - I) \end{vmatrix} = 0, \quad (6)$$

where:

g = potential parameter for CH_2F^- , taken as equal to the ionization potential of CH_3F , ((12.80 ev.) (23));

m = the potential parameter for $-\text{CH}_2-$, taken as equal to the ionization potential of CH_4 , ((12.98 ev.) (23));

h = the potential parameter for $-\text{OH}$, taken as equal to the ionization potential of H_2O , ((12.59 ev.) (23));

x = the C - O interaction, ((2.06 ev.) (9));

b = the C - C interaction, ((1.55 ev.) (9)).

The calculated ionization potential value for 2-fluoroethanol using this method is 10.24 ev., compared to the experimental value 11.0 ev.

No value for the C - F interaction was discovered in the literature survey. When reported ionization potentials are used for potential parameters,

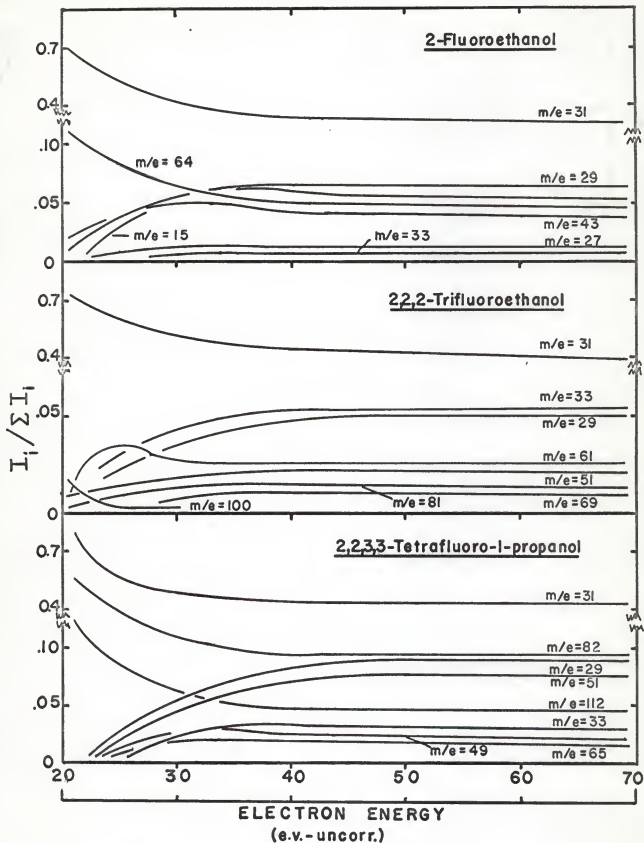


FIGURE 6.

CLASTOGRAMS

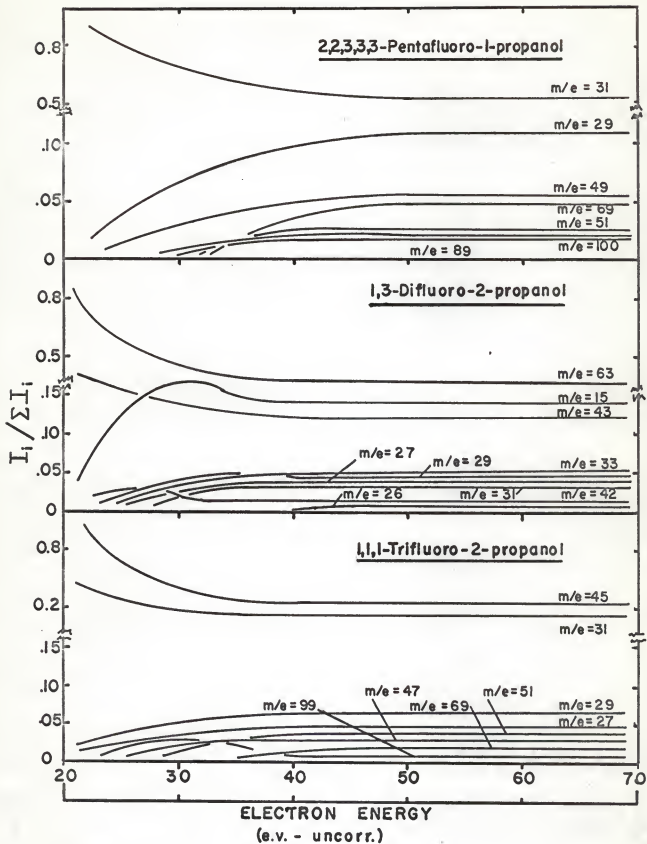


FIGURE 7.

CLASTOGRAMS

the C - F interaction value as shown in Table 7 differs greatly between these two compounds. Calculations of ionization potentials using an interpolated value proved unsuccessful.

A determinantal expression similar to Eq. (6) was used to calculate an ionization potential for 2,2,2-trifluoroethanol. The potential parameter for CF_3^- , taken as equal to $I(CHF_3)$ was substituted for the constant, g. Solution of the resulting equation gave 11.17 ev. as the ionization potential of 2,2,2-trifluoroethanol, a value which is low by approximately 1.5 ev.

Table 7. Summary of Constants Used to Determine Ionization Potentials of 2-Fluoroethanol and 2,2,2-trifluoroethanol.

		(Calc.)	(Meas.)
$t^2(CH_3F)$	(C - F)	0.53	
$t^2(CH_3CH_2F)$	(C - F)	-5.55	
x	(C - O)	1.55 ^a	
b	(C - C)	2.06 ^a	
g	$I(CH_3F)$		12.80 ^b
m	$I(CH_4)$		12.98 ^b
h	$I(H_2O)$		12.59 ^b
f	$I(HF)$		15.77 ^b
p	$I(CHF_3)$		13.84 ^b
	$I(CH_2FCH_2OH)$	11.24	11.0
	$I(CF_3CH_2OH)$	11.17	12.7

^aSee reference (9); ^bsee reference (23).

DISCUSSION

Mass Spectra

The mass spectra of the fluorine-substituted alcohols investigated are of two distinct types. The primary fluoro-alcohols show cracking patterns that are distinctly similar, with the relative abundance of the parent molecule-ion being low in the fluoroethanols and completely absent in the fluoro-propanols. The ion most abundant in these mass spectra is formed by cleavage of the C-C bond adjacent to the carbon containing the hydroxyl group and is characteristic of many low molecular weight non-fluorinated alcohols. The second most abundant peak in the primary alcohols corresponds to the CHO^+ ion at $m/e = 29$. This ion is formed by the removal of two hydrogen atoms from the dominant species.

The number of positive ions increases significantly in the spectra of the primary propanols in the upper ranges, although the abundances of these species are very low in all but a few instances. The CHF_2^+ and $\text{C}_2\text{H}_3\text{F}_3\text{O}^+$ ions are the only ones other than CHO^+ and CH_3O^+ that are common to more than one spectrum.

The spectra of the secondary fluoro-alcohols are qualitatively similar also. Three ions of quite large relative abundance are immediately identified in the mass spectrum of 1,3-difluoro-2-propanol at m/e values of 15, 43, and 63, corresponding to the CH_3^+ , $\text{C}_2\text{H}_3\text{O}^+$ and $\text{C}_2\text{H}_4\text{FO}^+$ ions, respectively. It is observed that the relative abundances of the group of ions in the vicinity of $m/e = 31$ are significantly smaller in the secondary alcohols; however, the number of ions in this range is notably larger. The mass spectrum of 1,1,1-trifluoro-2-propanol exhibits the same general pattern as that of 1,3-difluoro-2-propanol with the exception of the CH_3^+ ion. On the basis of the structures of these two compounds, the CH_3^+ ion might be expected to be present in greater

relative abundance in the mass spectrum of 1,1,1-trifluoro-2-propanol. No parent molecule-ion peak was discovered in the spectra of the secondary propanols.

Clastograms

The changes in ion abundances with the electron energy for all of the fluorine-containing compounds investigated are similar in many respects; however, they differ sufficiently to merit a separate consideration of each clastogram.

The intensities of the two ions, $m/e = 31$ and $m/e = 64$, in the spectrum of 2-fluoroethanol both increase significantly at lower electron energies. The ratio of the relative abundances of $m/e = 31$ to $m/e = 64$ varies only slightly over the entire electron energy scale though decreasing somewhat at lower values. Ions of $m/e = 29$, 15, and 43 closely parallel each other at the higher voltages and show only minor variations in the lower range. The ions at $m/e = 33$ and 27 show essentially the same behavior throughout the entire range and are characterized by very low intensities. These ions disappear from the spectrum at voltages somewhat in excess of the appearance potentials.

In the diagram for 2,2,2-trifluoroethanol the ion $m/e = 31$ shows nearly identical behavior to that observed in 2-fluoroethanol and in the two primary propanols. The molecule-ion for this compound is present in small quantity at low voltages, but disappears completely as the electron energy increases. At lower voltages the $m/e = 61$ ion increases and reaches a maximum at about 25 volts, then decreases and parallels the performance of the $m/e = 51$ ion. For $m/e = 33$ and 29 and $m/e = 81$ and 69 the same general trend is observed in that these pairs grow in at lower voltages, reach a maximum at approximately 35 volts and then remain in the spectrum at approximately the same proportions

as the ionizing electron energy is further increased.

The clastogram of 2,2,3,3-tetrafluoro-1-propanol shows three ions, $m/e = 31$, 82, and 112, that increase in relative abundances at the lower voltages. All other ions grow in at approximately 25 volts, approach the maximum in the vicinity of 35 volts and remain present in fairly constant proportions throughout the remainder of the electron energy scale.

The general appearance of the clastogram of 2,2,3,3-pentafluoro-1-propanol resembles that of 2,2,3,3-tetrafluoro-1-propanol with the notable exception that only one ion, $m/e = 31$, shows an increase in quantity at the lower voltages.

While only a few of the curves of the two clastograms represent the same ions, the general appearance and performance of the ions are quite similar, with the possible exception of $m/e = 69$ of 2,2,3,3-pentafluoro-1-propanol. This ion appears in the mass spectrum of the compound at a value in excess of 30 volts and increases to a maximum near 45 volts.

Clastograms of the secondary fluoro-alcohols are very much alike, with numerous ions of low intensities entering in the 25-30 volt range. These ions approach a maximum near 40 volts, somewhat higher than others discussed, then maintain very nearly constant intensities throughout the remaining section of the energy scale. The ion, $m/e = 15$, is of interest in the diagram of 1,3-difluoro-2-propanol. This ion must form through a rearrangement following the ionizing process. The CH_3^+ ion appears with increasing intensity at lower voltages. At 25 volts the intensity of the ion decreases somewhat but remains throughout the range in rather large abundances. The ions, $m/e = 42$ of 1,3-difluoro-2-propanol and $m/e = 99$ or 1,1,1-trifluoro-2-propanol, while not formed through rearrangements, follow the same general pattern but to a much lesser extent.

2-Fluoroethanol

The heat of formation of this compound in the gas phase has not been reported in the literature. A $\Delta H_f(\text{CH}_2\text{FCH}_2\text{OH}) = -101$ kcal/mole was used in calculations of the heats of formation of the ions produced from 2-fluoroethanol. Calculation of the heat of formation of 2-fluoroethanol involved the arithmetical operation of adding the heat content contributions of hydrocarbon groups (8) in the molecule and including a contribution for a single fluorine atom of -49 kcal/mole based on comparison of other fluorinated organic compounds. The reported value of -109.7 kcal/mole for liquid 2-fluoroethanol (38) makes the -101 kcal/mole (gas) reasonable. Throughout the discussion, heats of formation of the compounds will be determined using Franklin's group summation principle plus suitable correction factors to compensate for the presence of more than one fluorine atom on a single carbon atom.

m/e 15. The m/e 15 ion is CH_3^+ formed by a rearrangement in the molecule-ion as the single fluorine atom is ejected. The formation of CH_2O as the other neutral fragment gives $\Delta H_f^+(\text{CH}_3) = 273$ kcal/mole, a value in fair agreement with the 262 kcal/mole reported by Field and Franklin (7).

m/e 27. Only one ion in the mass spectrum of 2-fluoroethanol can have this m/e value. It is C_2H_3^+ . This ion is frequently observed in the mass spectra of various types of organic compounds including sulfur compounds and certain cyclic compounds. The value, $\Delta H_f^+(\text{C}_2\text{H}_3) = 312$ kcal/mole, is somewhat higher than other reported values (7).

m/e 29. Of the two possible ions with m/e 29, only the CHO^+ ion can logically result from electron impact of the 2-fluoroethanol molecule. The calculated heat of formation of this ion consistent with the energetics and the reported process is 201 kcal/mole.

m/e 31. Both the CF^+ and CH_3O^+ ions can appear in the mass spectrum of 2-fluoroethanol. The low appearance potential of 12.6 ev. and the large relative abundance of the ion makes the selection of CH_3O^+ tenable. A value of $\Delta H_f^+(CH_3O) = 173$ kcal/mole (7) was used to determine the heat of formation of the CH_2F radical equal to 17 kcal/mole.

m/e 33. One might expect the CH_2F^+ ion to appear in much greater abundance than the CH_3^+ ion in the spectrum of this compound, since this ion conceivably can be formed through a simple cleavage of a carbon-carbon bond. However, this was not the case even though the appearance potential of the CH_2F^+ ion is somewhat lower than that of the CH_3^+ ion. The reported heat of formation of the CH_2F^+ ion is 228 kcal/mole and is approximately 30 kcal/mole higher than the value listed for this ion by Lifshitz and Long (29).

m/e 43. A selection of $C_2H_3O^+$ over C_2F^+ for the ion at $m/e = 43$ and the process in which a hydrogen molecule and a fluorine atom are formed results in a calculated heat of formation for the $C_2H_3O^+$ ion of 201 kcal/mole. This value is about one electron volt high when compared with other values (7). No reason for the difference can be explained.

m/e 64. The heat of formation for the parent molecule-ion, $C_2H_5FO^+$, formed by the removal of a single electron from the molecule is 153 kcal/mole. The calculated heat of formation of the molecule-ion based on the experimentally determined ionization potential of 11.00 ± 0.15 ev. is about 35 kcal/mole more negative than the value of 188 kcal/mole reported for the $C_2H_6O^+$ ion from ethanol. Exchange of a hydrogen for fluorine in an ion of this type seems to increase the stability of the charged species by about 1.5 electron volts.

2,2,2-Trifluoroethanol

The heat of formation of 2,2,2-trifluoroethanol was taken as -205 kcal/mole for the calculation of heats of formation of the ions from this compound. The method used has been discussed earlier; however, an estimated stabilizing factor equal to -12 kcal/mole has been included to compensate for the three fluorine atoms attached to a single carbon atom.

m/e 29. This ion is formed by breaking the carbon-carbon bond and the expulsion of the two hydrogen atoms attached to the hydroxyl carbon. Using this process and an appearance potential of 17.7 ev., the calculated heat of formation of the CHO^+ ion is 214 kcal/mole. The heat of formation of the CF_3 radical equal to -115 kcal/mole was used in the calculation.

m/e 31. The relatively low appearance potential and the large abundance of this ion again make the selection of the CH_3O^+ ion most probable. The 173 kcal/mole mentioned earlier is used to calculate the heat of formation of the CF_3 radical equal to -71 kcal/mole. The value obtained is in poor agreement with the value used in the previous process, and the discrepancy cannot be explained by the author. Values in this vicinity have been reported (7); however, there is strong evidence in favor of -115 kcal/mole as the heat of formation of CF_3 (37, 39).

m/e 33. The ion at $m/e = 33$ is CH_2F^+ formed through a rearrangement involving a migration of a fluorine from the terminal carbon atom. Assuming the formation of CF_2 and OH as neutral radicals, the calculated heat of formation of the ion is then equal to 235 kcal/mole. This value is in good agreement with that obtained for this ion in the spectrum of 2-fluoroethanol.

m/e 51. The ion at this m/e value most assuredly is CHF_2^+ , although no process consistent with the listed appearance potential could be written that

gave an acceptable value for the heat of formation of this ion estimated to be around 190 kcal/mole.

m/e 61. This ion is $C_2H_2FO^+$. The process is considered to form a molecule of hydrogen fluoride plus a fluorine atom. The heat of formation of the $C_2H_2FO^+$ ion based on this process and the reported appearance potential is 210 kcal/mole.

m/e 69. This ion is probably CF_3^+ . Field and Franklin (7) have estimated a value for the heat of formation of this ion as 140-180 kcal/mole. The value obtained here is 118 kcal/mole. The general structure of the molecule leads one to expect this ion to be present in the mass spectrum in much larger relative abundance, since it can be formed through cleavage of the carbon-carbon bond. This expectation is not in agreement with the observed results as shown by the less than 4% relative abundance of this ion.

m/e 81. The ion at $m/e = 81$ is chosen to be $C_2H_3F_2O^+$, formed by the removal of a single fluorine atom from the molecule-ion. A calculated value, consistent with the observed appearance potential and the heat of formation of the single fluorine atom, for $\Delta H_F^+(C_2H_3F_2O) = 132$ is obtained.

m/e 100. Consideration of the extremely low relative abundance of this peak in the region of the Hg^{++} ion was expected to present minor problems. The appearance potential reported here contrasted with that of the mercury (II) ion definitely identifies the 12.7 ev. as the ionization potential of 2,2,2-trifluoroethanol. The $C_2H_3F_3O^+$ ion is formed by the removal of a single electron from the molecule. The calculated heat of formation of this molecule-ion is 88 kcal/mole.

2,2,3,3-Tetrafluoro-1-propanol

A calculated value of -250 kcal/mole for the heat of formation of 2,2,3,3-tetrafluoro-1-propanol includes an estimated contribution of about -3 kcal/mole for each instance where more than one fluorine atom is bonded to a single carbon atom. This value in conjunction with the listed appearance potentials was used to determine the heats of formation of ions in the cases where suitable processes consistent with calculated energetics could be determined.

Due to the increased complexity of the 2,2,3,3-tetrafluoro-1-propanol molecule, the number of neutral radicals and atoms possible and the generally high appearance potentials, suitable ion formation processes for $m/e = 29, 33, 49,$ and 51 were not readily discernable. The absence of known radical heats of formation eliminated even a qualitative conjecture concerning the heats of formation of these ions. However, these ions can be identified in the spectrum. The $m/e 29$ ion is CHO^+ ; the $m/e 33$ ion is CH_2F^+ ; the $m/e 49$ ion is CH_2FO^+ ; and the $m/e 51$ ion is CHF_2^+ , chosen over the only other possibility, CH_4FO^+ .

$m/e 31$. The calculated heat of formation of the CH_3O^+ ion based on the listed process is 154 kcal/mole. This value is considerably lower than that reported for $\Delta H_f^+(\text{CH}_3\text{O})$ (7).

$m/e 65$. A rearrangement involving the replacement of two fluorine atoms by two hydrogen atoms results in the formation of the $\text{C}_2\text{H}_3\text{F}_2^+$ ion at $m/e = 65$. The heat of formation of this ion determined using the process listed is 180 kcal/mole. The heat of formation of the C_2H_5^+ by comparison is given as 224 kcal/mole (7). An estimation of the change expected in the heat of formation of this ion when two hydrogen atoms are replaced by fluorine atoms makes the

reported $\Delta H_f^+(C_2H_3F_2)$ reasonable.

m/e 82. Two ions corresponding to $m/e = 82$ are possible in the mass spectrum of this compound, $C_2H_4F_2O^+$ and $C_2HF_3^+$. The $C_2H_4F_2O^+$ ion, necessarily formed through a rearrangement, plus the neutral CF_2 radical gives a calculated heat of formation of the ion equal to 92 kcal/mole. This value is approximately 100 kcal/mole lower than the value reported for the $C_2H_6O^+$ ion originating from ethanol (7). A second process in which the $C_2HF_3^+$ ion is formed can occur without rearrangement. The neutral fragments, HF and CH_2O , result in $\Delta H_f^+(C_2HF_3) = 149$ kcal/mole. This has been selected to represent the ion formation process.

m/e 112. Both the $C_3F_4^+$ and the $C_3H_3F_3O^+$ ions can occur at this m/e value. The formation of the $C_3H_3F_3O^+$ accompanied by the neutral HF fragment has been chosen as most probable. Based on this assumption the calculated heat of formation of the $C_3H_3F_3O^+$ ion is 80 kcal/mole.

2,2,3,3,3-Pentafluoro-1-propanol

The calculated heat of formation of 2,2,3,3,3-pentafluoro-1-propanol determined by Franklin's method includes a correction factor of -15 kcal/mole to -18 kcal/mole contributed by the carbon-fluorine bond arrangement. In the determination of heats of formation of ions, $\Delta H_f(CF_3CF_2CH_2OH) = -310$ kcal/mole was used.

The ions of $m/e = 49$, 51, and 69 are unquestionably CH_2FO^+ , CHF_2^+ , and CF_3^+ , respectively. No heats of formation were determined for these ions. Any attempt to justify a reasonable heat of formation for these ions involves estimations of heats of formation of the possible fragments, consequently no processes have been included.

m/e 29. The ion corresponding to $m/e = 29$ is CHO^+ . On the assumption

that C_2F_4 , F and H_2 are the neutral products resulting from ionization of the molecule followed by dissociation, $\Delta H_f^+(\text{CHO})$ is 227 kcal/mole. This value is considerably higher than other values for this ion determined in this work and the value reported by Franklin (7), but agrees favorably with results obtained for this ion observed in substituted oxiranes (41). Although the value reported here is rather high, the assigned process is considered reasonable.

m/e 31. The comparatively low appearance potential of this most abundant ion leads to the assumption that it is CH_3O^+ . The process listed is quite reasonable. The magnitude of the appearance potential indicates the ease with which the ion is formed. A calculated heat of formation of the C_2F_5 radical equal to -190 kcal/mole results when $\Delta H_f^+(\text{CH}_3\text{O}) = 173$ kcal/mole (7) is used.

m/e 83. The neutral fragments listed for this process must be regarded as a "best selection". It is not unreasonable to predict the formation of either CHO and F_2 or CHO and 2F as the fragments accompanying ionization of the molecule-ion followed by dissociation. Either of these choices result in an unrealistically low value for $\Delta H_f^+(\text{C}_2\text{H}_2\text{F}_3)$. Selection of FCO and HF is chosen. Although $\Delta H_f^+(\text{C}_2\text{H}_2\text{F}_3) = 158$ kcal/mole is somewhat higher than might be expected, a qualitative comparison to the heat of formation of $C_2H_3F_2^+$ equal to 180 kcal/mole from 2,2,3,3-tetrafluoro-1-propanol indicates the reported value is not unreasonable.

m/e 100. The ion corresponding to $m/e = 100$ might be either $C_2F_4^+$ or $C_2H_3F_3O^+$. However, since the $C_2F_5^+$ ion is absent from the mass spectrum, it was concluded that the $C_2F_4^+$ ion is the second choice. The neutral radical is then CF_2 . The $\Delta H_f^+(\text{C}_2\text{H}_3\text{F}_3\text{O})$ is 62 kcal/mole, a value of the same order of magnitude as the one reported for this ion observed in the mass spectrum of 2,2,2-trifluoroethanol.

1,3-Difluoro-2-propanol

A calculated heat of formation of this compound based on Franklin's method (8) is -155 kcal/mole. Here a -4 kcal/mole represented the estimated increase in molecular stability attributed to the position of the fluorine atoms within the molecule.

Only qualitative information for heats of formation of ions was obtainable from the mass spectrometric study of this compound. The generally high appearance potentials and the lack of reliable heat of formation data for certain of the numerous carbon-hydrogen-fluorine neutral radicals prevented the determination of any valid conclusions regarding either the ion formation process or the heat of formation of the ion.

m/e 15. Only a singular choice exists for this ion. It is CH_3^+ . This ion is formed through rearrangements within the molecule following the ionization process. The large relative abundance of this species shows that this ion forms easily. No realistic ion formation process could be assigned to evaluate the heat of formation of the ion.

m/e 26. One ion with $m/e = 26$ exists in the mass spectrum of 1,3-difluoro-2-propanol. It must be C_2H_2^+ . A heat of formation of the ion was not determined.

m/e 27. This ion is C_2H_3^+ . It logically is formed along with OH, F and CH_2F as neutral fragments; however, this assumption leads to the heat of formation of the ion equal to 188 kcal/mole. This value is much too low, and any attempt at further fragmentation reduces this value even more.

m/e 29. This ion is CHO^+ . A value for the heat of formation of the ion determined using the assumption that the neutral fragments are CH_3F and CH_2F , as shown in the first process in Table 5, is 251 kcal/mole. In the second pro-

cess, a somewhat irregular reaction, in which the terminal CH_2F groups of the parent molecule combine immediately following the ionization process to form $\text{C}_2\text{H}_4\text{F}_2$ and a single hydrogen atom gives a $\Delta H_f^+(\text{CHO}) = 223$. This value is in very close agreement with reported values for this ion observed in other compounds (10).

m/e 31. It was not possible to determine that this ion is not CF^+ . However, the CH_3O^+ ion is the one selected based on the results of earlier discussions. No suitable process was obvious that would give a reasonable value for the heat of formation of the ion.

m/e 33. This ion probably is CH_2F^+ . Consideration of the general structure of the molecule would show that this ion should be present in the mass spectrum of the compound in fairly large abundance. This is, indeed, the case. The relative abundance of this species is significantly greater than observed in the primary alcohols. Here the ion is formed by a simple process, whereas in the primary alcohols studied, with the exception of 2-fluoroethanol, it is formed through rearrangements.

m/e 42. No conclusive evidence for the presence of the $\text{C}_2\text{H}_2\text{O}^+$ can be established on the basis of the appearance potential. It is extremely unlikely that the other two possible ions at this m/e value can form during the short time interval following ionization of the molecule. Therefore, by a process of elimination this ion is concluded to be $\text{C}_2\text{H}_2\text{O}^+$.

m/e 43. The relative abundance of this species is considerably greater than that observed in the mass spectrum of 2-fluoroethanol. Three ions are possible at this m/e value; however, the best choice is $\text{C}_2\text{H}_3\text{O}^+$. If this selection is correct, then three equally likely processes can be written. The calculated heat of formation of the ion is 207 kcal/mole if the neutral fragments are as listed in the first process shown in Table 5. Consideration of

the second process results in a value equal to 193 kcal/mole. The third process yields $\Delta H_f^+(C_2H_3O) = 209$ kcal/mole. Any of these values agrees quite well with the heat of formation of this ion from ethanol (7).

m/e 63. This ion is the most abundant in the mass spectrum of 1,3-difluoro-2-propanol. The low appearance potential shows the ion is probably formed by a simple process. If the neutral radical is CH_2F , the heat of formation of the ion is 101 kcal/mole. In comparison, values for the heat of formation of the $C_2H_5O^+$ ion range from 148 kcal/mole to 218 kcal/mole, depending upon the source of the ion. When the lower value is considered, $\Delta H_f^+(C_2H_4FO)$ by comparison is very reasonable.

1,1,1-Trifluoro-2-propanol

The heat of formation of 1,1,1-trifluoro-2-propanol used to determine the heats of formation of the ion observed in the mass spectrum of the compound was -215 kcal/mole. This value was calculated using the methods discussed earlier.

m/e 15. The ion corresponding to $m/e = 15$ is CH_3^+ . Assuming the neutral products to be CHO, H and CF_3 , $\Delta H_f^+(CH_3)$ is calculated to be 321 kcal/mole. The large error in reproducibility necessarily makes the process questionable, and the heat of formation reported here is quite high compared to other results (7).

m/e 19. The ion quite obviously is F^+ . A process consistent with the listed energetics could not be written to represent the ionization process.

m/e 27. At this m/e value the only ion possible is $C_2H_3^+$. Acceptance of the process in which OH and CF_3H are the neutral radicals gives $\Delta H_f^+(C_2H_3) = 315$ kcal/mole. It is not understood why this value is significantly higher than that reported by other investigators (7).

m/e 29. The ion of $m/e = 29$ formed by the removal of all groups from the central carbon atom except the OH is CHO^+ . The calculated heat of formation of the ion based on the listed process is 190 kcal/mole.

m/e 31. If the ion at $m/e = 31$ is CH_3O^+ , it must be formed through a rearrangement in which a hydrogen is transferred from the adjacent methyl group. The expected radicals would be CF_3 and CH_2 . Calculation of $\Delta H_f^+(\text{CH}_3\text{O})$ based on this process is 138 kcal/mole. Any attempt at further fragmentation reduces this value even more. If an estimated heat of formation of $\text{C}_2\text{H}_2\text{F}_3$ equal to -75 kcal/mole is selected, $\Delta H_f^+(\text{CH}_3\text{O})$ becomes 167 kcal/mole.

m/e 33. This ion is CH_2F^+ . No process consistent with the energetics could be discovered. The ion is probably formed through a rearrangement involving the transfer of a fluorine, although the manner in which this migration occurs is not readily obvious. It was impossible to deduce a process identifying ion formation.

m/e 43. This ion is assumed to be $\text{C}_2\text{H}_3\text{O}^+$, the same as observed in 1,3-difluoro-2-propanol. The radicals, CF_2 , HF and H permit a calculated $\Delta H_f^+(\text{C}_2\text{H}_3\text{O}) = 183$ kcal/mole.

m/e 45. This most abundant ion is $\text{C}_2\text{H}_5\text{O}^+$, formed through the simple process of eliminating a CF_3 radical from the ion-molecule. The calculated heat of formation of the ion is 188 kcal/mole.

m/e 47. This ion conceivably could be CFO^+ at $m/e = 47$, however the $\text{C}_2\text{H}_4\text{F}^+$ ion has been selected as the most probable. If this assumption is accepted, then the ion must occur through replacement of the secondary OH group by a fluorine atom. Radicals expected would be CF_2 and OH. The calculated $\Delta H_f^+(\text{C}_2\text{H}_4\text{F}) = 188$ kcal/mole. Comparison of this value to that of $\Delta H_f^+(\text{C}_2\text{H}_5) = 224$ kcal/mole indicates that the reported heat of formation of this ion is

reasonable.

m/e 51. Only one ion sensibly can exist at this m/e value. It is CHF_2^+ . Multiple choices of radicals containing carbon, hydrogen and fluorine prevented the assigning of a suitable ionization process consistent with observed and reported energetics. The ion probably is formed by the transfer of a hydrogen atom from the central carbon atom.

m/e 69. The CF_3^+ ion occurs in the spectrum of 1,1,1-trifluoro-2-propanol in slightly greater intensity than the CH_3^+ . Both ions are formed by simple processes involving cleavage of the carbon-carbon bonds of the central carbon atom. If the radicals are as shown for this process in Table 6, then $\Delta H_f^+(\text{CF}_3) = 120$ kcal/mole, compared to $\Delta H_f^+(\text{CF}_3) = 118$ kcal/mole for this ion from 2,2,2-trifluoroethanol.

m/e 79. Both the $\text{C}_2\text{HF}_2\text{O}^+$ ion and the $\text{C}_3\text{H}_5\text{F}_2^+$ ion have this m/e value. It seems quite unlikely that the OF radical would occur as the only neutral product. Choice of the $\text{C}_2\text{HF}_2\text{O}^+$ ion and CH_3 plus HF neutral fragments yields $\Delta H_f^+(\text{C}_2\text{HF}_2\text{O}) = 163$ kcal/mole.

m/e 99. The ion at m/e = 99 can only be formed through the removal of a CH_3 radical from the molecule-ion. This simple process results in the formation of $\text{C}_2\text{H}_3\text{F}_3\text{O}^+$. The calculated heat of formation of this ion is 78 kcal/mole. This value is in fair agreement with that reported for the heat of formation of the molecule-ion of 2,2,2-trifluoroethanol.

SUMMARY

The appearance of the mass spectra of the primary fluoro-alcohols differs from that of the secondary fluorine-substituted alcohols. In the primary alcohols, the major ionic species was CH_3O^+ . The general pattern of these spectra

are qualitatively similar with the greater abundances occurring at the smaller m/e values. In addition, greatly reduced intensities of ions in the larger mass ranges were observed. No really significant differences appear among the spectra of the primary alcohols.

Depending on the molecule, the dominant ion observed in the secondary alcohols is other than CH_3O^+ . In 1,3-difluoro-2-propanol and in 1,1,1-trifluoro-2-propanol the major ions are $\text{C}_2\text{H}_4\text{FO}^+$ and $\text{C}_2\text{H}_5\text{O}^+$, respectively.

Heats of formation of these compounds were calculated using a modified Franklin method. Estimated corrections were included to compensate for increased molecular stability arising from carbon-fluorine bonding. The heats of formation of the compounds used to determine the heats of formation of the positive ions are: $\Delta H_f(\text{CH}_2\text{FCH}_2\text{OH}) = -101$ kcal/mole; $\Delta H_f(\text{CF}_3\text{CH}_2\text{OH}) = -205$ kcal/mole; $\Delta H_f(\text{CHF}_2\text{CF}_2\text{CH}_2\text{OH}) = -250$ kcal/mole; $\Delta H_f(\text{CF}_3\text{CF}_2\text{CH}_2\text{OH}) = -310$ kcal/mole; $\Delta H_f(\text{CH}_2\text{F})_2\text{CHOH} = -155$ kcal/mole; and $\Delta H_f(\text{CF}_3\text{CHOHCH}_3) = -215$ kcal/mole.

Interesting rearrangements were observed involving ions composed of carbon, hydrogen and oxygen as well as ions containing carbon, hydrogen, fluorine and oxygen.

Ionization potentials for 2-fluoroethanol and 2,2,2-trifluoroethanol were calculated and compared to experimentally determined values; $I(\text{CH}_2\text{FCH}_2\text{OH}) = 11.0$ ev. and $I(\text{CF}_3\text{CH}_2\text{OH}) = 12.7$ ev.

This mass spectrometric study of fluorine containing alcohols has provided useful data in an area where relatively little information is available. Also, this work indicates the necessity of additional mass spectrometric studies of fluorinated alcohols and other fluorine-containing organic compounds.

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REFERENCES

1. Beynon, J. H., "Mass Spectrometry and Its Application to Organic Chemistry", Elsevier Publishing Co., New York, 1960, p. 53.
2. Cameron, A. E., and D. F. Eggers, Jr., Rev. Sci. Instr., 19, 605 (1948).
3. Campbell, K. N., J. O. Knobloch and B. K. Campbell, J. Am. Chem. Soc., 72, 4380 (1950).
4. Cherbuliez, E., et al., Helv. Chim. Acta., 43, 1148 (1960).
5. Dibeler, V. H., Anal. Chem., 26, 58 (1954).
6. Daus, H. C., Ind. Eng. Chem., 47, 1445 (1955).
7. Field, F. H., and J. L. Franklin, "Electron Impact Phenomena and the Properties of Gaseous Ions", Academic Press, New York, N. Y., 1957.
8. Franklin, J. L., Ind. Eng. Chem., 41, 1070 (1949).
9. Franklin, J. L., J. Chem. Phys., 22, 1304 (1954).
10. Gallegos, E. J., and R. W. Kiser, J. Phys. Chem., 66, 136 (1962).
11. Gallegos, E. J., Doctor's Dissertation, "Mass Spectrometric Investigation of Saturated Heterocyclics", Kansas State University, 1962.
12. Gohlke, R. S., Anal. Chem., 31, 535 (1959).
13. Hall, G. G., Proc. Roy. Soc. (London), A205, 541 (1951).
14. Hall, G. G., Proc. Roy. Soc. (London), A213, 102 (1952).
15. Hall, G. G., Trans. Faraday Soc., 49, 113 (1953).
16. Hall, G. G., Trans. Faraday Soc., 50, 319 (1954).
17. Hall, G. G., and J. Lennard-Jones, Proc. Roy. Soc. (London), A202, 155 (1950).
18. Hall, G. G., and J. Lennard-Jones, Proc. Roy. Soc. (London), A205, 357 (1951).
19. Hoffman, F. W., F. J. Ess and R. P. Usinger, Jr., J. Am. Chem. Soc., 78, 5817 (1956).
20. Husted, D. R., and A. H. Ahlbrecht, J. Am. Chem. Soc., 74, 5422 (1952).
21. Katzenstein, H. S., and S. S. Friedland, Rev. Sci. Instr., 26, 324 (1955).
22. Kiser, R. W., and E. J. Gallegos, J. Phys. Chem., 66, 947 (1962).

23. Kiser, R. W., "Tables of Ionization Potentials", U. S. Atomic Energy Commission, TID-6142, 1963.
24. Knunyants, I. L., O. V. Kil'disheva and I. P. Petrov, Zhur. Obshechi. Khim., 19, 95 (1949), [see Chem. Abstr., 43:6163c (1949)].
25. Lennard-Jones, J., Proc. Roy. Soc. (London), A198, 1 (1949).
26. Lennard-Jones, J., Proc. Roy. Soc. (London), A198, 14 (1949).
27. Lennard-Jones, J., and G. G. Hall, Discussions Faraday Soc., 10, 18 (1951).
28. Lennard-Jones, J., and J. A. Pople, Proc. Roy. Soc. (London), A202, 166 (1950).
29. Lifshitz, C., and F. A. Long, "Appearance Potentials and Mass Spectra of Fluorinated Olefins", presented at The Tenth Annual ASTM Committee E-14 Meeting on Mass Spectrometry, New Orleans, La., June 3-8, 1962.
30. Lossing, F. P., A. W. Tickner and W. A. Bryce, J. Chem. Phys., 19, 1254 (1951).
31. McBee, E. T., C. E. Hathaway and C. W. Roberts, J. Am. Chem. Soc., 78, 3851 (1956).
32. Majer, J. R., in "Advances in Fluorine Chemistry", Vol. 2, edited by M. Stacey, J. C. Tatlow and A. G. Sharpe, Butterworths, Washington, 1961, pp. 55-103; and C. R. Patrick, *ibid.*, pp. 1-34.
33. Majer, J. R., and C. R. Patrick, Nature, 192, 866 (1961).
34. Margrave, J. L., Nature, 197, 376 (1963).
35. Moore, C. E., "Atomic Energy Levels", National Bureau of Standards Circular 467, Vol. III, 1958.
36. Neugebauer, C. A., and J. L. Margrave, J. Phys. Chem., 62, 1043 (1958).
37. Reed, R. I., and W. Snedden, Trans. Faraday Soc., 54, 301 (1958).
38. Rossini, F. D., D. D. Wagman, W. H. Evans, S. Levine and I. Jaffee, "Selected Values of Chemical Thermodynamic Properties", National Bureau of Standards Circular 500, U. S. Government Printing Office, Washington, D. C., 1952.
39. Steele, W. C., and F. G. A. Stone, J. Am. Chem. Soc., 84, 3450 (1962).
40. Szwarc, M., Chem. Revs., 47, 75 (1950).
41. Wada, Y., and R. W. Kiser, J. Phys. Chem., 66, 1652 (1962).
42. Warren, J. W., Nature, 165, 810 (1950).

43. Wiley, W. C., Science, 124, 817 (1956).
44. Wiley, W. C., and I. H. McLaren, Rev. Sci. Instr., 26, 1150 (1955).
45. Zwolinski, B. J., A. Danti, B. S. Darrow and A. L. Risinger, "Mass Spectral Data", Manufacturing Chemists Association Research Project, Agricultural and Mechanical College of Texas, College Station, Texas, 1961.

MASS SPECTROMETRIC INVESTIGATION
OF SOME FLUORINATED ALCOHOLS

by

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Certain qualitative similarities exist among the mass spectra of the primary fluoroalcohols. In the mass spectra of 2-fluoro- and 2,2,2-trifluoroethanol and 2,2,3,3-tetrafluoro- and 2,2,3,3,3-pentafluoro-1-propanol the dominant species is the CH_2O^+ ion formed by cleavage of the $-\text{CH}_2\text{OH}$ group from the parent molecule. Differences by comparison noted in the mass spectra of 1,3-difluoro- and 1,1,1-trifluoro-2-propanol are that ions other than CH_2O^+ are most abundant and that a significantly greater number of ions form in the lower mass ranges. The ion of greatest relative abundance in the mass spectrum of 1,3-difluoro-2-propanol is $\text{C}_2\text{H}_4\text{FO}^+$. In 1,1,1-trifluoro-2-propanol the dominant species is the $\text{C}_2\text{H}_5\text{O}^+$ ion.

No general pattern exists for the ion formation processes. Increased possibilities for various carbon-hydrogen-fluorine radicals resulting from the high appearance potential values made selection of a valid process uncertain for several ions observed in the substituted propanol spectra. Limited heat of formation data was also a contributing factor.

Experimentally determined ionization potentials agreed poorly with the values calculated using the group orbital treatment. Observed ionization potentials for 2-fluoroethanol and 2,2,2-trifluoroethanol were $11.0_0 \pm 0.1_5$ ev. and 12.7 ± 0.3 ev., respectively. Parent molecule-ion peaks were absent in the spectra of the other fluorine substituted alcohols investigated. Rearrangements were observed for certain fluorohydrocarbon ion formations.

This mass spectrometric investigation of fluorine containing alcohols has provided useful information on ionization and appearance potentials, probable ion formation processes and heats of formation of resulting ions. Also, this study has indicated the somewhat anomalous behavior of many fluorine-containing ions, and has suggested additional studies aimed at improving our understanding of this class of interesting compounds.