

respectively. The distributed dipole approximation requires that ζ_N vary considerably from compound to compound for the best fit. The average value of $\zeta_N = 0.77$ gives a small improvement over the point-dipole approximation. However, such a value for ζ_N is inconsistent with the fact that compounds **3** and **6**, which have different geometries for the N-O groups than **2**, **4** and **5**, all fall on an extremely good least-squares line for a plot of D_{obsd} vs. $1/r_{\text{NN}}^3$.

These difficulties can be resolved if, for the distance range examined here (5.7–8.1 Å), the nitroxide biradicals are not 100% in the triplet state. The slope of eq 4 implies that the nitroxide biradicals are 72% in the triplet state and 28% in the singlet state. For $r_{\text{NN}} > 8.1$ Å the fraction in the triplet state should increase, thereby increasing the slope of the plot of D_{obsd} vs. $1/r_{\text{NN}}^3$. Ultimately the curve should pass through the origin of the plot. For $r_{\text{NN}} < 5.7$ Å the fraction of molecules in the triplet state should decrease, with the slope of the D_{obsd} vs. $1/r_{\text{NN}}^3$ also decreasing. Consequently, eq 4 will give the upper limit for r_{NN} for $r_{\text{NN}} < 5.7$ Å ($D_{\text{obsd}} > 121$ G) and lower limit for $r_{\text{NN}} > 8.1$ Å ($D_{\text{obsd}} < 50$ G).

Assuming that the compounds used in this study are a reasonable sample of nitroxide biradicals, eq 4 can be used to calculate r_{NN} with an average error of 1.4% for $5.7 \text{ Å} \leq r_{\text{NN}} \leq 8.1 \text{ Å}$ ($121 \text{ G} \geq D_{\text{obsd}} \geq 50 \text{ G}$). A dipolar splitting of

50 G is the practical lower limit for which D_{obsd} can be accurately determined (Figures 4b and 5), and so distances between nitroxides more than 8 Å apart cannot be readily determined by ESR.

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Photoionization Mass Spectrometry of 2-Fluoropropane and 2,2-Difluoropropane. A Novel Determination of the Proton Affinity of Vinyl Fluoride and 1,1-Difluoroethylene

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Abstract: Photoionization efficiency curves for the parent and abundant fragment ions from 2-fluoropropane and 2,2-difluoropropane are reported in the energy region between threshold and 13 eV. For 2-fluoropropane an adiabatic ionization potential of 11.08 ± 0.02 eV is determined, with appearance thresholds of 11.23 ± 0.03 , 11.53 ± 0.03 , and 11.75 ± 0.03 eV for the fragment ions $(\text{CH}_3)_2\text{CF}^+$, CH_2CHF^+ , and CH_3CHF^+ , respectively. For 2,2-difluoropropane an adiabatic ionization potential of 11.42 ± 0.02 eV is determined, with appearance thresholds of 11.57 ± 0.03 and 11.81 ± 0.03 eV for the fragment ions CH_2CF_2^+ and CH_3CF_2^+ , respectively. These data are interpreted in terms of the thermochemistry of the neutrals and ions involved. From the difference in thresholds for the loss of CH_4 and CH_3 , a thermochemical cycle yields the proton affinities of vinyl fluoride (173.6 kcal/mol) and 1,1 difluoroethylene (174.8 kcal/mol), independent of the heats of formation of any neutral species.

There have been several recent studies of gas-phase acid-base chemistry which provide insight into the thermochemistry of organic molecules and ions containing fluorine. Fluoride transfer reactions between substituted carbonium ions have been shown to be fast, providing relative $\text{R}^+ - \text{F}^-$ heterolytic bond energies and hence heats of formation of fluorine-substituted cations.²⁻⁴ Proton affinities of fluoroethylenes have been measured, yielding heats of formation of the corresponding conjugate acids, which are fluorinated ethyl cations.⁵ The enthalpy of formation of CF_2 and the difluoromethyl cation have been interrelated by studying proton transfer reactions involving CF_2H^+ .⁶ Thermochemical data for fluorine-substituted anions have been derived from studies of the reactions of F^- and other bases with fluoroalkenes⁷ and fluoroalkanes⁸ in the gas phase. A factor hindering interpretation of experimental results in these studies is the lack of thermo-

chemical data for molecules and ions containing fluorine. This in part can be attributed to experimental difficulties associated with making accurate calorimetric measurements involving fluorinated species. Thus it is not surprising that previous studies^{2,3,6} have uncovered inconsistencies which can be resolved only if the heats of formation used for neutral species are considered to be in error.

Although systematic studies of photoionization efficiencies have been reported for parent and fragment ions derived from lower alkanes,⁹ ketones,¹⁰ and alcohols,¹¹ none of the alkyl fluorides have been studied except methyl fluoride.¹² In view of the ability of photoionization mass spectrometry to determine accurate appearance potentials for fragmentation processes, we have undertaken a series of studies in our laboratories directed at providing more precise thermochemical data for fluorine-substituted neutrals and ions. We wish to report

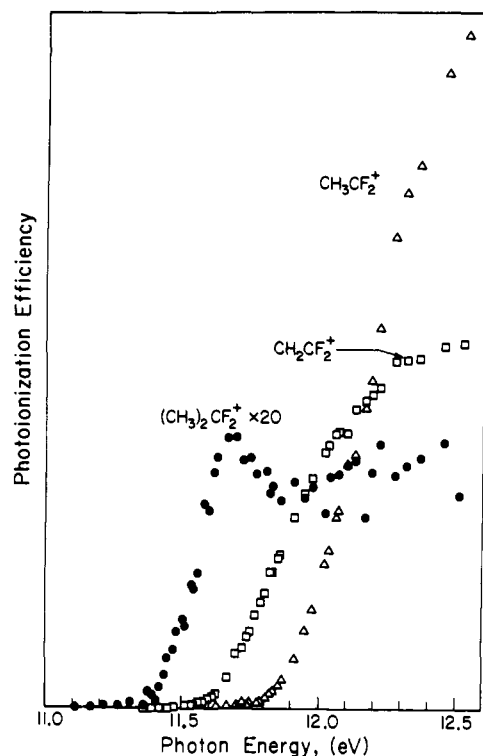


Figure 1. Photoionization efficiency curves for the molecular ion, CH_2CF_2^+ , and CH_3CF_2^+ in 2,2-difluoropropane.

measurements on 2-fluoropropane and 2,2-difluoropropane. Heats of formation of neutral and ionic species in these systems are derived. In addition, a novel measurement of the proton affinities of vinyl fluoride and 1,1-difluoroethylene without reference to the heats of formation of the neutral species is presented.

Experimental Section

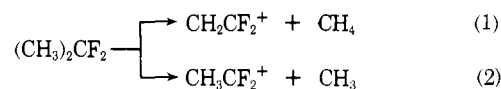
The photoionization mass spectrometer used for these studies has been described in detail.^{13,14} For these studies the hydrogen molecular spectrum at 1 Å fwhm resolution was used as the source of ionizing radiation. Sample pressures were $\sim 8 \times 10^{-5}$ Torr as measured by an MKS Baratron capacitance manometer. Repeller voltages of ~ 0.1 V were used, yielding an ion residence time of approximately 50 μs . When appropriate, ion signals were corrected for ^{13}C isotope contributors. All experiments were performed at ambient temperature (20–25 °C).

2-Fluoropropane was prepared in our laboratory from the reaction of AgF and isopropyl iodide¹⁵ and purified by gas chromatography. The sample of 2,2-difluoropropane was purchased from Cationics, Inc.

Results

2,2-Difluoropropane. Photoionization efficiency data for the molecular ion and the two abundant low-energy fragments of 2,2-difluoropropane are shown in Figure 1. The onset of the molecular ion occurs at 1086 Å, giving a value of 11.42 ± 0.02 eV for the adiabatic ionization potential of the parent neutral. The ionization efficiency rises with photon energy as higher vibrational levels of the ground state ion are populated, peaks at a photon energy slightly above the onset of the first fragmentation, and declines slightly for higher photon energies.

The major fragmentation pathways of (1) and (2) account



for the observed fragment ions. The CH_2CF_2^+ ion formed by loss of CH_4 from the molecular ion (process 1) exhibits an

Table I. Appearance Thresholds and Derived Heats of Formation

Molecule	Ion	AP or IP, eV	$\Delta H_f^\circ_{298}$, kcal/mol
$(\text{CH}_3)_2\text{CF}_2$	$(\text{CH}_3)_2\text{CF}_2^+$	11.42 ± 0.02	-129.8 ± 3.0^a
	CH_2CF_2^+	11.57 ± 0.03	133.5 ± 3.5
	CH_3CF_2^+	11.81 ± 0.03	154.8 ± 2.6^b
$(\text{CH}_3)_2\text{CHF}$	$(\text{CH}_3)_2\text{CHF}^+$	11.08 ± 0.02	108.5 ± 3.2
	$(\text{CH}_3)_2\text{CF}^+$	11.23 ± 0.03	-69.0 ± 1.0^b
	CH_2CHF^+	11.53 ± 0.03	186.5 ± 1.5
$\text{CH}_3\text{CH}_2\text{F}$	CH_3CHF^+	11.75 ± 0.03	138.0 ± 1.7
	CH_3CF_2^+	12.04 ± 0.03	214.9 ± 1.7^c
CH_3CHF_2	CH_3CHF^+	12.18 ± 0.03	168.0 ± 1.7^c
	CH_3CF_2^+	12.18 ± 0.03	-62.9 ± 0.4^b
			162.6 ± 1.1
			-119.7 ± 1.5^b
			109.1 ± 2.2

^a Derived from thermochemical cycle using $\Delta H_f^\circ_{298}(\text{CH}_2\text{CF}_2^+)$.
^b Table II. ^c These values appear to be too high. There is a possibility that kinetic shift effects may be significant.

Table II. Selected Thermochemical Data

Compd	$\Delta H_f^\circ_{298}^a$	Compd	$\Delta H_f^\circ_{298}^a$
$\text{CH}_3\text{CH}_2\text{F}$	-62.9 ± 0.4^b	CH_3	34.0^g
CH_3CHF_2	-119.7 ± 1.5^b	H	52.1^h
CH_3CF_3	-178.2 ± 0.4^b	IP(H)	13.598 eV^h
$(\text{CH}_3)_2\text{CHF}$	-69.0 ± 1.0^c	IP(CH_2CHF)	$10.36 \pm 0.01 \text{ eV}^i$
$(\text{CH}_3)_2\text{CF}_2$	-129.8 ± 3.0^d	IP(CH_2CF_2)	$10.29 \pm 0.01 \text{ eV}^i$
CH_2CHF	-33.2 ± 0.4^e		
CH_2CF_2	-82.5 ± 2.4^f		

^a Units kcal/mol except as noted. ^b S. S. Chen, A. S. Rodgers, J. Chao, R. S. Wilhoit, and B. J. Zwolinski, *J. Phys. Chem. Ref. Data*, **4**, 441 (1975). ^c J. R. Lacher, *J. Phys. Chem.*, **60**, 1454 (1956). ^d Derived relative to $\Delta H_f^\circ_{298}(\text{CH}_2\text{CF}_2^+)$. See text for details. ^e V. P. Kolesov and T. S. Papina, *Russ. J. Phys. Chem.*, (Engl. Transl.), **44**, 611 (1970). Corrected for the value of $\Delta H_f^\circ_{298}[\text{HF}, 40\text{H}_2\text{O}]$ given in footnote f. ^f J. R. Lacher and H. A. Skinner, *J. Chem. Soc. A*, 1034 (1968). ^g J. A. Kerr, *Chem. Rev.*, **66**, 465 (1966). ^h Reference 20. ⁱ Reference 17.

onset at 1072 ± 3 Å, corresponding to an appearance potential of 11.57 ± 0.03 eV, and rises continually with photon energy above this point. The onset of the CH_3CF_2^+ cation, formed by loss of a methyl radical (process 2), occurs at 1050 ± 3 Å, or 11.81 ± 0.03 eV.

The thresholds observed in the present study are summarized in Table I. Also included in Table I are ion heats of formation derived from the measured thresholds. Thermochemical data for neutral species utilized in these calculations are summarized in Table II.

Since the heat of formation of 2,2-difluoropropane is not available, the $\Delta H_f^\circ_{298}$ values quoted in Tables I and II for the parent molecule and its fragment ions are referenced to the value $\Delta H_f^\circ_{298}(\text{CH}_2\text{CF}_2) = -82.5 \pm 2.4$ kcal/mol quoted in Table II. Using the ionization potential of CH_2CF_2 and the appearance potential of the CH_2CF_2^+ fragment ion from the present study, we assign the heat of formation of 2,2-difluoropropane to be -129.8 ± 3.0 kcal/mol. This value is consistent with an estimate of -125.8 kcal/mol obtained by the assumption that the change in enthalpy of formation resulting from replacement of H with CH_3 is the same for $\text{CH}_3\text{CF}_2\text{H}$ as for CH_3CH_3 . The difference in the appearance potentials

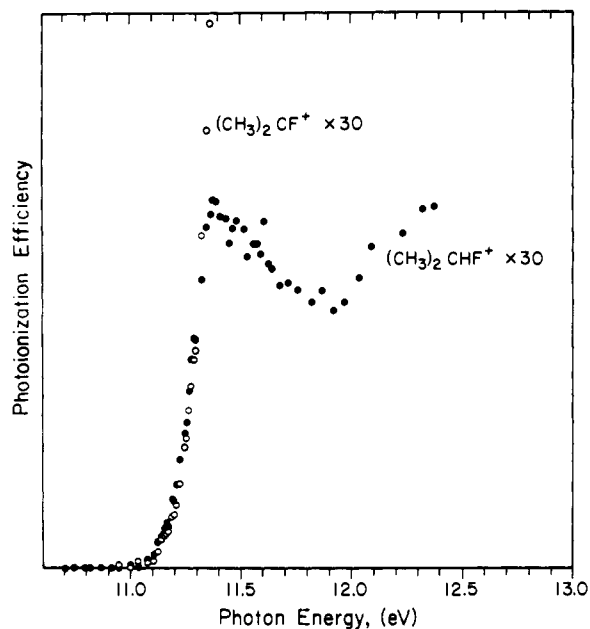
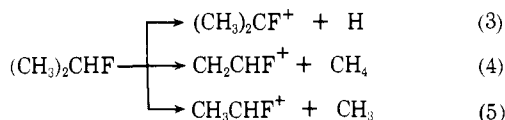


Figure 2. Photoionization efficiency curves for the molecular ion and $(\text{CH}_3)_2\text{CF}^+$ fragmentation ion in 2-fluoropropane.

for processes 1 and 2 allows calculation of $\Delta H_f^\circ_{298}(\text{CH}_3\text{CF}_2^+) = 108.5 \pm 3$ kcal/mol. An independent determination of this quantity is provided by the appearance potential of CH_3CF_2^+ from $\text{CH}_3\text{CF}_2\text{H}$. The measured threshold of 12.18 ± 0.03 eV gives $\Delta H_f^\circ_{298}(\text{CH}_3\text{CF}_2^+) = 109.1 \pm 2.2$ kcal/mol. The excellent agreement between the two values gives further confidence in our assignment of the heat of formation for 2,2-difluoropropane as well as the published value for CH_2CF_2 .

2-Fluoropropane. In 2-fluoropropane processes 3–5 were



detected. Photoionization efficiency data for the parent ion and $(\text{CH}_3)_2\text{CF}^+$ fragment ion in 2-fluoropropane are shown in Figure 2. The threshold for ionization occurs at 1119 ± 2 Å, corresponding to an adiabatic ionization potential of 11.08 ± 0.02 eV. As in the 2,2-difluoropropane case, the parent curve reaches a maximum and declines as photon energy is increased. The $(\text{CH}_3)_2\text{CF}^+$ ion formed by process 3 shows an onset exactly coincident with the ionization potential. The ionization efficiency of the fragment essentially coincides with that of the parent ion from threshold to about 1095 Å, then continues to rise as the parent ion curve reaches a maximum. The behavior of the $(\text{CH}_3)_2\text{CF}^+$ ion is shown with a smaller magnification in Figure 3.

The appearance threshold of $(\text{CH}_3)_2\text{CF}^+$ is assigned as 1104 ± 3 Å (11.23 ± 0.03 eV), the wavelength at which the slopes of the parent and fragment ionization efficiency curves become equal. This point corresponds to the crossing point of the ion curves on a breakdown diagram.^{9b} This system is unusual in that the appearance potential for process 3 lies only 3.5 kcal/mol above the adiabatic ionization potential. Since the thermal vibrational energy distribution of the parent molecule at room temperature is expected to include a significant population at energies greater than this difference, the onset of fragmentation coincides with the ionization potential. The threshold for process 3 gives the heat of formation of $(\text{CH}_3)_2\text{CF}^+$ as 138.0 ± 1.7 kcal/mol. This result is consistent with the value of 143 ± 7 kcal/mol determined from limits set by ion–molecule reactions in 2-fluoropropane.¹⁶

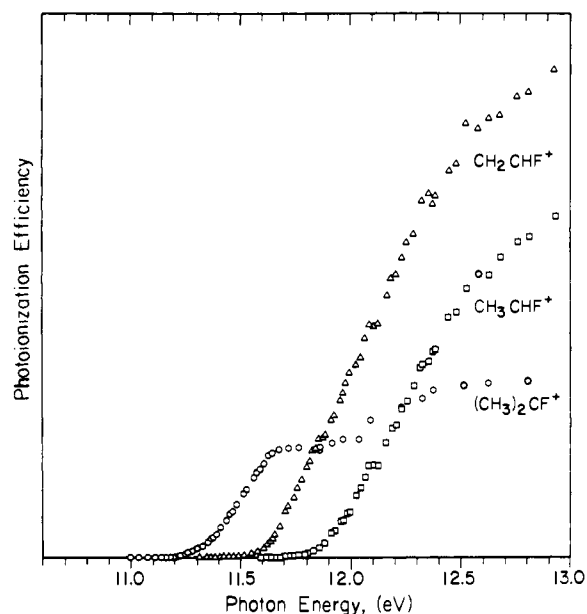


Figure 3. Photoionization efficiency curves for $(\text{CH}_3)_2\text{CF}^+$, CH_2CHF^+ , and CH_3CHF^+ fragment ions in 2-fluoropropane. With the indicated scale changes the data of Figures 2 and 3 can be directly compared.

Figure 3 also shows the fragment ions of processes 4 and 5, analogous to processes 1 and 2 in 2,2-difluoropropane. The apparent onset of process 4 is 1075 ± 3 Å (11.53 ± 0.03 eV), and that for the α -cleavage process 5 is 1055 ± 3 Å (11.75 ± 0.03 eV). These thresholds would indicate heats of formation of 214.9 and 168.0 kcal/mol, respectively, for CH_2CHF^+ and CH_3CHF^+ . The former value implies a heat of formation of vinyl fluoride of -24.0 kcal/mol, since the ionization potential of vinyl fluoride is well known.¹⁷ There are indications that these values and thus the appearance potentials used to derive them may be too high. In particular, the literature contains various values for the heat of formation of vinyl fluoride,^{18,19} but the highest published number is -28 kcal/mol,²⁰ and we favor the value of -33.2 ± 0.4 quoted in Table II.

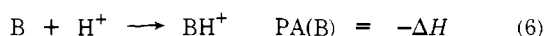
As was done for the CH_3CF_2^+ ion, an independent study of the heat of formation of CH_3CHF^+ was performed by measuring the appearance potential of this ion from $\text{CH}_3\text{CH}_2\text{F}$. The observed threshold of 12.04 ± 0.03 eV yields 162.6 ± 1.1 kcal/mol for the heat of formation of CH_3CHF^+ . Thus the appearance potentials of both processes 4 and 5 appear to be too high. As discussed below, these findings are consistent with a significant kinetic shift for the two processes, or alternatively an error in the published heat of formation of 2-fluoropropane. As a result the derived heats of formation quoted in Table I are upper limits to the true values.

Interestingly, neither 2-fluoropropane nor 2,2-difluoropropane exhibits an abundant fragment ion resulting from the thermochemically favorable loss of HF from the molecular ion. In 2-fluoropropane, for example, this process has a computed threshold of 10.10 eV, which lies below the observed molecular ionization potential, yet the only ion observed at m/e 42 was clearly due to a trace propylene impurity in the sample.

Proton Affinities of 1,1-Difluoroethylene and Vinyl Fluoride. The most abundant fragment ions derived from the fluorinated propanes considered in this study correspond to the molecular ions and protonated parent of the appropriate fluorinated ethylene. A thermodynamic cycle can be established which depends only on the difference in the thresholds for these fragmentations and yields the proton affinities of the olefins. The proton affinity of a base B is defined as the negative of the enthalpy change for the protonation reaction 6. Table III summarizes the appropriate thermochemical cycle for both

Table III. Proton Affinities of CH₂CFX by Fragmentations of (CH₃)₂CFX (X = F, H)

Process	ΔH (X = H), kcal/mol	ΔH (X = F), kcal/mol
(CH ₃) ₂ CFX → CH ₃ CFX ⁺ + CH ₃	271.0	272.3
CH ₄ + CH ₂ CFX ⁺ → (CH ₃) ₂ CFX	-265.9	-266.8
CH ₂ CFX → CH ₂ CFX ⁺	238.9	237.3
CH ₃ + H → CH ₄	-104.0	-104.0
H ⁺ → H	-313.6	-313.6
CH ₂ CFX + H ⁺ → CH ₃ CFX ⁺	-173.6	-174.8



fluorinated propanes studied. As is evident, the cycle yields the proton affinity for the relevant olefins using only the measured appearance potentials and well-known thermochemical relationships. In particular, the heats of formation of neither the parent neutral nor the neutral fluoroethylene appear. The calculations of Table III give for 1,1-difluoroethylene a proton affinity of 174.8 ± 1.0 kcal/mol. For vinyl fluoride a proton affinity of 173.6 kcal/mol is computed, but error estimates are difficult to make in light of the uncertainty in the accuracy of the thresholds used.

The proton affinities of the fluoroethylenes have been determined by Ridge,⁵ using ion cyclotron resonance spectroscopy to investigate proton transfer reactions in mixtures. He finds that the proton affinity of 1,1-difluoroethylene is greater than that of ethyl iodide and less than that of methanol, assigning it a value of 177 ± 3 kcal/mol. Likewise he finds that vinyl fluoride has a proton affinity greater than water, less than formaldehyde, and approximately equal to hydrogen sulfide. Assigning these limits using an extensive tabulation of recently determined relative proton affinities²¹ gives 171 ± 2 kcal/mol for the proton affinity of vinyl fluoride. The agreement between our data and the direct proton affinity measurements is excellent. In the case of 2-fluoropropane there seems to be a cancellation of errors in the difference of the thresholds used. It is interesting to note that if the heat of formation of CH₂CHF quoted in Table II is combined with the heat of formation of the proton and that of CH₃CHF⁺ determined by H atom loss from CH₃CH₂F, a value of 171.4 kcal/mol is calculated for the proton affinity of vinyl fluoride.

Discussion

Evaluation of ionization thresholds requires consideration of the contribution of thermal internal energy of the neutral to the dissociation process as well as the possibility of a significant kinetic shift. These phenomena have been discussed in detail in the literature.^{22,23}

The initial thermal energy in the parent neutral contributes to the total internal energy of the molecular ion and folds a Maxwellian energy distribution into the threshold curve. The resulting low-energy "tail" on the fragment ionization efficiency curve causes the apparent threshold to be shifted to lower energies by an amount equal to the mean thermal energy content of the parent molecule. These effects have been confirmed for fragmentations in the lower alkanes.²³

The second effect, that of kinetic shift, is defined as the displacement of the apparent threshold to higher energy by an amount appropriate to raise the dissociation rate to the level at which the fragment ions can be detected. This effect is opposite in direction and often comparable in magnitude to the

effect of thermal energy, leading to fortuitous cancellation of error. In our instrument the fragmentation rate must be greater than 10^4 – 10^5 s⁻¹ to enable detection of the lowest energy fragment. This is an order of magnitude less than the rates necessary for detection on magnetic sector instruments. For fragmentations analogous to processes 1 and 3 in systems of similar size, kinetic shift effects have been calculated to be less than the quoted error of our thresholds.²²

For higher energy fragmentations the situation is quite different; decomposition rates must compete not only with the rate of extraction from the ion source but in addition with the higher rate of fragmentation in the decomposition channel with the lower threshold, and kinetic shifts may be substantial.

Applying these principles to our systems sheds light on the interpretation of our data. The 2,2-difluoropropane fragmentations are typical of many systems in which the lowest energy fragmentation is a rearrangement process and the higher is a simple bond fission. Here entropic factors strongly favor the "loose" intermediate of the higher energy process over the "tight" four-center intermediate for the rearrangement. If this factor is great enough in the present system, the difference in kinetic shifts will be negligible and the relative thresholds will be accurate. One factor that suggests that matters may not be this simple is the continued rise of the CH₂CF₂⁺ efficiency curve above the threshold for CH₃CF₂⁺ production, suggesting that the two fragmentation rates are comparable over a large energy range. In any case the threshold for process 2, AP2, represents an upper bound. A lower bound can be determined from the fact that the CH₄ loss (with threshold AP1) must be a lower energy process in order to compete with the α cleavage. Using these considerations we can state with assurance that $0 < AP2 - AP1 \lesssim 0.24$ eV, resulting in the relationship 174.1 kcal/mol $\lesssim PA(CH_2CF_2) < 179.6$ kcal/mol. As noted above, the consistency with other measurements suggests that the measured thresholds are reasonably accurate.

The 2-fluoropropane case is somewhat different in that both fragmentations 4 and 5 must compete with process 3, which has a very low threshold. The ionization efficiency curve for process 3 does stop rising abruptly slightly above the onset for process 4, indicating that the rate of fragmentation 4 is varying rapidly with excess energy. However, as noted above, ion heats of formation calculated from thresholds for fragmentations 4 and 5 are clearly inconsistent with those derived from other sources. The discrepancies can be attributed to kinetic shifts of about 7–9 kcal/mol for processes 4 and 5. In this event the cancellation of the kinetic shifts for the two thresholds to give a close estimate of the proton affinity must be considered fortuitous. Alternatively, the possibility exists that the heat of formation of 2-fluoropropane is actually lower than the -69.0 kcal/mol quoted in Table II, as is suggested by recent flame calorimetry measurements of Kabo and Andreevskii.²⁴

Recommended Heats of Formation and Related Thermochemical Properties. There are several experiments which provide additional limits on the thermochemistry of fluorine-substituted ions considered in this study. Ridge has observed equilibrium in the fluoride transfer reaction 7 for which a value



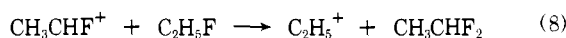
$\Delta H = -1.4 \pm 0.2$ kcal/mol was determined.²⁵ Using the average value of $\Delta H_f^\circ(298)(CH_3CF_2^+) = 108.8$ kcal/mol from threshold measurements on CH₃CF₂H and (CH₃)₂CF₂, the enthalpy change for reaction 7 yields $\Delta H_f^\circ(298)(CH_3CHF^+) = 165.9$ kcal/mol. This value is intermediate between the threshold measurements for this ion from CH₃CH₂F and (CH₃)₂CHF and agrees well with the estimate of 163 ± 2 kcal/mol calculated from $PA(CH_2CHF) = 171 \pm 2$ kcal/mol. In addition, reaction 8 is known to occur in ethyl fluoride with

Table IV. Recommended Heats of Formation for Fluorine-Substituted Carbonium Ions and Related Thermochemical Data

R ⁺	ΔH_f° ₂₉₈ (R ⁺) ^a	ΔH_f° ₂₉₈ (R) ^a	IP(R) ^b	$D(R^+-H^-)$ ^{a,g}	$D(R^+-F^-)$ ^{a,g}
CH ₃ CH ₂ ⁺	218.9	25.7 ^c	8.38 ^c	272.5	220.5
CH ₃ CHF ⁺	165.9 ^d	-17.0 ^e	7.93	262.2	224.3
CH ₃ CF ₂ ⁺	108.8 ^d	-73.8 ^e	7.92	261.9	225.7
(CH ₃) ₂ CH ⁺	191.7	17.6 ^c	7.55 ^c	249.9	199.4
(CH ₃) ₂ CF ⁺	138.0 ^d	-26.6 ^f	7.14	240.4	206.5

^a Data in kcal/mol. ^b Ionization potentials in eV. ^c F. P. Lossing and G. P. Semeluk, *Can. J. Chem.*, **48**, 955 (1970). ^d Estimated uncertainty ± 3 kcal/mol (see text). ^e $D(\text{CH}_3\text{CHF}-\text{H}) \approx D(\text{CH}_3\text{CF}_2-\text{H}) \approx D(\text{CH}_3\text{CH}_2-\text{H}) = 98.0$ kcal/mol assumed to calculate ΔH_f° ₂₉₈(R). ^f $D[(\text{CH}_3)_2\text{CF}-\text{H}] \approx D[(\text{CH}_3)_2\text{CH}-\text{H}] = 94.5$ kcal/mol assumed to calculate ΔH_f° ₂₉₈[(CH₃)₂CF]. ^g Heterolytic bond dissociation energies $D(R^+-X^-) = \Delta H_f^\circ$ ₂₉₈(R⁺) + ΔH_f° ₂₉₈(X⁻) - ΔH_f° ₂₉₈(RX) for X = H, F.

a thermal rate constant of $k = 4 \times 10^{-10}$ cm³ molecule⁻¹ s⁻¹.^{25,26} For reaction 8 to be exothermic it is required that



ΔH_f° ₂₉₈(CH₃CHF⁺) ≥ 162.1 kcal/mol, which is also consistent with the derived value of 165.9 kcal/mol.

Recommended heats of formation for the various fluorine-substituted ions considered in this study are summarized in Table IV. Although differences in thermochemical properties are more accurately determined in several instances, it appears reasonable to assign uncertainties of ± 3 kcal/mol to the derived heats of formation.

Included in Table IV are several related thermochemical properties. As is observed in the methyl series,^{2,3} fluorine substitution on the carbonium ion center results in a reduction of the ionization potential of the corresponding radical. In addition, fluorine substitution at the carbonium ion center consistently results in an increase in the $D(R^+-F^-)$ and a decrease in the $D(R^+-H^-)$ heterolytic bond dissociation energies.

The origin of this phenomenon and its interesting consequences have been previously discussed.^{2,3,16}

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Extrinsic Circular Dichroism in Twisted Nematic Mesophases

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Abstract: Extrinsic wavelength dependent circular dichroism (CD) has been observed in twisted nematic mesophases produced by placing an achiral nematic liquid crystalline material between rubbed surfaces held at an angle between 0 and 90°. The extrinsic CD was extracted from the combination of linear dichroism (LD) and CD by summing signal intensities on a Cary 61 CD spectropolarimeter taken at cell rotation angles (normal to the light beam) of 90° with respect to each other. The sign of the CD is dependent on the chirality of the twist as well as the polarization of the optical transition dipole moment of the matrix or aligned solute molecules. Nematic mesophases between rubbed surfaces placed at 90° relative to each other produce CD of either positive or negative sign due to the apparently equal probability of forming left- or right-handed helical structures. It is concluded from this investigation that the twisted nematic mesophase is cholesteric in nature.

The prebiotic generation of optical activity, i.e., a racemic mixture enriched in one enantiomer, is not fully understood.¹ Recently we have reported an asymmetric synthesis in an an-

isotropic cholesteric liquid crystal solvent² in which an achiral reactant was thermally rearranged to a chiral product. Several other processes for the creation of chiral species have been