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Competition between Proton Transfer and Elimination in the Reactions of Strong Bases with Fluoroethanes in the Gas Phase. Influence of Base Strength on Reactivity

S. A. Sullivan^{1a} and J. L. Beauchamp*^{1b}

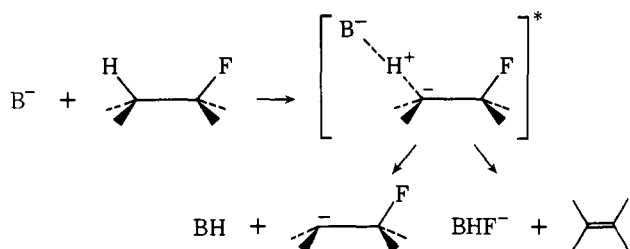
Contribution No. 5100 from the Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, California 91125.

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Abstract: Fluoroethanes react with strong bases in the gas phase by proton transfer, elimination of HF, and production of F^- . Ion cyclotron resonance spectroscopy has been used to examine the relative importance of these processes for a series of bases of varying strength, including NH_2^- , OH^- , CH_3O^- , $CH_3CH_2O^-$, $(CH_3)_2CHO^-$, $(CH_3)_3CO^-$, F^- , and CN^- . Reactant base strength is the principal factor determining product distributions. With decreasing base strength, the amount of proton transfer decreases relative to elimination. Observed proton transfer reactions establish limits for the acidities of the fluoroethanes. In addition, binding energies of F^- to the fluoroethanes, fluoroethylenes, and HF have been determined. With these thermochemical data, a satisfactory explanation of the effect of base strength on reactivity is provided by the application of straightforward concepts of unimolecular reaction kinetics.

With the development of ion cyclotron resonance spectroscopy (ICR), it has become possible to examine organic reaction mechanisms without solvent mediation. In particular, the result of a bimolecular encounter between a reagent ion and a neutral molecule can be observed. We have recently demonstrated, for example, that strong bases such as CH_3O^- can effect elimination reactions in the gas phase.² These studies are summarized in Scheme I. The interaction

Scheme I



of a base with an acidic hydrogen of the fluoroalkane leads to the formation of a chemically activated intermediate which can decompose either by cleavage of the C-H bond (proton transfer) or by cis elimination with HF remaining bound to the attacking base. With several fluoroethanes F^- is also observed. It was proposed that this product results from the breakup of either the intermediate or ionic products in Scheme I rather than from a nucleophilic displacement reaction. The ionic products in Scheme I react further, transferring F^- to the neutral fluoroethane. When ob-

served, the product F^- effects HF elimination from the neutral fluoroethane to form the bihalide ion FHF^- .

We wish to report an extension of the above studies in which reactivity has been examined with a range of gases of varying strength. With different bases it is expected that the internal excitation of the reaction intermediate, as well as the exothermicities of the different reaction pathways, can be varied significantly. The reactants selected include NH_2^- , OH^- , CH_3O^- , $CH_3CH_2O^-$, $(CH_3)_2CHO^-$, $(CH_3)_3CO^-$, F^- , and CN^- , which cover a wide range of base strengths (Table I).

Experimental Section

Experiments were performed using both a modified Varian V-5900 ICR spectrometer with a 9-in. magnet system and a spectrometer, built in this laboratory, incorporating a 15-in. magnet and capable of operating up to m/e 750. The general aspects of instrumentation and experimental techniques of ICR have been detailed elsewhere.³

In a typical experiment the precursor of the reagent base was admitted to the analyzer and maintained at a constant pressure. The fluoroethane was subsequently added through another inlet so that its pressure could be varied independently. Relative ion intensities were measured as a function of the fluoroethane partial pressure. To determine the relative acidities of the fluoroethanes, a reagent base is added to a mixture of two ethanes. The fluoroethyl carbanions are formed and their reactions with neutral ethanes can be observed. These experiments were performed using three inlets which allowed independent pressure variation of all components. Pressure measurements were made using a Schulz-Phelps ion gauge, calibrated against a MKS Baratron Model 90H1-E capaci-

Table I. Thermodynamic Properties of Reactant Bases^a

BH	$\Delta H_f(\text{BH})^b$	PA(B ⁻) ^c	$\Delta H_f(\text{B}^-)^f$
NH ₃	-11.0	403.8 ^d	25.6
H ₂ O	-57.8	390 ^e	-36
CH ₃ OH	-48.1	376.8	-38.5
CH ₃ CH ₂ OH	-56.2	374.9	-48.5
(CH ₃) ₂ CHOH	-65.1	373.5	-58.8
(CH ₃) ₃ COH	-74.7	372.7	-69.2
HF	-65.1	371.3 ^f	-61.0 ^g
HCN	-32.3	348.9 ^f	15.5 ^h

^a All values in kcal/mol at 298 K. ^b Neutral heats of formation are from J. D. Cox and G. Pilcher, "Thermochemistry of Organic and Organometallic Compounds", Academic Press, New York, N.Y., 1970, and D. R. Stull and H. Prophet, *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand.*, No. 37 (1971). ^c The proton affinities of the alkoxide anions are taken from R. T. McIver, Jr., and J. S. Miller, *J. Am. Chem. Soc.*, 96, 4325 (1974). ^d Calculated from $D(\text{NH}_2-\text{H}) = 107.4$ kcal/mol and $\text{EA}(\text{NH}_2) = 0.744$ eV; see D. K. Bohme, R. S. Hemswoorth, and H. W. Rundle, *J. Chem. Phys.*, 59, 77 (1973). ^e Calculated using eq 11 with $D(\text{HO}-\text{H}) = 119$ kcal/mol from J. A. Kerr, *Chem. Rev.*, 66, 465 (1966); $\text{EA}(\text{HO}) = 42.20$ kcal/mol from J. I. Brauman and K. C. Symth, *J. Am. Chem. Soc.*, 91, 7778 (1969); and $\text{IP}(\text{H}) = 313.58$ kcal/mol from J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, K. Draxl, and F. H. Field, *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand.*, No. 26 (1969). ^f Calculated, except as noted, from data in this table using $\Delta H_f(\text{H}^+) = 367.2$ kcal/mol. ^g Calculated using $\text{EA}(\text{F}) = 3.398$ eV from R. Milstein and R. S. Berry, *J. Chem. Phys.*, 55, 4140 (1971). ^h $\Delta H_f(\text{CN}^-) = 15.5$ kcal/mol from R. T. McIver and J. R. Eyler, *J. Am. Chem. Soc.*, 93, 6334 (1971).

tance manometer at higher pressures. Double resonance experiments were used to identify reacting ions.

Alkoxide ions were produced by thermal electron attachment to alkyl nitrites.⁴ Small amounts of the enolate anions *m/e* 43 (CH_2CHO^-) and *m/e* 57 ($\text{CH}_2\text{C}(\text{CH}_3)\text{O}^-$) are produced in ethyl and isopropyl nitrite, respectively, along with *m/e* 31 (HNO^-). Alkoxide anions react with the alkyl nitrites forming *m/e* 46 (NO_2^-). This reaction is minimized by maintaining the pressure of the nitrite at $\sim 10^{-6}$ Torr. Double resonance experiments indicate that only the alkoxide anions participate in reactions with fluoroethanes.

Low-energy dissociative electron capture processes⁵ yield NH_2^- from NH_3 , F^- from NF_3 and $\text{CH}_2\text{CHCFH}_2$, and CN^- from HCN . The base OH^- was generated in H_2O by the reaction of H^- , formed by dissociative electron capture.^{5,6}

Alkyl nitrites were prepared from the corresponding alcohols using standard methods.⁷ Allyl fluoride was provided by Professor F. S. Rowland of the University of California at Irvine. The fluoroethanes were from Peninsular Chemresearch with the exception of $\text{CH}_3\text{CF}_2\text{H}$ (Matheson) and CF_3CFH_2 (provided by Dr. R. F. Hein of the Du Pont de Nemours Co.). All other compounds were from commercial sources and were used as supplied. Noncondensable impurities were removed from all samples prior to use by repeated freeze-pump-thaw cycles.

Results

Product distributions for the reactions of fluoroethanes with different bases are summarized in Table II. From these data it is evident that the ratio of proton transfer to elimination decreases with decreasing base strength. For each fluoroethane there is a minimum base strength such that weaker bases effect only elimination. Fluoride ions are produced only with the strongest bases and again the minimum base strength necessary to observe the reaction depends on the fluoroethane.

Since the purpose of this study was to determine the influence of base strength on product distributions, reaction rates were not accurately measured. Total reaction rates are qualitatively described in Table II as fast (10^{-9} – 10^{-10} cm^3 molecule⁻¹ s⁻¹), slow (10^{-10} – 10^{-11} cm^3 molecule⁻¹ s⁻¹), or very slow ($< 10^{-11}$ cm^3 molecule⁻¹ s⁻¹). These are estimates based on the total conversion of reactants to products as a function of pressure.

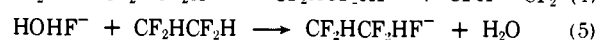
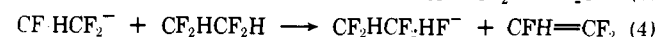
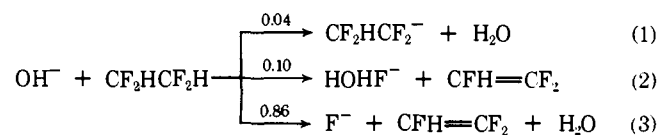
Table II. Product Distributions for Reactions of Bases with Fluoroethanes^a

Fluoroethane	Base ^b	Total rate ^d	Elimination	Proton transfer	F ⁻ production
CH ₃ CH ₂ F	OH ⁻	f	0.09	0.01	0.90
	CH ₃ O ⁻	f	0.29	0.34	0.37
	CH ₃ CH ₂ O ⁻	s	0.17	0.14	0.69
CH ₃ CHF ₂	(CH ₃) ₂ CHO ⁻	vs	1.00		
	OH ⁻	f	0.71	0.01	0.28
	CH ₃ O ⁻	f	0.71	0.29	
	CH ₃ CH ₂ O ⁻	f	0.94	0.06	
CH ₃ CF ₃	(CH ₃) ₂ CHO ⁻	s	1.00		
	NH ₂ ⁻	f	0.12	0.36	0.52
	OH ⁻	f	0.70	0.30	
	CH ₃ O ⁻	f	0.93	0.07	
CH ₂ FCHF ₂	CH ₃ CH ₂ O ⁻	f	0.98	0.02	
	(CH ₃) ₂ CHO ⁻	s	1.00		
	OH ⁻	f	0.08	0.07	0.85
	CH ₃ O ⁻	f	0.50	0.33	0.17
	CH ₃ CH ₂ O ⁻	f	0.79	0.21	
	(CH ₃) ₂ CHO ⁻	s	0.82	0.18	
CHF ₂ CHF ₂	(CH ₃) ₃ CO ⁻	s	0.89	0.11	
	F ⁻	s	1.00		
	NH ₂ ⁻	f	0.05	0.07	0.88
	OH ⁻	f	0.10	0.04	0.86
	CH ₃ O ⁻	f	0.11	0.89	
	CH ₃ CH ₂ O ⁻	f	0.28	0.72	
	(CH ₃) ₂ CHO ⁻	f	0.47	0.53	
	(CH ₃) ₃ CO ⁻	f	0.40	0.60	
CH ₂ FCF ₃	F ⁻	s	1.00		
	CN ⁻	vs	1.00		
	NH ₂ ⁻	f		0.44	0.56
	OH ⁻	f	0.79	0.21	
	CH ₃ O ⁻	f	0.61	0.39	
	(CH ₃) ₃ O ⁻	f	0.97	0.03	
CHF ₂ CF ₃	F ⁻	f	1.00		
	NH ₂ ⁻	f		1.00	
	OH ⁻	f		1.00	
	CH ₃ O ⁻	f		1.00	
	(CH ₃) ₃ O ⁻	f		1.00	
	F ⁻	f	1.00		

^a Product ion abundance normalized to 1.00. ^b Bases listed in order of decreasing base strength. The data for CH_3O^- are taken from ref 2; the reagent base actually used was CD_3O^- to avoid interference from HNO^- (see text). ^c $\text{CD}_3\text{CD}_2\text{O}^-$ was used in this case since the products $\text{C}_2\text{H}_5\text{OHF}^-$ and CH_3CF_2^- are both at *m/e* 65. ^d Qualitative total rates of reaction; fast (f) $k = 10^{-9}$ – 10^{-10} cm^3 molecule⁻¹ s⁻¹, slow (s) $k = 10^{-10}$ – 10^{-11} cm^3 molecule⁻¹ s⁻¹, and very slow (vs) $k \leq 10^{-11}$ cm^3 molecule⁻¹ s⁻¹.

The reactions of $\text{CF}_2\text{HCF}_2\text{H}$ with several bases illustrate the experimental methods and exemplify the reaction processes observed in other fluoroethanes. Analyzed in detail below are the reactions of $\text{CF}_2\text{HCF}_2\text{H}$ with OH^- , $\text{CH}_3\text{CH}_2\text{O}^-$, and CN^- .

Reactions of OH^- with $\text{CF}_2\text{HCF}_2\text{H}$. The product ions *m/e* 19 (F^-), 37 (HOHF^-), 39 (FHF^-), 101 ($\text{CF}_2\text{HCF}_2^-$), and 121 ($\text{CF}_2\text{HCF}_2\text{HF}^-$) appear as the partial pressure of $\text{CF}_2\text{HCF}_2\text{H}$ is increased (Figure 1). Double resonance experiments indicate that OH^- is the precursor of the secondary product ions HOHF^- , $\text{CF}_2\text{HCF}_2^-$, and F^- , that F^- reacts to produce FHF^- , and that $\text{CF}_2\text{HCF}_2^-$ and HOHF^- react to yield $\text{CF}_2\text{HCF}_2\text{HF}^-$. The sequence of reactions 1–6 is consistent with these results. Both $\text{CF}_2\text{HCF}_2^-$ (eq 4)



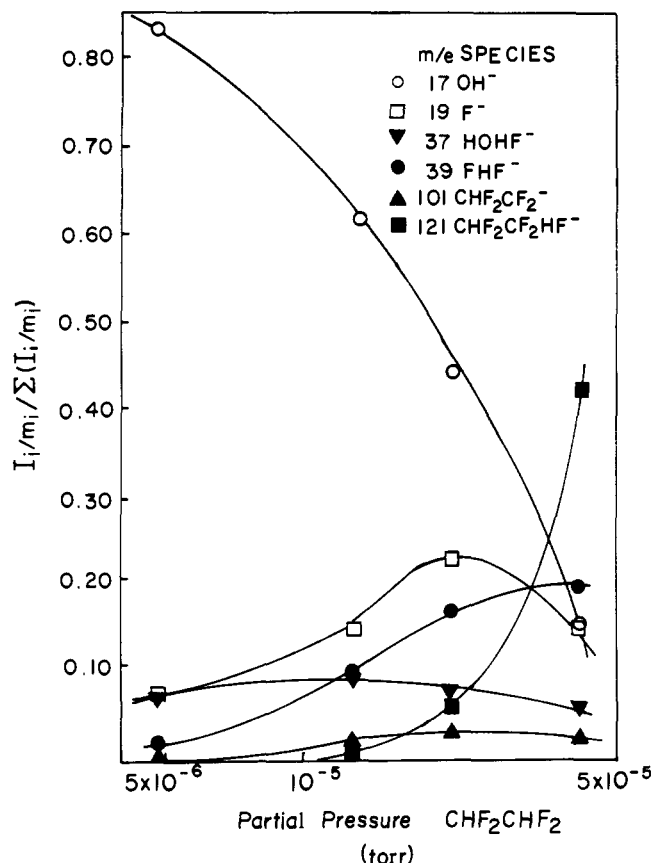
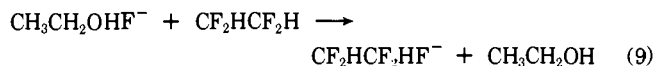
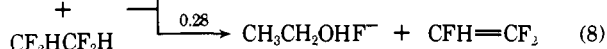


Figure 1. Relative negative ion abundance as a function of CHF_2CHF_2 partial pressure in a mixture of CHF_2CHF_2 and H_2O at 70.0 eV electron energy. The pressure of H_2O is held constant ($\sim 10^{-5}$ Torr) as the CHF_2CHF_2 pressure is varied.

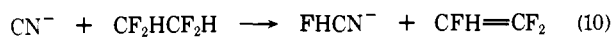
and HOHF^- (eq 5) transfer F^- to the neutral fluoroethane. In contrast, the bihalide ion FHF^- , produced in the elimination reaction (eq 6), does not transfer F^- .

Reactions of $\text{CH}_3\text{CH}_2\text{O}^-$ with $\text{CF}_2\text{HCF}_2\text{H}$. With $\text{CH}_3\text{CH}_2\text{O}^-$ as the reactant base, the product ions m/e 65 ($\text{CH}_3\text{CH}_2\text{OHF}^-$), 101 ($\text{CF}_2\text{HCF}_2^-$), and 121 ($\text{CF}_2\text{HCF}_2\text{HF}^-$) appear as the partial pressure of $\text{CF}_2\text{HCF}_2\text{H}$ is increased (Figure 2). The ethoxide ion is the precursor of the two secondary product ions $\text{CF}_2\text{HCF}_2^-$ and $\text{CH}_3\text{CH}_2\text{OHF}^-$ which subsequently react with the neutral fluoroethane to form $\text{CF}_2\text{HCF}_2\text{HF}^-$. Reactions 7-9 in



addition to the F^- transfer (eq 4) are consistent with these data. Significantly, F^- is not observed as a product.

Reactions of CN^- with $\text{CF}_2\text{HCF}_2\text{H}$. With the relatively weak base CN^- only the elimination reaction 10 is ob-



served. This is analogous to reaction 6 of F^- with $\text{CF}_2\text{HCF}_2\text{H}$. The product ion m/e 46 (FHCN^-) appears only at high pressures of $\text{CF}_2\text{HCF}_2\text{H}$, indicating a very slow reaction ($k \approx 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$). At 1.6×10^{-4} Torr of $\text{CF}_2\text{HCF}_2\text{H}$, FHCN^- is only 3% of total ionization.

Generation of Negative Ions from the Fluoroethanes. In general the reactions of $\text{CF}_2\text{HCF}_2\text{H}$ typify those of the

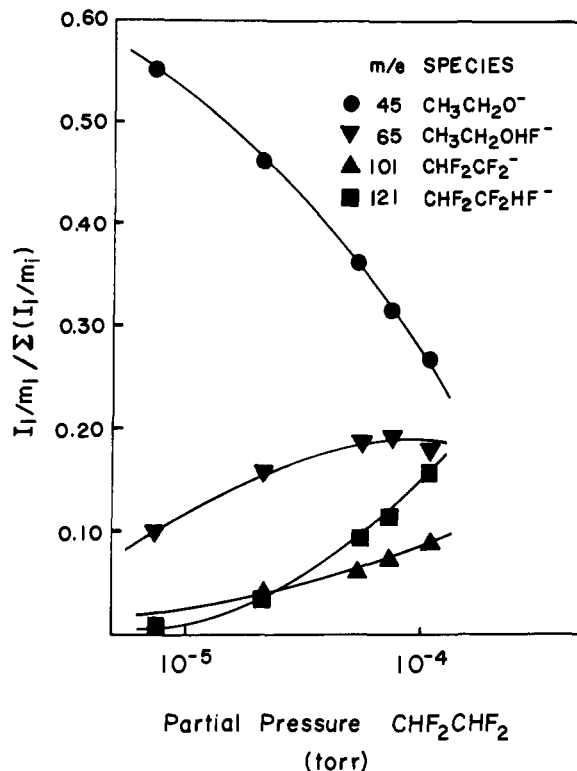


Figure 2. Relative negative ion abundance as a function of CHF_2CHF_2 partial pressures in a mixture of CHF_2CHF_2 and $\text{CH}_3\text{CH}_2\text{ONO}$ at 70.0 eV electron energy.

other fluoroethanes. In the case of $\text{CF}_3\text{CF}_2\text{H}$, however, several observations deserve special comment. To examine the possible formation of negative ions directly from fluoroethanes the neutral precursor of the reagent base was removed at the highest fluoroethane pressure employed in each study. Pentafluoroethane is the only case in which a negative ion m/e 119 (CF_3CF_2^-) is formed directly at 70 eV electron energy. Pentafluoroethane is further distinguished in that elimination and F^- production do not occur with any of the bases used. In addition, the carbanion product CF_3CF_2^- does not transfer F^- to the neutral fluoroethane.

Mixtures of Fluoroethanes. If it is assumed that failure to observe a proton transfer reaction indicates that the process is endothermic, then the proton affinities of the fluoroethyl carbanions relative to the alkoxide anions can be estimated (Table III), based on data in Table II. Attempts were made to confirm this ordering of acidities by determining the preferred direction of proton transfer in mixtures of fluoroethanes with reference acids. These studies were complicated by the rapid transfer of F^- from the fluorocarbanion to acidic species (e.g., reaction 4) which occurs in competition with proton transfer. While this prevented a complete ordering, the relative acidities $\text{CF}_3\text{CH}_3 > \text{CF}_2\text{HCFH}_2 > \text{CF}_2\text{HCH}_3$ were determined. These results are consistent with the order obtained from product distribution data. No reaction of CF_3CF_2^- with other fluoroethanes was observed, suggesting that $\text{CF}_3\text{CF}_2\text{H}$ is the strongest acid. The proton affinities of fluoroethyl carbanions are bounded by those of $\text{CH}_3\text{CH}_2\text{O}^-$ and F^- , a surprisingly small range of only 4 kcal/mol. Therefore the error in the estimated proton affinities in Table III cannot be large, even though the exact order of acidities is not firmly established.

Discussion

Thermochemical Inferences. The acidities of the fluoroethanes have not previously been considered in detail. It is

Table III. Proton Affinities of the Fluoroethanes^a

B ⁻	PA(B ⁻) ^b
CH ₃ O ⁻	376.8
CH ₃ CH ₂ O ⁻	374.9
CH ₂ FCH ₂ ⁻	374 ^c
CHF ₂ CH ₂ ⁻	
CF ₃ CH ₂ ⁻	
(CH ₃) ₂ CHO ⁻	
(CH ₃) ₃ CO ⁻	373.5
CHF ₂ CHF ⁻	372.7
CHF ₂ CF ₂ ⁻	372
CF ₃ CHF ⁻	372 ^c
CF ₃ CF ₂ ⁻	
CF ₃ CF ₂ ⁻	372
F ⁻	371.3

^a The proton affinity (PA) is defined as the enthalpy for the reaction $BH \rightarrow B^- + H^+$. ^b All values in kcal/mol. The proton affinities of the alkoxides are from M. T. McIver and J. S. Miller, *J. Am. Chem. Soc.*, **96**, 4323 (1974). Data for the fluoroethyl carbanions are estimates based on the ordering relative to the alkoxides and F⁻. ^c The order of acidities for these fluoroethanes has not been established.

Table IV. F⁻ Binding Energies to Fluorine Substituted Olefins and Ethanes^a

Ethane	Olefin	Binding energies to F ⁻	
		To olefin ^b	To ethane ^c
CH ₃ CH ₂ F	CH ₂ CH ₂	6	41
CH ₃ CHF ₂	CH ₂ CHF	19	41
CH ₃ CF ₃	CH ₂ CF ₂	31	41
CH ₂ FCHF ₂	CHFCHF	22	43
CHF ₂ CHF ₂	CHF ₂ CF ₂	25 ^d	43
CH ₂ F ₂ CF ₃	CHF ₂ CF ₂	35 ^d	43
CHF ₂ CF ₃	CF ₂ CF ₂	44	43

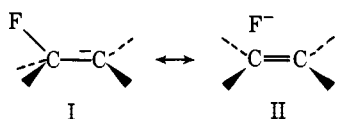
^a Bond energies in kcal/mol. ^b Calculated using data in Tables III and V. ^c Calculated using data in Table III and eq 15. ^d Binding energies of F⁻ to the different carbons of CHF₂CF₂.

expected that C₂H₆ is only weakly acidic, with PA(C₂H₅⁻) greater than 404 kcal/mol.⁸ If this is correct, then our data indicate that addition of a single fluorine leads to an increase in acidity of ~30 kcal/mol. No large effects are then observed with further fluorine substitution. The proton affinity of an anion B⁻ is related to the homolytic bond dissociation energy $D(B-H)$ and the electron affinity EA(B) by eq 11. The C-H bond dissociation energies of CF₃CH₃

$$PA(B^-) = D(B-H) - EA(B) + IP(H) \quad (11)$$

(106.7 ± 1.1 kcal/mol)⁹ and CF₃CF₂H (103.0 ± 1.0 kcal/mol)¹⁰ are both somewhat higher than ethane (98 kcal/mol).¹¹ Using these data and proton affinities in Table III, eq 11 gives an electron affinity of 2.0 ± 0.2 eV for both CF₃CH₂ and CF₃CF₂.¹²

Reported gas-phase studies of fluorinated ethanols and acetic acids¹³ indicate a large stepwise increase in acidity with increasing β-fluorine substitution. This is adequately explained by the interaction of the negative charge with C-F bond dipoles. The fluoroethanes exhibit contrasting behavior, with a range of acidities much smaller than electrostatic arguments predict. The major effect is observed on addition of one fluorine. If the fluoroethyl carbanion I is



significantly stabilized by charge delocalization as indicated in II (negative fluorine hyperconjugation),^{14,15} then simple electrostatic arguments will be inappropriate to explain the observed relative acidities.

Table V. Thermodynamic Properties of the Fluoroethanes and Ethylenes^a

Fluoroethane	ΔH_f^c	Ethylene	ΔH_f^c	ΔH_f^f
CH ₃ CH ₂ F	-61	CH ₂ =CH ₂	12.5	8
CH ₃ CHF ₂	-118	CH ₂ =CHF	-28	25
CH ₃ CF ₃	-178	CH ₂ =CF ₂	-80	33
CHF ₂ CH ₂ F ^b	-159	CH ₂ =CF ₂	-80	14
		CHF=CHF	-72 ^d	22
CHF ₂ CHF ₂	-209	CHF=CF ₂	-119	25
CH ₂ FCF ₃	-219 ^d	CHF=CF ₂	-119	35
CHF ₂ CF ₃	-266 ^e	CF ₂ =CF ₂	-157	44

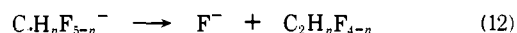
^a All values in kcal/mol at 298 K. ^b There are two possible modes of removal of HF from CHF₂CH₂F. The formation of CH₂CF₂ is less endothermic. ^c The heats of formation of the fluoroethanes and olefins are taken from J. R. Skinner and H. A. Lacher, *J. Chem. Soc. A*, 1034 (1968); G. E. Millward, R. Hortig, and E. Tschuikow-Roux, *J. Phys. Chem.*, **75**, 3195 (1971); and T. Smail, R. S. Iyer, and F. S. Rowland, *J. Am. Chem. Soc.*, **94**, 1041 (1972). The heat of formation of C₂H₄ is taken from ref 20. ^d Estimate based on trends in heats of formation of other fluorinated ethanes and ethylenes. ^e Calculated from $\Delta H_f(CF_3CF_2)$ of -214.9 kcal/mol, R. E. Marcotte and T. O. Tiernan, *J. Chem. Phys.*, **54**, 3385 (1971), and a $D(CF_3CF_2-H)$ of 103.0 kcal/mol from ref 10. ^f Enthalpy for removal of HF from the fluoroethane.

Table VI. Hydrogen Bond Strengths in BHF^{-a}

BH	$D(BH \cdots F^-)$		Calcd using eq 15
	Lower limit	Upper limit	
NH ₃	1	3	2
H ₂ O	17	26	20
CH ₃ OH	30	39	37
CH ₃ CH ₂ OH	32	41	40
(CH ₃) ₂ CHOH	33	42	41
(CH ₃) ₃ COH	34	43	42
HF	44	50 ^c	44
HCN	48 ^b		73

^a Bond strengths in kcal/mol. ^b This limit is based on results of mixture of CN⁻ with CHF₂CHF₂ in which elimination was observed; no upper limit was determined. ^c The upper limit is taken as 50 kcal/mol (see ref 16).

Binding energies of F⁻ to fluoroolefins (given by the enthalpy change for eq 12, where $n = 0-4$) can be calculated



from the proton affinities of the fluoroethyl carbanions. These data, summarized in Table IV, indicate an increase in binding energy with increased fluorine substitution on the olefinic carbon to which F⁻ is bound.

For the general process 13 (where $n = 1-5$) to be exo-



thermic, the binding energy of HF to the reactant base must be greater than the enthalpy change for elimination of HF from the fluoroethane (Table V). For example, observation of the elimination of HF from CF₃CFH₂ by CH₃O⁻ indicates $D(CH_3O^- - HF) \geq 35$ kcal/mol, from which a lower limit of 30 kcal/mol can be calculated for $D(CH_3OH - F^-)$. Although not rigorously established, upper limits to these hydrogen bond strengths may be derived from the failure to observe particular eliminations. For example, CH₃O⁻ fails to effect elimination of HF from CF₃CF₂H, establishing upper limits of 44 kcal/mol for $D(CH_3O^- - HF)$ and 39 kcal/mol for $D(CH_3OH - F^-)$. Limits for the binding energies of F⁻ to NH₃, H₂O, HF,¹⁶ HCN, and the alcohols are listed in Table VI.

Yamdagni and Kebarle¹⁷ have measured hydrogen bond strengths for a variety of anionic dimers. Their results indicate that the hydrogen bond strength $D(BH-X^-)$ will increase with the acidity of BH as well as the basicity of X⁻.

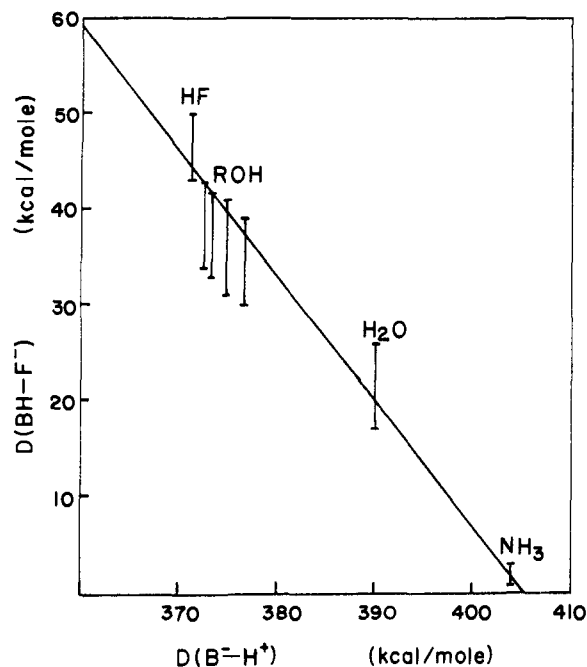


Figure 3. Variation of hydrogen bond strengths $D(\text{BH}-\text{F}^-)$ with proton affinity of B^- . The hydrogen bond strengths in each case are the limits summarized in Table VI.

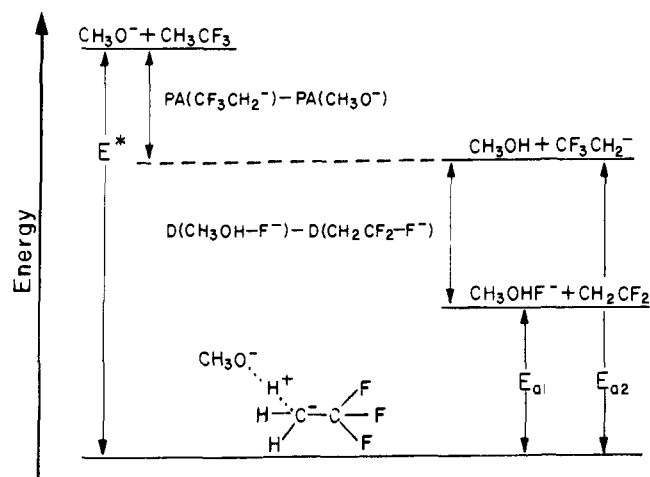


Figure 4. The energetics of the reaction of CH_3O^- with CH_3CF_3 . E^* is the internal energy of the intermediate while E_{a1} and E_{a2} are the activation energies for elimination and proton transfer, respectively.

$$D(\text{BH}-\text{X}^-) = aD(\text{H}^+-\text{X}^-) + bD(\text{B}^--\text{H}^+) \quad (14)$$

Kebarle has proposed the empirical eq 14 to correlate hydrogen bond strengths. Derived limits for the binding energy of F^- to various acids BH are displayed in Figure 3. All of the experimental limits can be accommodated by eq 15,

$$D(\text{BH}-\text{F}^-) = 1.41D(\text{H}^+-\text{F}^-) - 1.29D(\text{B}^--\text{H}^+) \quad (15)$$

which is indicated by the straight line in Figure 3.

The acidities given in Table III can be used with eq 15 to calculate binding energies of F^- to the fluoroethanes. With the exception of pentafluoroethane, these binding energies are all higher than those calculated for the binding energies of F^- to the corresponding olefins (Table IV). These results are consistent with observed F^- transfer reactions from the conjugate bases of the fluoroethanes to the parent neutral. In addition, F^- transfer from FHF^- to all of the fluoroethanes is expected to be endothermic. This is also corroborated by experiment.

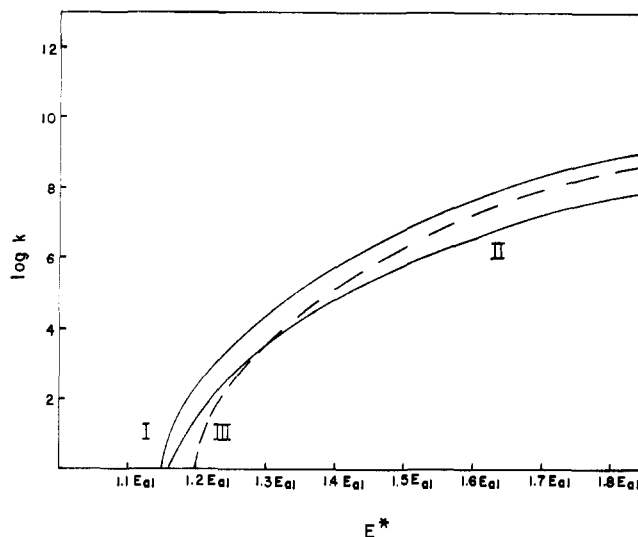


Figure 5. Qualitative variation of rate constant for proton transfer and elimination as a function of the relative activation energies for the two processes, calculated using eq 16. E^* is given in terms of E_{a1} , the activation energy for elimination. The solid lines I and II represent the two processes with the same activation energy. The dashed line III represents proton transfer occurring with an activation energy 5% higher than elimination ($E_{a2} = 1.05E_{a1}$).

Effect of Base Strength on Reactivity. Base strength is seen to be the single most important factor in determining reactivity. The data in Table II indicate that the ratio of proton transfer to elimination decreases in a consistent fashion with decreasing base strength. These processes occur as a result of the competitive fragmentation of the chemically activated intermediate formed by interaction of the reactant base and fluoroethane as illustrated in Scheme I. The influence of base strength on reactivity can be readily understood by first considering the effect it has on internal excitation (E^*) of the reaction intermediate and the activation energies (relative exothermicities) of the elimination (E_{a1}) and proton transfer (E_{a2}) processes and then applying straightforward concepts of unimolecular reaction kinetics.

The energetic changes associated with the reaction of CH_3O^- with CH_3CF_3 are illustrated in Figure 4. In Figure 4 the relative energies of the products are determined by the difference in proton affinity between CH_3O^- and CF_3CH_2^- and the difference in binding energies of F^- to the alcohol and the fluoroolefin. For a given fluoroethane, the difference in activation energies $E_{a1} - E_{a2}$ depends in general only on $D(\text{BH}-\text{F}^-)$. Since $D(\text{BH}-\text{F}^-)$ is proportional to $D(\text{B}^--\text{H}^+)$ (eq 14), the activation energy for elimination relative to proton transfer *decreases* with decreasing base strength. For the same reason, E_{a2} *increases* with decreasing base strength.

Reactivity can be related to reaction energetics using the simplified RRR eq 16,¹⁸ where ν and E_a are the frequency

$$k = \nu([E^* - E_a]/E^*)^{s-1} \quad (16)$$

factor and activation energy for the process, E^* is the internal energy of the reaction intermediate, and $s - 1$ may be regarded as the effective number of oscillators.¹⁹ Frequency factors of 10^{13} – 10^{14} s^{-1} are typical for simple bond cleavage. For the more complex elimination reaction, frequency factors an order of magnitude lower are reasonable.²⁰ Using frequency factors of 10^{14} for proton transfer and 10^{13} for elimination, the dependence of relative rates on the difference in activation energies for the two processes is illustrated in Figure 5, where E^* is given in units of E_{a1} . If the activation energies for the two processes are equivalent,

Table VII. Enthalpy Changes for Reaction 17^a

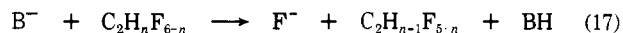
Fluoroethane	Reagent bases					
	NH ₂ ⁻	OH ⁻	CH ₃ O ⁻	CH ₃ CH ₂ O ⁻	(CH ₃) ₂ HCO ⁻	(CH ₃) ₃ CO ⁻
CH ₃ CH ₂ F	-24	-10 ^c	3 ^c	5 ^c	6	7
CH ₃ CHF ₂	-8	7 ^c	19	21	23	24
CH ₂ FCHF ₂ ^b	-18 ^c	-4 ^c	8	10	12	13
CHF ₂ CHF ₂	-7 ^c	7 ^c	19	21	23	24
CH ₂ CF ₃	1 ^c	15	27	29	31	32
CH ₂ FCF ₃	3 ^c	17	29	31	33	34
CHF ₂ CF ₃	13	26	39	41	42	43

^a Enthalpies in kcal/mol; calculated using data in Tables I and V. ^b Calculated, assuming that CH₂CF₂ is the product. ^c In these cases, F⁻ is observed as a reaction product (Table II). Note that not every base was reacted with each fluoroethane. It is expected that the reaction of NH₂⁻ with CH₃CH₂F and CH₃CHF₂ will also produce F⁻.

then proton transfer will always predominate over elimination (Figure 5). If, however, the activation energy for proton transfer is greater than that for elimination (e.g., $E_{a1} = 1.05E_{a2}$ as illustrated by the dashed line in Figure 5), there will be a range of E^* for which elimination predominates. The amount of elimination relative to proton transfer is expected to increase (1) with the increase in the activation energy of proton transfer relative to that of elimination and (2) with a decrease in the excitation energy of the intermediate. These two requirements are fulfilled by a decrease in reactant base strength as seen in Figure 4. With sufficiently weak bases, proton transfer becomes endothermic and only elimination is observed.

Using an estimated $E^* = 43$ kcal/mol for the reaction of CH₃O⁻ with CH₃CF₃ and the experimental product distribution (Table II), a difference in activation energies of 3 kcal/mol is predicted, with $E_a = 34$ and 37 kcal/mol for elimination and proton transfer, respectively. This is in good agreement with the difference in activation energies, $D(\text{CH}_3\text{OH}-\text{F}^-) - D(\text{CH}_2\text{CF}_2-\text{F}^-)$, which is calculated as 4 kcal/mol from data in Tables IV and VI. The changes expected in the relative energetics of proton transfer and elimination with variation of base strength qualitatively explain reactivity in the systems considered in this study.

F⁻ Production. A slow ($k \sim 10^{-12}$ cm³ molecule⁻¹ s⁻¹) nucleophilic displacement of F⁻ by CD₃O⁻ is the only reaction observed with CH₃F and CH₂F₂.²¹ Proton transfer is not observed. Reactions of H⁻, NH₂⁻, OH⁻, and CN⁻ with CH₃F confirm a generally slow rate for gas-phase substitution reactions in which F⁻ is the leaving group.²² In the reactions of the strongest bases with several of the fluoroethanes (Table II), F⁻ comprises a major fraction of the total product distribution. This is inconsistent with a slow rate for displacement of F⁻ and suggests that another mechanism is operating. It is proposed that loss of F⁻ occurs directly from the intermediate or from the dissociation of the ionic products. In either case the products (eq 17, $n =$



1-5) and energetics (Table VII) are equivalent. Considering the possible uncertainties in the thermochemical data employed, there is a reasonably good correlation (Table VII) between the predicted exothermicity of reaction 17 and the observation of F⁻ as a product. This correlation is not expected for nucleophilic displacement reactions, which

would be quite exothermic in many instances where F⁻ is not observed as a product.²³

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