Gas-Phase Ion Chemistry of Fluoromethanes by Ion Cyclotron Resonance Spectroscopy. New Techniques for the Determination of Carbonium Ion Stabilities
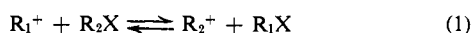
R. J. Blint,[1] T. B. McMahon,[2] and J. L. Beauchamp*[3]

Contribution No. 4554 from the Department of Chemistry, California Institute of Technology, Pasadena, California 91109. Received November 16, 1972

Abstract: The gas-phase ion chemistry of the fluoromethanes $CH_{4-n}F_n$ (n = 1–4) has been investigated using the techniques of ion cyclotron resonance spectroscopy. The kinetics of reactions involving parent and fragment ions have been determined over a range of pressure and electron energies using trapped ion techniques complemented by the more usual method of examining the variation of ion abundance with pressure. Fluoride-transfer reactions between substituted carbonium ions are a dominant feature of the observed ion chemistry. A detailed examination of these processes provides information relating to carbonium ion stabilities. Several criteria, including hydride affinities of carbonium ions (R^+-H^- heterolytic bond dissociation energies) and adiabatic ionization potentials of the corresponding free radicals, indicate the order of decreasing stability of fluoromethyl cations to be $CHF_2^+ >$ $CH_2F^+ > CF_3^+ > CH_3^+$. A second important feature of the observed ion chemistry concerns halonium ion formation. While $(CH_3)_2F^+$, $(CH_2F)_2F^+$, and $(CHF_2)_2F^+$ are readily formed in nucleophilic displacement reactions involving the protonated parent and corresponding neutral of CH_3F, CH_2F_2, and CHF_3, respectively, the species $(CF_3)_2F^+$ is not observed. The binding energies of fluoromethyl cations to fluoromethanes decrease with increasing fluorine substitution in the neutral. The basicities (proton affinities) of the fluoromethanes also decrease with increasing fluorine substitution.

Fluorine is unique in its ability as a substituent to modify molecular properties and reactivity. To explore the effects of fluorine substituents on the properties and reactions of gaseous ions, we have extended our earlier study[4] of monosubstituted methyl and ethyl halides with an examination of the gas-phase ion chemistry of the fluoromethanes $CH_{4-n}F_n$ (n = 1–4) using the techniques of ion cyclotron resonance spectroscopy (icr).[5]

In a preliminary account[6] of the present work we reported that exothermic and thermoneutral fluoride-transfer reactions between carbonium ions are relatively fast, permitting the equilibrium indicated in eq 1 (X =

$$R_1^+ + R_2X \rightleftharpoons R_2^+ + R_1X \qquad (1)$$

F) to be established in favorable instances. Thermodynamic data obtained from such experiments are useful in assessing the relative stabilities of the two carbonium ions R_1^+ and R_2^+ in the absence of complicating solvent effects. Absolute scales of carbonium ion stabilities can be established with appropriate reference data.[7] Both the reactions observed in the present study and the available thermochemical data make it convenient to define fluoride and hydride affinities as the negative of the enthalpy change of reactions 2 and 3,

$$R^+ + F^- \longrightarrow RF \qquad (2)$$
$$R^+ + H^- \longrightarrow RH \qquad (3)$$

respectively, and use such data for quantifying considerations of carbonium ion stability. In the present study the stabilizing (F $\rightarrow$ C π donation) and destabilizing (C $\rightarrow$ F σ polarization) effects of α-fluorine substituents on carbonium ions are considered. In subsequent

(1) Supported by the Department of Health, Education and Welfare, National Defense Education Act.

(2) Supported by National Research Council of Canada, 1970–1973.

(3) Dreyfus Teacher-Scholar.

(4) J. L. Beauchamp, D. Holtz, S. D. Woodgate, and S. L. Patt, J. Amer. Chem. Soc., 94, 2798 (1972).

(5) For a recent review of ion cyclotron resonance spectroscopy, see J. L. Beauchamp, Annu. Rev. Phys. Chem., 22, 527 (1971).

(6) T. B. McMahon, R. J. Blint, D. P. Ridge, and J. L. Beauchamp, J. Amer. Chem. Soc., 94, 8934 (1972); for a related study, see J. H. J. Dawson, W. G. Henderson, R. M. O'Mally, and K. R. Jennings, Int. J. Mass Spectrom. Ion Phys., 11, 61 (1973).

(7) For related studies interpreting the effects of substituents on amine basicity, see D. Holtz, J. L. Beauchamp, W. G. Henderson, and R. W. Taft, Inorg. Chem., 10, 201 (1971); M. Taagepera, W. G. Henderson, R. T. C. Brownlee, D. Holtz, J. L. Beauchamp, and R. W. Taft, J. Amer. Chem. Soc., 94, 4728 (1972); E. M. Arnett, F. M. Jones III, M. Taagepera, W. G. Henderson, J. L. Beauchamp, D. Holtz, and R. W. Taft, ibid., 94, 4727 (1972).

reports we will consider the more complicated combined effects of α- and β-fluorine substituents using the methodology developed in the present study.[8]

The gas-phase ion chemistry of methyl fluoride has been extensively investigated using both icr[4,9] and conventional mass spectrometric techniques,[10,11] the latter including most recently a study of reaction kinetics using the technique of trapping ions in the space charge of an electron beam.[11] Due to the low methyl cation affinity of HF, protonated methyl fluoride has been shown in icr studies to be an excellent alkylating reagent for studies of gas-phase nucleophilic displacement reactions.[4,12–14] Methyl fluoride is briefly reinvestigated in the present work using new icr trapped ion techniques developed in our laboratory.[6,15] Harrison and McAskill[16,17] have examined the ion chemistry of methylene fluoride, fluoroform, and carbon tetrafluoride using high pressure and trapped ion mass spectrometry and have reported reaction rates for the primary ions. In addition the gas-phase basicity (PA) of carbon tetrafluoride has been found by Roche, et al.,[18] to be between methane and nitrogen. The gas-phase ion chemistry of numerous perfluoroalkanes,[19–24] including perfluoroethane[20–22] and perfluoropropane,[23,24] has been investigated.

Useful information relevant to the interpretation of our results is provided by the available studies of the mass spectrometry[25–29] and electronic structures of the fluoromethanes and their associated molecular and fragment ions.[30–34]

(8) D. P. Ridge, J. Y. Park, and J. L. Beauchamp, to be submitted for publication.

(9) A. G. Marshall and S. E. Buttrill, Jr., J. Chem. Phys., 52, 2752 (1970).

(10) N. A. McAskill, Aust. J. Chem., 23, 2301 (1970).

(11) A. A. Herod, A. G. Harrison, and N. A. McAskill, Can. J. Chem., 49, 2217 (1971).

(12) D. Holtz, J. L. Beauchamp, and S. D. Woodgate, J. Amer. Chem. Soc., 92, 7484 (1970).

(13) D. Holtz and J. L. Beauchamp, Nature (London), 231, 204 (1971).

(14) D. Holtz and J. L. Beauchamp, Science, 173, 1237 (1971).

(15) T. B. McMahon and J. L. Beauchamp, Rev. Sci. Instrum., 43, 509 (1972).

(16) N. A. McAskill, Aust. J. Chem., 23, 893 (1970).

(17) A. G. Harrison and N. A. McAskill, Aust. J. Chem., 24, 1611 (1971).

(18) A. E. Roche, M. M. Sutton, D. K. Bohme, and H. I. Schiff, J. Chem. Phys., 55, 5480 (1971).

(19) Chemical ionization studies using CF4 as a reagent gas have been reported by N. Einolf and B. Munson, Int. J. Mass Spectrom. Ion Phys., 9, 141 (1972). The only ion ≥5% of the total ionization at high pressures (∼1 Torr) is CF3+.

(20) J. King and D. Elleman, J. Chem. Phys., 48, 412 (1968).

(21) D. Smith and L. Kevan, J. Chem. Phys., 46, 1586 (1967).

(22) R. E. Marcotte and T. O. Tiernan, J. Chem. Phys., 54, 3385 (1971).

(23) T. Su, L. Kevan, and T. O. Tiernan, J. Chem. Phys., 54, 4871 (1971).

(24) T. Su, L. Kevan, and T. O. Tiernan, J. Phys. Chem., 75, 2534 (1971).

(25) D. C. Frost and C. A. McDowell, Proc. Roy. Soc., Ser. A, 241, 194 (1957); R. W. Taft, R. H. Martin, and F. W. Lampe, J. Amer. Chem. Soc., 87, 2490 (1965).

(26) C. J. Noutary, J. Res. Nat. Bur. Stand., Sect. A, 479 (1968).

(27) M. Krauss, J. A. Walker, and V. H. Dibeler, J. Res. Nat. Bur. Stand., Sect. A, 72, 281 (1968).

(28) T. Walter, C. Lifshitz, W. Chupka, and J. Berkowitz, J. Chem. Phys., 51, 3531 (1969).

(29) F. P. Lossing, Bull. Soc. Chim. Belg., 81, 125 (1972).

(30) B. P. Pullen, T. A. Carlson, W. E. Moddeman, G. K. Schweitzer, W. E. Bull, and F. A. Grimm, J. Chem. Phys., 53, 768 (1970).

(31) C. R. Brundle, M. B. Robin, and H. Basch, J. Chem. Phys., 53, 2196 (1970).

(32) A. W. Potts, H. K. Lempka, D. G. Streets, and W. C. Price, Phil. Trans. Roy. Soc. London, Ser. A, 268, 59 (1970).

(33) N. C. Baird and R. K. Datta, Can. J. Chem., 49, 3708 (1971).

(34) L. D. Kispert, et al., J. Amer. Chem. Soc., 94, 5979 (1972).

Experimental Section

Methyl fluoride and methylene fluoride were obtained from Peninsular Chemresearch. Fluoroform and carbon tetrafluoride were obtained from Matheson. Other chemicals were obtained from commercial sources and used as supplied with the exception of degassing with freeze–pump–thaw cycles at 77°K. Purities as ascertained by mass spectrometric analysis were acceptable.

The general features and operating characteristics of icr instrumentation have been previously described in detail.[5] All experiments were performed at ambient temperature in a modified Varian V-5900 icr spectrometer utilizing a flat cell equipped for trapped ion studies.[5,15] The control unit for the icr spectrometer has been redesigned to incorporate pulse circuitry for performing trapped ion experiments.[15] This circuitry, which allows for switching between trapped ion and normal drift modes of operation, will be described in detail elsewhere.[35]
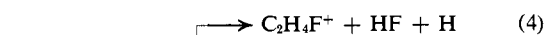
Spectral intensities reported in tables and figures have been corrected to ion abundance by dividing the measured icr single resonance peak heights by ion mass.[5,15] In the case of trapped ion experiments this represents an exact ion abundance.[15] The same procedure for drift operation yields can approximate ion abundance depending on the operating pressure.[5]

Trapped ion experiments are generally performed in the pressure range 10^{-7}–10^{-5} Torr.[15] To accurately measure absolute pressures we have installed a Schulz–Phelp type gauge adjacent to the icr cell in the magnetic field.[36] This gauge is then calibrated for a given emission current (10 μA) and magnetic field (usually 6 kG) against an MKS Instruments Baratron Model 90H1-E capacitance manometer. The manometer is connected directly to the cell housing, independent of the pumping lead. Pumping is reduced from the usual 8 l./sec by a throttle valve during calibration in order to avoid overloading the ion pump. The extent of throttling and hence the pumping speed has no effect on gauge calibration. A linear variation of ion gauge current with pressure is observed over three orders of magnitude (10^{-6}–10^{-3} Torr). The method has proved to work extremely well for a wide range of gases and has produced rate constants in good agreement with literature values for many systems. The major error in rate constants (estimated to be ±10%) arises from uncertainties in absolute pressure determination.
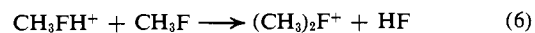
Gas mixtures were prepared either manometrically on a high-vacuum gas handling system or directly in the instrument using two sample inlets and the calibrated Schulz–Phelp gauge. In the case of equilibrium studies described below, equivalent results were obtained with both methods.

Results and Discussion

CH₃F. The gas-phase ion chemistry of CH₃F has been discussed in detail elsewhere.[4,9–11] The variation of ion abundance with time is shown in Figure 1 at a pressure of 1.25×10^{-6} Torr and an electron energy of 70 eV. The parent ion reacts to yield $C_2H_4F^+$ as the minor and CH_3FH^+ as the major product ion (reactions 4 and 5).[4,8] The product of reaction 5 participates in the nucleophilic displacement[4,12–14] reaction 6 to yield the dimethylfluoronium ion, $(CH_3)_2F^+$

$$CH_3F^+ + CH_3F \longrightarrow \begin{cases} C_2H_4F^+ + HF + H & (4) \\ CH_3FH^+ + CH_2F & (5) \end{cases}$$

$$CH_3FH^+ + CH_3F \longrightarrow (CH_3)_2F^+ + HF \qquad (6)$$

As noted before,[4] a small fraction of the $(CH_3)_2F^+$ product ion is formed in a vibrationally excited state and decomposes by loss of CH₄ (reaction 7). The

$$[(CH_3)_2F^+]^* \longrightarrow CH_2F^+ + CH_4 \qquad (7)$$
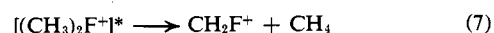
major contribution to the increase in CH_2F^+ abundance at long times in Figure 1 comes from CH_3^+ in reaction 8, which has been shown with isotopic labeling to pro-

(35) T. B. McMahon, M. S. Foster, and J. L. Beauchamp, to be submitted for publication.

(36) The gauge is similar in construction to that described in F. Rosenbury, "Handbook of Electron Tube and Vacuum Techniques," Addison-Wesley, Reading, Mass., 1965, p 471.

$$CH_3{}^+ + CH_3F \longrightarrow [CH_3\overset{+}{F}CH_3]^* \longrightarrow CH_2F^+ + CH_4 \quad (8)$$

ceed as indicated through a halonium ion intermediate.[4] No reaction of CH_2F^+ with CH_3F has been identified, accounting for its predominance at long reaction times.

For simple bimolecular kinetics, the total reaction rate constant for a particular ion can be obtained from the limiting slope in a plot of the log of ion abundance vs. time (e.g., Figure 1).[15] For primary ions the decay should be represented entirely by a straight line such as is observed for CH_3F^+ in Figure 1. This expected behavior is not observed in the case of $CH_3{}^+$, however. The upward curvature could result from $CH_3{}^+$ being a reaction product of one of the remaining primary ions. Herod, et al., have shown that reaction 9 becomes promi-

$$CH_3F^+ + CH_3F \longrightarrow CH_3{}^+ + \text{neutral products} \quad (9)$$
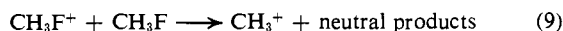
nent at high-ion kinetic energies (≥ 0.2 eV). We found no evidence indicating that $CH_3{}^+$ was an important product in the reaction of CH_3F^+ with CH_3F and favor an alternative explanation.

It is known that $CH_3{}^+$ is generated from CH_3F only with ionizing energy considerably in excess of the thermodynamic threshold.[27] In recent experiments in our laboratory[37] utilizing both icr and photoionization mass spectrometry to determine the partitioning of this excess energy, we have ascertained that the average kinetic energy of methyl cations from CH_3F is 0.5 eV at 70 eV electron energy with the distribution centered at this value. Interestingly, this explains why Herod, et al., were unable to observe $CH_3{}^+$ using the technique of trapping ions in the space charge of an electron beam.[38] Apparently, in their experiments the well depth is insufficient to confine ions formed with appreciable kinetic energy. In icr trapped ion experiments we observe an appreciable loss of $CH_3{}^+$ with trapping voltages below ~ 1.0 V. Double resonance experiments indicate that the rate of reaction 8 decreases with increasing ion kinetic energy (negative dk/dE[39]). Hence, the upward curvature in the decay of $CH_3{}^+$ likely results from a translational deexcitation of $CH_3{}^+$ in nonreactive collisions followed by rapid reaction in subsequent encounters. Although no attention was given to this matter in our earlier investigation, similar behavior is evident in the variation of ion abundance with pressure as determined by icr methods.[4]

Total reaction rates from the limiting slopes in Figure 1 for CH_3F^+, CH_3FH^+, and $CH_3{}^+$ are summarized in Table I. The total rate constant for reactions 4 and 5 of the parent ion is compared in Table II to other values reported in the literature. Recently, in our lab we have developed[40] a trapped ion analyzer which utilizes a combination of electrostatic and magnetic fields similar to those used for trapped ion icr experiments with the exception that ions are withdrawn for mass analysis using a quadrupole mass spectrometer. The total reaction rate determined for CH_3F^+ in CH_3F is in excellent agreement with the trapped ion icr results

(37) P. G. Miasek, P. LeBreton, W. T. Huntress, and J. L. Beauchamp, unpublished results.

(38) For a more complete discussion of the techniques, see A. A. Herod and A. G. Harrison, Int. J. Mass Spectrom. Ion Phys., 4, 415 (1970).

(39) For a discussion of the significance of the sign of dk/dE, see J. L. Beauchamp and S. E. Buttrill, Jr., J. Chem. Phys., 48, 1783 (1968). It is important to note that a positive dk/dE does not imply that a reaction is endothermic.

(40) P. G. Miasek and J. L. Beauchamp, unpublished results.
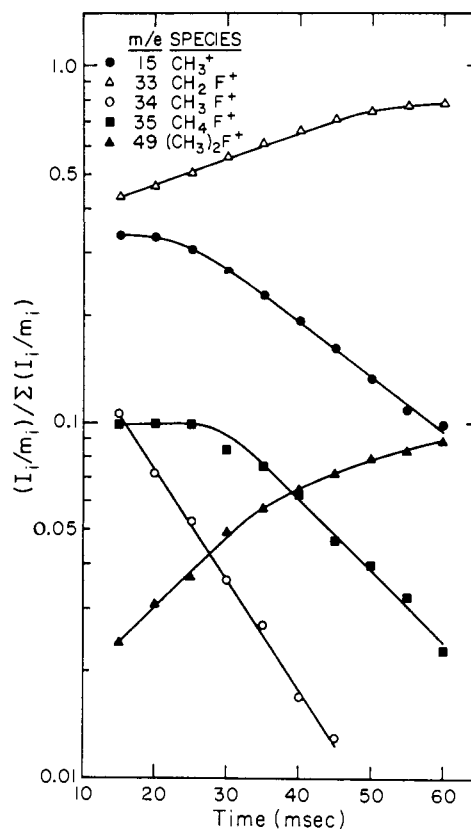
Figure 1. Variation of ion abundance with time for CH_3F at 70 eV and 1.25×10^{-6} Torr with a 10-msec electron beam pulse. The minor ion $C_2H_4F^+$, which rises to a constant fraction (0.007) of the total ionization, is not shown.

Table I. Rate Constants for Ion–Molecule Reactions of the Fluoromethanes

Species	Reactions observed	$k_{total}{}^a$
CH_3F	$CH_3F^+ + CH_3F \begin{cases} \rightarrow CH_3FH^+ + CH_2F \\ \rightarrow C_2H_4F^+ + HF + H \end{cases}$	17.3
	$CH_3{}^+ + CH_3F \rightarrow CH_2F^+ + CH_4$	10.2
	$CH_3FH^+ + CH_3F \begin{cases} \rightarrow (CH_3)_2F^+ + HF \\ \rightarrow CH_2F^+ + CH_4 + HF \end{cases}$	9.9
CH_2F_2	$CHF_2{}^+ + CH_2F_2 \rightarrow CH_2F^+ + CF_3H$	1.9
	$CH_2F^+ + CH_2F_2 \rightarrow CHF_2{}^+ + CH_3F$	0.068
	$CH_2F_2{}^+ + CH_2F_2 \rightarrow CH_2F_2H^+ + CF_2H$	13.0
	$CH_2F_2H^+ + CH_2F_2 \rightarrow (CH_2F)_2F^+ + HF$	14.0
CF_3H	$CF_3{}^+ + CHF_3 \rightarrow CHF_2{}^+ + CF_4$	2.1
	$CHF_3H^+ + CF_3H \rightarrow (CHF_2)_2F^+ + HF$	0.82^b
CF_4	$CF_2{}^+ + CF_4 \rightarrow CF_3{}^+ + CF_3$	1.7

^{a} Units 10^{-10} cm^3 molecule^{-1} sec^{-1}. ^{b} The rate constant for this process was measured in a mixture of CH_4 and CHF_3 (see text).

and both of these determinations are in the middle of the general range of literature values summarized in Table II.

CH_2F_2. The ion chemistry of CH_2F_2 is similar to that observed for CH_3F. The important ions observed at all electron energies are CH_2F^+, $CHF_2{}^+$, and $CH_2F_2{}^+$. The variation of ion abundance with time at 17 eV electron energy and 3.2×10^{-6} Torr is shown in Figure 2. The parent ion reacts rapidly to form the protonated parent ion (reaction 10) which in turn reacts to generate

$$CH_2F_2{}^+ + CH_2F_2 \longrightarrow CH_2F_2H^+ + CHF_2 \quad (10)$$

the bis(fluoromethyl)fluoronium ion (reaction 11).
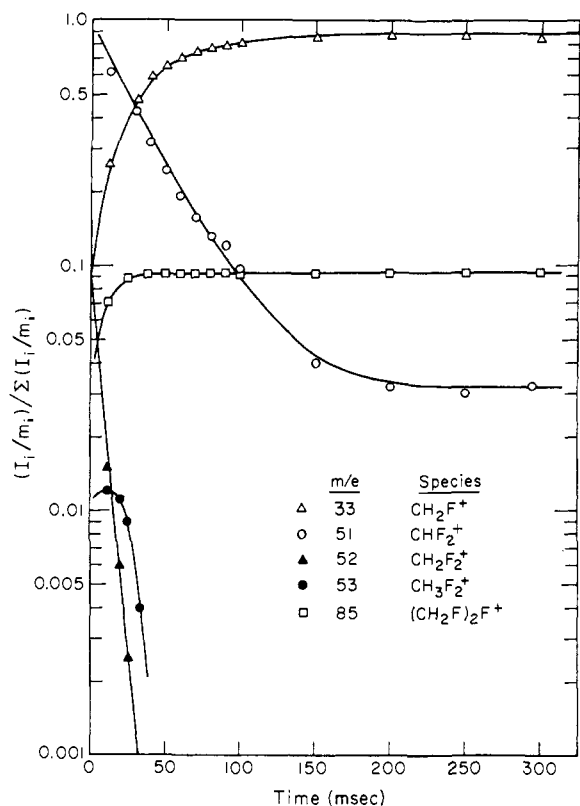
Figure 2. Variation of ion abundance with time for CH_2F_2 at 17.0 eV and 3.2×10^{-6} Torr with a 10-msec electron beam pulse.

Table II. Comparison of Total Rate Constants for Reaction of the Parent Ion of Methyl Fluoride

Method	Av ion energy	k_{total},[a] 10^{-10} cm³ molecule⁻¹ sec⁻¹	Ref
Icr (pressure variation)	Thermal[b]	14.6	9
Icr (pressure variation)	Thermal[b]	13.8	4
Icr (trapped ion)	Thermal[b]	17.3	This work
High-pressure mass spectrometry	0.24–1.1 eV[c]	15.3–22.7[c]	11
High-pressure mass spectrometry	0.2 eV	22.0	10
Mass spectrometry (trapped ion)	0.45 eV	18.7	11
Mass spectrometry (trapped ion)	Thermal	17.0	40

[a] In cases where the individual rates were measured for the production of CH_3FH^+ and $C_2H_4F^+$, they are summed to yield the quoted value of the total rate constant. [b] Rate measurements using icr techniques yield data appropriate for thermal ion energies. However, a small fraction of the ions (those formed near the trapping plates) may have excess kinetic energy due to their motion in the trapping well. [c] In the high-pressure mass spectrometry experiments the total rate constant was observed to increase with increasing average ion energy, with the latter being determined by varying the repeller voltage.

$$CH_2F_2H^+ + CH_2F_2 \longrightarrow (CH_2F)_2F^+ + HF \quad (11)$$
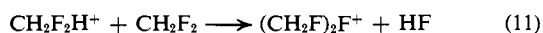
The fluoride transfer reaction 12 involving the two most

$$CHF_2^+ + CH_2F_2 \longrightarrow CH_2F^+ + CHF_3 \quad (12)$$

prevalent ions CH_2F^+ and CHF_2^+ accounts for the initial decay of the latter. The ion abundance ratio CH_2F^+–CHF_2^+ reaches a constant value of 28:1 at long times. The hydride transfer reaction 13 accounts

$$CH_2F^+ + CH_2F_2 \longrightarrow CHF_2^+ + CH_3F \quad (13)$$
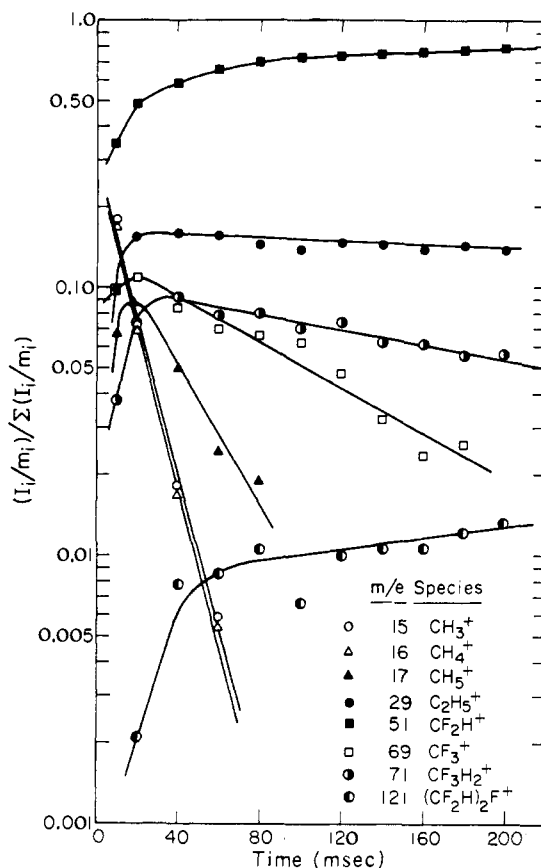
Figure 3. Variation of ion abundance with time for a 1.1:1 mixture of CHF_3 and CH_3 at 70 eV and 2.4×10^{-6} Torr total pressure with a 10-msec electron beam pulse.

for this behavior. When CH_2F^+ is ejected from the cell, CHF_2^+ is observed to entirely decay. Total reaction rate constants for CHF_2^+ (derived from the initial slope), $CH_2F_2^+$, and $CH_2F_2H^+$ are summarized in Table I. The kinetics of reaction 12 is discussed in greater detail below, where CHF_3 is added and the process is shown to occur reversibly. The rate constant for reaction 13 is estimated to be 6.8×10^{-12} cm³ molecule⁻¹ sec⁻¹ from the measured rate constant for reaction 12 and the ratio of CH_2F^+ and CHF_2^+ observed at long times. Mass spectral analysis showed no more than 0.3% CHF_3 in CH_2F_2. This is considerably below the amount required (5%) for the reverse of reaction 12 to be important relative to reaction 13 as a source of CHF_2^+.

CHF_3. The principal fragment ions derived from CHF_3 at all pressures and electron energies are CF_3^+ and CHF_2^+. Although the parent ion has been previously reported,[26] our sensitivity did not permit its detection. Only the fluoride-transfer reaction 14 is

$$CF_3^+ + CHF_3 \longrightarrow CHF_2^+ + CF_4 \quad (14)$$

observed, where the product CHF_2^+ is unreactive toward CHF_3. Fluoronium ion formation is effected by adding CH_4 and using chemical ionization processes to generate the protonated parent ion and initiate the sequence of reactions 15–17. This sequence, identified

$$CH_4^+ + CHF_3 \longrightarrow CHF_3H^+ + CH_3 \quad (15)$$

$$CH_5^+ + CHF_3 \longrightarrow CHF_3H^+ + CH_4 \quad (16)$$

$$CHF_3H^+ + CHF_3 \longrightarrow (CHF_2)_2F^+ + HF \quad (17)$$

using icr double resonance, is illustrated with the trapped ion data shown in Figure 3 for a 1:1.1 mixture
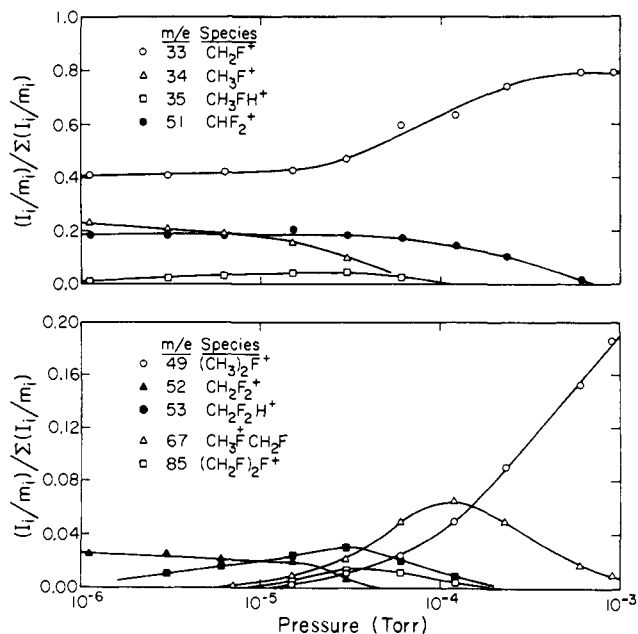
Figure 4. Variation of ion abundance with pressure for a 1:1 mixture of CH_3F and CH_2F_2 at 70 eV.

Figure 5. Variation of ion abundance with pressure for a 6.2:1 mixture of CH_2F_2 with CHF_3 at 70 eV. For the range of pressures indicated the species shown are the only ionic species present in abundance greater than 5% of the total ionization. Above 5.0×10^{-4} Torr the ratio CH_2F^+/CHF_2^+ is found to be independent of electron energy.

of CH_4 with CHF_3 at 70 eV. The reaction of CH_4^+ with CH_4 generates the chemical ionization reagent ion CH_5^+. The ion $C_2H_5^+$ generated in the reaction of CH_3^+ with CH_4 is not observed to react with CHF_3. Reaction 18 of CH_3^+ with CHF_3 accounts partially for

$$CH_3^+ + CHF_3 \longrightarrow CHF_2^+ + CH_3F \qquad (18)$$
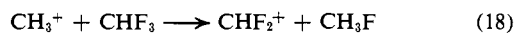
the observed decay of CH_3^+ in this mixture. Rate constants for the fluoride transfer reaction 13 and reaction 17 forming the bis(difluoromethyl)fluoronium ion are included in Table I. The latter process is significantly slower than the nucleophilic displacement reactions leading to fluoronium ion formation in CH_3F and CH_2F_2, possibly suggesting that the reaction is slightly endothermic. Consistent with this suggestion, the rate of reaction 17 is observed to increase with increasing ion energy (positive dk/dE^{39}).

CF$_4$. Electron impact ionization of CF_4 leads to CF_3^+ as the most abundant ion at all electron energies with no observable parent ion. The minor ion CF_2^+ reacts rapidly to produce CF_3^+. Reaction 19 may in-
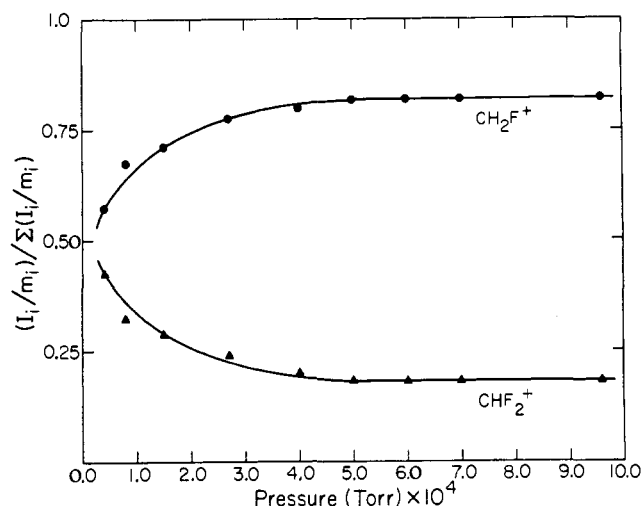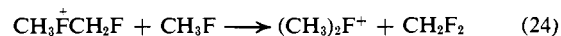
$$CF_2^+ + CF_4 \longrightarrow CF_3^+ + CF_3 \qquad (19)$$
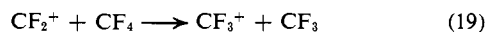
volve either fluoride ion or fluorine atom transfer, the two being indistinguishable. The ion CF_3^+ is unreactive toward CF_4.[19] Addition of CH_4 to CF_4 leads to the formation of CF_4H^+ in reaction 20. The species

$$CH_4^+ + CF_4 \longrightarrow CF_4H^+ + CH_3 \qquad (20)$$
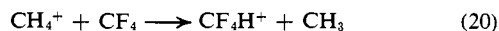
CF_4H^+ in turn undergoes proton transfer to CH_4, consistent with relative proton affinity studies of Roche, et al.[18] The bis(trifluoromethyl)fluoronium ion is not observed.

Binary Mixtures of Fluoromethanes. Binary mixtures of fluoromethanes (including methane) were investigated with the goals of determining the preferred direction for fluoride and hydride transfer reactions, examining the effects of fluorine substituents on halonium ion formation and stability, and determining the relative basicities of the fluoromethanes.

CH$_3$F and CH$_2$F$_2$. The variation of ion abundance

with pressure at 70 eV in a 1:1 mixture of CH_3F and CH_2F_2 is shown in Figure 4. Attention is to be focussed on halonium ion formation. Initially, the three halonium ions $(CH_3)_2F^+$, $(CH_2F)_2F^+$, and $CH_3FCH_2F^+$ are observed, the latter being produced in both reactions 21 and 22. With increasing pressure, however, the

$$CH_3FH^+ + CH_2F_2 \longrightarrow CH_3\overset{+}{F}CH_2F + HF \qquad (21)$$

$$CH_3F + CH_2F_2H^+ \longrightarrow CH_3\overset{+}{F}CH_2F + HF \qquad (22)$$

halonium ions $(CH_2F)_2F^+$ and $CH_3FCH_2F^+$ disappear as a result of the sequential reactions 23 and 24, iden-

$$(CH_2F)_2F^+ + CH_3F \longrightarrow CH_3FCH_2F + CH_2F_2 \qquad (23)$$

$$CH_3\overset{+}{F}CH_2F + CH_3F \longrightarrow (CH_3)_2F^+ + CH_2F_2 \qquad (24)$$

tified by double resonance. Reactions 23 and 24 proceed in such a manner as to reduce the number of fluorine atoms in the fluoronium ion product.

CH$_2$F$_2$ and CHF$_3$. As noted above, the reaction sequence for CH_2F_2 and CHF_3 leads to the formation of CH_2F^+ and CHF_2^+ as abundant ions at long times. In a mixture of CH_2F_2 and CHF_3, reaction 12 can occur reversibly. This is in fact suggested by the variation of ion abundance with pressure at 70 eV shown for a 6.2:1 mixture of CH_2F_2 with CHF_3 in Figure 5. Above 5×10^{-4} Torr, the ratio of CH_2F^+ and $CH_2F_2^+$ attains a constant value, leading to an equilibrium constant for reaction 12 of 0.74. At 10^{-3} Torr the measured equilibrium constant was observed to be independent of electron energy in the range 13-70 eV, even though the fragmentation patterns of both neutrals change markedly over this range, and the internal energies of the fragments are likely to vary considerably. Trapped ion studies (Figure 6) indicate an equilibrium constant of 0.65, with the ratio of CH_2F^+ and CHF_2^+ exhibiting no significant change beyond 100 msec at a total pressure of 3.2×10^{-6} Torr in a 4.5:1 mixture of CH_2F_2 with CHF_3.

To check that equilibrium is established, a time delay ion ejection technique is used. In the trapped ion timing sequence an irradiating radiofrequency field

(a)

(b)
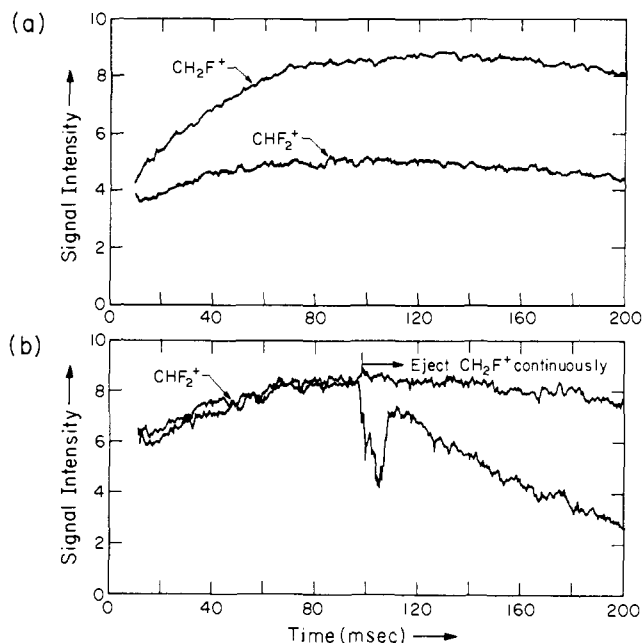
Figure 6. (a) Variation with time of CH_2F^+ and CHF_2^+ ion abundances in a 4.5:1 mixture of CH_2F_2 and CHF_3. Other conditions are a 10-msec 70-eV electron beam pulse, total pressure 3.15×10^{-6} Torr. Initial build-up of CH_2F^+ and CHF_2^+ is due to reaction of CF_3^{3+} (decay not shown). (b) Repeat of CHF_2^+ scan with and without continuous ejection of CHF_2^+ after 100 msec. The anomalous feature in the CHF_2^+ decay curve results from transients generated by turning on the irradiating oscillator in the timing sequence.

is switched on at 100 msec (Figure 6b) and used to continuously remove CH_2F^+ in a time short compared to the time between collisions. Thus, reaction 12 can proceed only to the right, causing the subsequent decay of CHF_2^+. Similarly, by ejecting CHF_2^+, reaction 12 proceeds exclusively to the left, causing the decay of CH_2F^+. The ratio I/I_0, where I and I_0 are respectively the intensity with and without the ejection field, exhibits an exponential decay with time after the irradiating field is switched on (Figure 7). From an analysis of the resulting kinetic data, the forward ($k_f = 1.3 \times 10^{-10}$ cm^3 molecule^{-1} sec^{-1}) and reverse ($k_r = 2.2 \times 10^{-10}$ cm^3 molecule^{-1} sec^{-1}) rate constants have been independently obtained for reaction 12. Both processes are sufficiently fast to neglect the slow hydride transfer reaction 13 in these considerations. The rate constant for the forward reaction is close to that oberved in CH_2F_2 alone (1.9 $\times$ 10^{-10} cm^3 molecule^{-1} sec^{-1}, Table I). The calculated equilibrium constant $K = k_f/k_r = 0.64$ is in excellent agreement with those obtained above. These data are summarized in Table III. The equilib-

Table III. Summary of Equilibrium Data for the Reaction $CHF_2^+ + CH_2F_2 \rightleftharpoons CH_2F^+ + CHF_3$

Method	K_{eq}
Pressure variation	0.74
Trapped ion	0.65
Ratio of forward and reverse rate constants	0.64

rium constant $K = 0.64$ corresponds to $\Delta G°_{298} = 0.25$ kcal/mole for reaction 12 as written. The entropy
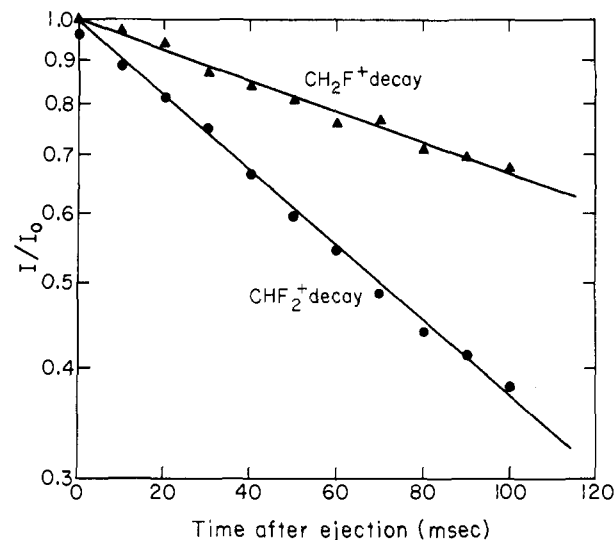
Figure 7. Illustration of exponential decay of CH_2F^+ and CHF_2^+ following ejection of the reaction partner after equilibrium is established for the process $CH_2F^+ + CHF_3 \rightleftharpoons CHF_2^+ + CH_2F_2$. The slopes for CH_2F^+ and CHF_2^+ give respectively the forward and reverse reaction rate constants. Other conditions are indicated in Figure 6.

change, $\Delta S°_{298} = -1.86$ eu, is estimated using the standard entropy data of Benson[41] for the neutral molecules and calculating the entropies of the ions assuming the geometry obtained by Baird and Datta,[33] giving $\Delta H°_{298} = -0.3$ kcal/mol.

To examine halonium ion formation in the mixture of CH_2F_2 and CHF_3, CD_4 was added to generate the protonated parent ions as described above for CHF_3 alone. The three halonium ions $(CH_2F)_2F^+$, CHF_2F-CH_2F^+, and $(CHF_2)_2F^+$ are observed with the mixed halonium ion being formed in processes analogous to reactions 21 and 22. Also in analogy with reactions 23 and 24, observed in the mixture of CH_3F and CH_2F_2, the latter two ions react sequentially to form $(CH_2F)_2F^+$, which is the only halonium ion remaining at high pressure. Significantly, no deuterium appears in the halonium ion products. Thus, the fluoromethanes CH_3F,[4] CH_2F_2, and CHF_3 all protonate on fluorine and not on carbon.

Additional Mixtures to Determine Relative Fluoride and Hydride Affinities. Only in the mixture of CH_2F_2 and CHF_3 was equilibrium observed in a fluoride or hydride transfer reaction. The dynamic range of icr experiments permits observation of equilibria at ambient temperatures only when $\Delta G \le 3$ kcal/mol.[7] Double resonance experiments allow, however, for the relative ordering of fluoride and hydride affinities to be determined by examining the variation of rate constants k with ion energy E. Empirically, it has been observed that dk/dE is negative for exothermic reactions. It must be positive for strongly endothermic reactions. For near thermoneutral reactions the expectations are less clear, although it is generally observed that dk/dE is negative for both forward and reverse processes.[42] This is the case for reaction 12.

(41) S. W. Benson, "Thermochemical Kinetics," Wiley, New York, N. Y., 1968.
(42) D. Holtz, W. G. Henderson, and J. L. Beauchamp, unpublished results in conjunction with the studies reported in ref 7. See also J. I. Brauman, J. M. Riveros, and L. K. Blair, *J. Amer. Chem. Soc.*, **93**, 3914 (1971).

Table IV. Summary of Fluoride- and Hydride-Transfer Reactions Involving Fluoromethyl Cations

Species or mixture	Reaction[a]	k, 10^{-10} cm³ molecule⁻¹ sec⁻¹ [b]	dk/dE	ΔH^c
CH₃F	CH₃⁺ + CH₃F → CH₂F⁺ + CH₄	10.2	−	−22.6
	CH₂F⁺ + CH₃F → CH₃⁺ + CH₂F₂		NR[d]	+8.4
CH₂F₂	CHF₂⁺ + CH₂F₂ → CH₂F⁺ + CHF₃	1.9	−	−0.3
	CH₂F⁺ + CH₂F₂ → CHF₂⁺ + CH₃F	0.10	−	−5.7
CHF₃	CF₃⁺ + CHF₃ → CHF₂⁺ + CF₄	2.1	−	−8.1
	CHF₂⁺ + CHF₃ → CF₃⁺ + CH₂F₂		NR	+15.1
CH₄ and CH₂F₂	CH₃⁺ + CH₂F₂ → CH₂F⁺ + CH₃F	6.4	−	−8.4
	CH₃⁺ + CH₂F₂ → CHF₂⁺ + CH₄		+[e]	−28.3
	CHF₂⁺ + CH₄ → CH₃⁺ + CH₂F₂		NR	+28.3
	CH₂F⁺ + CH₄ → CH₃⁺ + CH₃F		NR	+8.4
CH₄ and CHF₃	CH₃⁺ + CHF₃ → CF₃⁺ + CH₄		NR	−13.2
	CH₃⁺ + CHF₃ → CHF₂⁺ + CH₃F	7.6	−	−8.1
	CF₃⁺ + CH₄ → CH₃⁺ + CHF₃		NR	+13.2
	CHF₂⁺ + CH₄ → CH₃⁺ + CH₂F₂		NR	+28.3
CH₄ and CF₄	CH₃⁺ + CF₄ → CF₃⁺ + CH₃F		−	+4.5[f]
	CF₃⁺ + CH₄ → CH₃⁺ + CHF₃		NR	+13.2
CH₂F₂ and CHF₃	CHF₂⁺ + CH₂F₂ → CH₂F⁺ + CHF₃	2.2	−	−0.3
	CH₂F⁺ + CHF₃ → CHF₂⁺ + CH₂F₂	1.4	−	+0.3
CH₃F and CF₄	CF₃⁺ + CH₃F → CH₃⁺ + CF₄		+	−4.5[f]
	CH₃⁺ + CH₃F → CH₂F⁺ + CH₄		−	−22.6
	CH₂F⁺ + CF₄ → CF₃⁺ + CH₂F₂		+	+12.9
	CH₃⁺ + CF₄ → CF₃⁺ + CH₃F		−	+4.5[f]

[a] Not every reaction observed in the mixture is reported. Only those processes pertinent to determining relative fluoride and hydride affinities were examined. [b] Rate constants measured using trapped ion techniques. [c] ΔH calculated using thermochemical data summarized in Table V. [d] NR (no reaction) indicates the process was examined using double resonance techniques and not observed. [e] Even though exothermic this process gave a positive double resonance response. This likely results from the competition of exothermic fluoride- and hydride-transfer reactions, suggesting that the latter process is more favorable only at high ion kinetic energies. [f] Double resonance results are consistent with $D(\text{CH}_3^+\text{-F}^-) > D(\text{CF}_3^+\text{-F}^-)$. This is in disagreement with the calculated enthalpy change using data from Table V (see discussion in text).

The fluoride- and hydride-transfer reactions observed in this study are summarized in Table IV along with the sign of dk/dE as determined by double resonance. In mixtures it is observed that exothermic fluoride-transfer reactions occur to the virtual exclusion of hydride transfer even when the latter process is significantly exothermic. Hydride-transfer reactions involving fluoromethane neutrals (e.g., reaction 8) may all proceed through halonium ion intermediates. From the results summarized in Table IV, it is apparent that the relative fluoride affinities[43] of the fluoromethyl cations are CH₃⁺ > CF₃⁺ > CHF₂⁺ > CH₂F⁺. Although it is less clear due to the competing fluoride-transfer reactions, the only order which can be constructed which is consistent with all observations gives the relative hydride affinities as CH₃⁺ > CF₃⁺ > CH₂F⁺ > CHF₂⁺.

All thermochemical data used and arrived at in this study are summarized in Table V. All data refer to species in the gas phase at 298°K. The present results in conjunction with available literature data permit construction of Table VI for the properties of fluoromethyl cations. For a reference point we have arbitrarily chosen the determination of the photoionization threshold for the production of CH₂F⁺ from CH₃F which gives $\Delta H_f(\text{CH}_2\text{F}^+) = 200.3$ kcal/mol.[27] Combining this value with $\Delta H = -0.3$ kcal/mol for reaction 12 gives $\Delta H_f(\text{CHF}_2^+) = 142.4$ kcal/mol. This is in good agreement with the value $\Delta H_f(\text{CHF}_2^+) = 142.1$ kcal/mol derived from Lossing's study of the fragmentation processes in CH₂F₂ using monoenergetic electron impact techniques.[29] The ionization potential of the radical R is related to the heats of formation or R⁺

Table V. Summary of Thermochemical Data Used in This Study[a]

Neutral species	ΔH_f	Ref	Ionic species	ΔH_f	Ref
CH₄	−17.89	b	CH₄⁺	276.1	h
CH₃F	−55.9	b	CH₃F⁺	233.3	h
CH₂F₂	−108.1	b	CH₂F₂⁺	185.2	h
CHF₃	−166.3	b	CHF₃⁺	151.9	h
CF₄	−223.0	c	CF₄⁺	131.0	h
CH₃	34.0	b	CH₃⁺	260.9	i
CH₂F	−4.9	d	CH₂F⁺	200.3	d
CHF₂	−59.2	b	CHF₂⁺	142.4	d
CF₃	−112.2	b	CF₃⁺	99.3	j
CF₂	−39.0	e	CF₂⁺	223.7	k
HF	−65.3	f	F⁻	−61.3	f
F	18.72	f	H⁻	33.39	g
H	52.09	g	H⁺	365.7	g

[a] All data in kcal/mol at 298°K. [b] J. A. Kerr and D. M. Timlin, Int. J. Chem. Kinet., **3**, 427 (1971). [c] J. R. Lacher and H. A. Skinner, J. Chem. Soc. A, 1034 (1968). [d] See text for discussion. [e] J. Heicklen, Advan. Photochem., **7**, 57 (1969). [f] W. A. Chupka and J. Berkowitz, J. Chem. Phys., **54**, 5126 (1971). [g] D. D. Wagman, W. H. Evans, V. B. Parker, I. Halow, S. M. Bailey, and R. H. Schumm, National Bureau of Standards Technical Note 270-3, U. S. Government Printing Office, Washington, D. C., 1968. [h] Calculated using the neutral heats of formation and the adiabatic ionization potentials given by C. R. Brundle, M. B. Robin, and H. Basch, J. Chem. Phys., **53**, 2196 (1970). [i] G. Herzberg and J. Shoosmith, Can. J. Phys., **34**, 523 (1956). [j] T. A. Walter, C. Lifshitz, W. A. Chupka, and J. Berkowitz, J. Chem. Phys., **51**, 3531 (1969). [k] T. Su, L. Kevan, and T. O. Tiernan, J. Chem. Phys., **54**, 4871 (1971).

and R as indicated in eq 25. Lossing has determined

$$\text{IP(R)} = \Delta H_f(\text{R}^+) - \Delta H_f(\text{R}) \qquad (25)$$

the adiabatic ionization potential of CH₂F to be 8.90 eV.[29] Although he was able to observe only upper limits for the ionization potentials of CHF₂ and CF₃, Lossing provides evidence from competitive

(43) ΔH and ΔG have opposite signs for the nearly thermoneutral fluoride-transfer reaction 12. Since fluoride affinities have been defined as the negative of the enthalpy change for the process R⁺ + F⁻ → RF, it is the sign of ΔH which determines the relative fluoride affinities.

Table VI. Thermochemical Properties Related to Fluoromethyl Cation Stabilities[a]

R	$\Delta H_f(R)$	$\Delta H_f(RH)$	$\Delta H_f(RF)$	$D(R-H)$	$D(R-F)$	$IP(R)$	$\Delta H_f(R^+)$	$D(R^+-H^-)$	$D(R^+-F^-)$
CH_3	34.0	−17.89	−55.9	104.0	108.6	9.84[b]	260.9	312.2	255.5
CH_2F	−4.9	−55.9	−108.1	103.1	121.9	8.90[c]	200.3	289.6	247.1
CHF_2	−59.2	−108.1	−166.3	101.0	125.8	8.74[d]	142.4	283.9	247.4
CF_3	−112.2	−166.3	−223.0	106.2	129.5	9.17[e]	99.3	299.0	260.0

[a] All thermochemical data in kcal/mol at 298 °K except ionization potentials which are given in eV. Except as noted all data are taken from Table V. [b] G. Herzberg and J. Shoosmith, *Can. J. Phys.*, **34**, 523 (1956). [c] F. P. Lossing, *Bull. Soc. Chim. Belg.*, **81**, 125 (1972). [d] Calculated from $IP(R) = \Delta H_f(R^+) - \Delta H_f(R)$ (see text). [e] T. A. Walker, C. Lifshitz, W. A. Chupka, and J. Berkowitz, *J. Chem. Phys.*, **51**, 3531 (1969). [f] The present work suggests that this value is too high (see text for discussion).

mass spectral fragmentation processes that $8.80 \geq IP(CHF_2) \geq 8.45$ eV. Combining our value for ΔH_f-(CHF_2^+) with $\Delta H_f(CHF_2) = -59.2 \pm 2$ kcal/mol reported by Kerr and Timlin, [44] eq 25 gives $IP(CHF_2) = 8.74$ eV consistent with the limits determined by Lossing. Using the value $\Delta H_f(CH_2F^+) = 200.3$ kcal/mol adopted in the present work and $IP(CH_2F) = 8.90$ eV gives $\Delta H_f(CH_2F) = -4.9$ kcal/mol, which is somewhat higher than the value -7.8 ± 2 kcal/mol reported by Kerr and Timlin.[44] There are obvious uncertainties on the order of ±2 kcal/mol in many of these data. It is to be emphasized, however, that the methodology developed in the present study can yield differences in fluoride affinities accurate to ±0.1 kcal/mol.

While the calculated hydride affinities are in agreement with the observed hydride-transfer reactions, the relative fluoride affinities given in Table VI are not entirely consistent with the experimentally determined order as quoted above. In particular, the data in Table IV indicate that CH_3^+ reacts with CF_4 to yield CF_3^+, a reaction calculated to be 4.5 kcal/mol endothermic. It is not possible at present to resolve this discrepancy, which could be attributed to several sources. For example, $\Delta H_f(CH_3F)$ has never been measured, the value quoted in Table V being an estimate. However, changing $\Delta H_f(CH_3F)$ would also alter several of the quantitative data given above. With these reservations in mind, several criteria may be used in conjunction with the data in Table VI to evaluate the effects of fluorine substituents on carbonium ion stabilities. These include, in addition to relative fluoride and hydride affinities, the effect of successive fluorine substitutions on ionic heats of formation and the ionization potentials of the corresponding radicals. A much smaller decrease (20 kcal/mol less) in ionic heat of formation is observed in proceeding from CHF_2^+ to CF_3^+ than from CH_3^+ to CH_2F^+ and CH_2F^+ to CHF_2^+. Relative ionization potentials of the radicals decrease in the same order $CH_3 > CF_3 > CH_2F > CHF_2$ as the hydride affinities of the corresponding carbonium ions. The different ordering of fluoride and hydride affinities can be understood with the thermochemical cycle of Scheme I described by

Scheme I

$$D(R^+-X^-) = D(R-X) + IP(R) - EA(X) \quad (26)$$
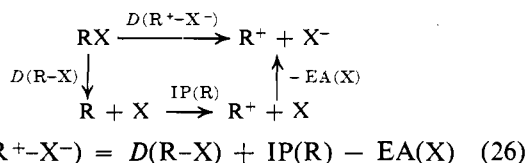
eq 26. Unlike the relatively constant C–H dissociation energies, the C–F bond dissociation energies in the fluoromethanes vary considerably with the number of

(44) J. A. Kerr and D. M. Timlin, *Int. J. Chem. Kinet.*, **3**, 427 (1971).

fluorines present (Table VI). Hence, only the hydride affinities parallel the changes in the radical ionization potentials. A reasonably consistent picture of the effects of fluorine substituents on carbonium ion stability emerges from these data. Dative π bonding is apparently most significant in CH_2F^+ relative to CH_3^+ and to a lesser extent in CHF_2^+ and CF_3^+ relative to CH_2F^+. Destabilization of the carbonium ion by electron withdrawal increases with increasing fluorine substitution, causing CF_3^+ to be less stable than CH_2F^+ and CHF_2^+.

Gas-Phase Basicity of the Fluoromethanes. In our earlier study of the gas-phase ion chemistry of the methyl and ethyl halides, it was observed that even small differences in thermochemical properties are important in determining reactivity, particularly with regard to halonium ion formation and other nucleophilic displacement reactions involving protonated n-donor bases such as the alkyl halides.[4,12-14] The proton affinity of a species, PA(M), defined as the negative of the enthalpy change for the process $M + H^+ \rightarrow MH^+$, quantifies the energetics of reactions involving MH^+ and serves also as a measure of the absolute basicity of the species M.[5] Using well-established methods, the relative proton affinities of a number of species including the fluoromethanes have been determined and are listed in Table VII in the order of decreasing basicity.

Table VII. Relative Proton Affinities of the Fluoromethanes and Other Compounds[a]

Species	Proton affinity, kcal/mol	Ref
C_2H_2	154	b
CH_3F	151	c
$\left\{\begin{array}{l}CH_2F_2\\CHF_3\end{array}\right.$		
CO	142	d
HCl	141	d
CH_4	126	d, e
CF_4		e
N_2	116	e, f

[a] In order of decreasing proton affinity. Brackets indicate compounds could not be distinguished, with proton transfer occurring in both directions with negative dk/dE. [b] F. P. Lossing, *Can. J. Chem.*, **49**, 357 (1971); calculated using $\Delta H_f(C_2H_3^+) = 266$ kcal/mol. [c] J. L. Beauchamp, D. Holtz, S. D. Woodgate, and S. L. Patt, *J. Amer. Chem. Soc.*, **94**, 2798 (1972). [d] M. A. Haney and J. L. Franklin, *J. Phys. Chem.*, **73**, 4329 (1969). [e] A. E. Roche, M. M. Sutton, D. K. Bohme, and H. I. Schiff, *J. Chem. Phys.*, **55**, 5480 (1971). [f] D. K. Bohme, A. E. Roche, and H. I. Schiff, paper presented at the 18th Annual Conference on Mass Spectrometry and Allied Topics, San Francisco, Calif., 1970.

Increased fluorine substitution leads not unexpectedly to a general decrease in basicity. Although the error

limits are quite wide (± 5 kcal/mol), we can assign numerical values to the proton affinities (Table VII) of the fluoromethanes using the known values for the bracketing compounds.

Thermochemical properties related to the proton affinities of the fluoromethanes are summarized in Table VIII, including the ionization potential of the

Table VIII. Thermochemical Data Related to the Gas-Phase Basicities of Fluoromethanes[a]

Species (RF)	IP(RF)[b]	PA(RF)[c]	HA-(RF$^+$)[c]	ΔH_f-(RFH$^+$)	D-(HF-R$^+$)
CH$_3$F	12.54	151	127	159	37
CH$_2$F$_2$	12.72	147	127	111	24
CHF$_3$	13.8	147	152	53	24
CF$_4$	15.35	121	161	22	12

[a] All thermochemical data in kcal/mol at 298°K except ionization potentials which are given in eV. [b] Data correspond to best available estimates of adiabatic ionization potentials, from C. R. Brundle, M. B. Robin, and H. Basch, *J. Chem. Phys.*, **53**, 2196 (1970). [c] Estimated uncertainty ± 5 kcal/mol.

neutral and the hydrogen affinity of the molecular ion, HA(M$^+$). The latter quantity is the MH$^+$ bond dissociation energy (MH$^+ \rightarrow$ M$^+$ + H). It is of interest to note that the hydrogen affinities increase markedly with fluorine substitution. This is in contrast to earlier studies in which hydrogen affinities have been found to be invariant to substituent changes for many other homogous series of compounds including alcohols,[45] amines,[7] ethers,[46] aldehydes,[45,46] and ketones.[45,46] The fluoromethanes are unusual in comparison to these other series in that the adiabatic ionization potential does not correspond to removal of an electron from the n-donor pair to which the proton binds in forming the conjugate acid.[30-32] The assumption that hydrogen affinities are invariant to substituent changes provides a useful basis for extending and correlating[7,45] gas-phase proton affinity data. It should be applied with caution, however, when unusual features of the electronic structure of the n-donor base affect the lowest adiabatic ionization potential. Interaction of lone pairs in bifunctional molecules may represent an unusual case in which this caution is required.[47]

Also included in Table VIII are the calculated binding energies of fluoromethyl cations to HF. As noted before,[12-14] the binding energy of methyl cations to n-donor bases (methyl cation affinity) serves to quantify the thermochemical changes attending gas-phase nucleophilic displacement reactions in which methyl cations are transferred between n-donor bases.[48] Inspection of Table VIII indicates that the binding energies of fluoromethyl cations decrease appreciably with increasing fluorine substitution from 37 kcal/mol for CH$_3^+$ to 11 kcal/mol for CF$_3^+$. Using HF as a

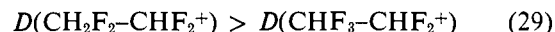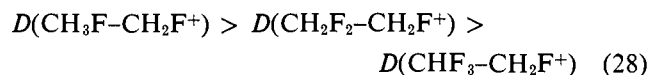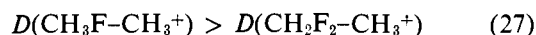(45) M. C. Caserio and J. L. Beauchamp, *J. Amer. Chem. Soc.*, **94** 2638 (1972).

(46) J. L. Beauchamp, Ph.D. Thesis, Harvard University, 1967.

(47) See, for example, D. A. Sweigart and D. W. Turner, *J. Amer. Chem. Soc.*, **94**, 5599 (1972), and references contained therein.

(48) Examples of such processes were observed in mixtures of CO with CHF$_3$ and CH$_2$F$_2$ utilized to determine relative proton affinities. The fluoro-substituted acyl cations CHF$_2$CO$^+$ and CH$_2$FCO$^+$ were formed in nucleophilic displacement reactions entirely analogous to those responsible for the generation of CH$_3$CO$^+$ in a mixture of CO with CH$_3$F as reported previously.[13]

reference base (rather than F$^-$ and H$^-$ as above) thus implies an order of carbonium ion stabilities CF$_3^+$ > CHF$_2^+$ $\cong$ CH$_2$F$^+$ > CH$_3^+$. The unfavorable interactions of the positive charge with the fluorine substituents in the species RFH$^+$ undoubtedly account for the observed relative binding energies of HF to the fluoromethyl cations and thus for the derived order of carbonium ion stabilities being quite different from those derived from relative fluoride and hydride affinities.

From the nucleophilic displacement reactions observed in mixtures of CH$_3$F with CH$_2$F$_2$ and CH$_2$F$_2$ with CHF$_3$, we can write the relative fluoromethyl cation binding energies as in eq 27–29. Thus, it can be

$$D(CH_3F-CH_3^+) > D(CH_2F_2-CH_3^+) \qquad (27)$$

$$D(CH_3F-CH_2F^+) > D(CH_2F_2-CH_2F^+) >$$
$$D(CHF_3-CH_2F^+) \qquad (28)$$

$$D(CH_2F_2-CHF_2^+) > D(CHF_3-CHF_2^+) \qquad (29)$$

inferred that the binding energies of the fluoromethyl cations decrease with increasing fluorine substitution in the neutral fluoromethane. This parallels the observed basicities of the methyl halides toward binding a proton. The stabilization derived from π donation in the fluoromethyl cations is likely to be substantially reduced when these species bind an n-donor base (*e.g.*, HF or RF). The destabilizing effects due to C–F σ withdrawal remain, however.

General Discussion

Positive Ion Chemistry. The gas-phase ion chemistry of the fluoromethanes follows the systematic trends established for the monosubstituted methyl and ethyl halides. The main reaction sequences are seen to involve the parent ion (when it is present) reacting to form the protonated parent (reaction 30, X = F) and in turn,

$$RX^+ + RX \longrightarrow RXH^+ + R'X \qquad (30)$$
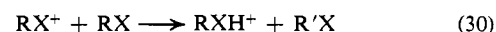
with the exception of CF$_4$, the fluoronium ion R$_2$F$^+$ (reaction 31, X = F). In the absence of a parent ion,

$$RXH^+ + RX \longrightarrow R_2X^+ + HX \qquad (31)$$
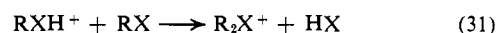
reaction 31 is observed when the protonated parent ion is formed in reactions involving suitable proton donors.

The major fragment ions are fluoro-substituted methyl cations. The interactions of a fluoro-substituted methyl cation R$_1^+$ with a fluoromethane neutral R$_2$F proceeds by nucleophilic attack on the carbonium ion center with formation of an intermediate halonium ion (Scheme II).

Scheme II

$$R_1^+ + R_2X \rightleftharpoons [R_1XR_2^+]^* \rightleftharpoons R_1X + R_2^+$$
$$\downarrow$$
$$\text{other products}$$
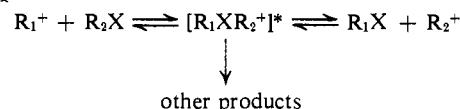
This species may decompose by breaking the bond R$_2$X–R$_1^+$ to regenerate the reactants or the bond R$_1$X–R$_2^+$ to generate the carbonium ion R$_2^+$. In the presence of both neutrals, R$_1$F and R$_2$F, the reaction can proceed reversibly, with the relative abundance of R$_1^+$ and R$_2^+$ being determined by the free energy change for the fluoride-transfer process. Only in the case where an exothermic fluoride transfer is not possible do other exothermic reaction channels appear to compete with these relatively fast processes. The important addi-

tional reaction channel in these instances involves elimination of RH across the RX–R⁺ bond in what has the overall appearance of a hydride-transfer reaction. Collisional stabilization of intermediates involved in fluoride-transfer reactions is not observed at pressures approaching 10^{-2} Torr, even when such reactions are thermoneutral. This implies that the lifetime of the intermediate halonium ion in Scheme II is relatively short ($<10^{-6}$ sec).

Thermochemistry. The present studies demonstrate the effects of fluorine substituents on the stability and reactivity of protonated fluoromethanes, dimethylfluoronium ions, and fluoromethyl cations.

The basicities of the fluoromethanes toward both methyl cations and protons decrease with increasing fluorine substitution. This can be attributed to the unfavorable interaction of the positive charge in the ions with the highly polar and electronegative fluorine substituents.

The important result of the present study relates to the use of relatively fast fluoride-transfer reactions to determine carbonium ion stabilities. We originally attempted to observe hydride-transfer reactions (e.g., reaction 1, X = H) between carbonium ions as a means of determining carbonium ion stabilities.[49] The rates of these reactions for many interesting pairs of carbonium ions (e.g., tert-butyl and isopentyl) are too slow to permit the establishment of equilibrium at convenient pressures and reaction times. Our observations in this matter are in agreement with results of other recent investigations of hydride-transfer reactions.[50] The rationale for the observation of rapid fluoride-transfer reactions is a simple one, namely that the carbonium ion interacts at long range with the C–F bond dipole so as to favorably approach and bind to fluorine, thus forming the postulated fluoronium ion intermediate (Scheme II). This site selectivity in the collision of the carbonium ion with the fluorine-substituted species has no parallel in the case of the analogous hydride-transfer reaction.

With a sufficiently large number of reference species it should be possible to accurately determine the stability of many carbonium ions of chemical interest. The

present method of examining fluoride-transfer reactions directly complements other techniques such as electron impact and photoionization mass spectrometry of neutrals and free radicals for determining ion thermochemical properties. While it is not without problems in its application, the thermochemical kinetic method employed here does not suffer from the difficulties known to be associated with particle and photon impact spectroscopy. Such problems include inability to accurately identify ionization thresholds[28,29] and assess the contributions of thermal energy to ionization and fragmentation processes,[51] and ambiguities associated with the time scale of the experiment in which it is necessary to relate the decomposition rate near threshold with excess energy present in the decomposing ion ("kinetic shifts").[52] The present "adiabatic" method of examining halide- (and other functional group) transfer reactions is especially well suited for measuring *small* differences in ion stability and hence assessing substituent effects.

Considering carbonium ions as Lewis acids, it is to be emphasized that there is no absolute scale of carbonium ion stabilities. As with any acid–base interaction, the scale is dependent on the reference base. Hence, we have shown that different orders of stability, which can be reasonably accounted for, are derived for the reference bases H⁻, F⁻, HF, and RF. The observed reversal of relative binding energies of F⁻ and H⁻ for different pairs of carbonium ions has interesting consequences in the case of CH_2F_2. Processes 12 and 13 comprise a chain reaction sequence which converts CH_2F to a mixture of CH_3F and CHF_3, the overall process (reaction 32) being exothermic by 6.0 kcal/mol.

$$2CH_2F_2 \longrightarrow CH_3F + CHF_3 \qquad (32)$$
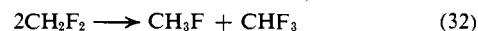
Similar reversals of fluoride and hydride affinities have been observed for other pairs of carbonium ions along with the occurrence of chain reactions analogous to reactions 12 and 13.[8] These interesting processes are being further investigated.[53]

(49) D. P. Ridge and J. L. Beauchamp, unpublished results.

(50) P. Ausloos and S. G. Lias, *J. Amer. Chem. Soc.*, **92**, 5037 (1970); L. Hellner and L. W. Sieck, *J. Res. Nat. Bur. Stand., Sect. A*, **75**, 487 (1971).

(51) W. A. Chupka, *J. Chem. Phys.*, **54**, 1936 (1971).

(52) W. A. Chupka, *J. Chem. Phys.*, **30**, 191 (1959).

(53) For a discussion of the importance of radiation-induced ionic chain reactions in gases, see K. M. Bansal and G. R. Freeman, *Radiat. Res. Rev.*, **3**, 209 (1971).