

Reactions of Strong Bases with Alkyl Halides in the Gas Phase. A New Look at E2 Base-Induced Elimination Reactions without Solvent Participation

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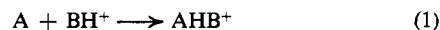
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Abstract: The kinetics and mechanism of a newly identified class of ion-molecule reactions, base-induced elimination reactions, is investigated using the techniques of ion cyclotron resonance spectroscopy. Strong bases, such as CH_3O^- , are observed to interact with the acidic β hydrogen of fluorinated ethanes, forming a chemically activated intermediate which decomposes either by elimination of HF yielding the proton bound dimer CH_3OHF^- and the corresponding olefin or by cleavage of the C-H bond (proton transfer). The fluorine-substituted carbanions formed in the latter process are observed to transfer F^- to the neutral fluoroethane. Although base-induced elimination reactions are observed in other systems, including dehydrochlorination of 1,1,1-trichloroethane and β -chloroethanol, they are most prominent in the case of the fluoroethanes.

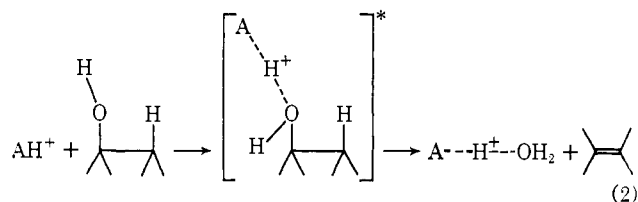
Studies of reactions in the gas phase permit the release and utilization of energy in exoergic chemical transformations to be envisioned in terms of a meaningful potential energy surface. Atomic motions on such a surface, however complicated, serve to characterize the "mechanism" of the reaction, in the absence of solvation phenomena which moderate reactivity in condensed phase reactions. To better understand the role which solvation phenomena play in chemical reactions, it is of general interest to examine processes in the gas phase which occur or have analogies in solution. In this regard, elimination reactions represent an important class of reactions amenable to study in the gas phase. An investigation of the reactions of strong bases with alkyl halides in the gas phase, using the techniques of ion cyclotron resonance spectroscopy,² has revealed a general class of base-induced elimination reactions which form the subject matter for this paper.³

The reasoning which led to the expectation that base-induced elimination reactions could be observed resulted from our continuing investigations of the chemical consequences of strong hydrogen bonding. The strong hydrogen bond, formed by the binding of two *n*-donor bases to a labile proton, participates in a variety of gas phase ion-molecule reactions. Bimolecular⁴ processes in which strong hydrogen bonding has been observed to play an important role include nucleophilic substitution reactions,⁵⁻⁷ acid-induced elimination reactions,^{7,8} and a novel class of associative fragmentation reactions.⁹ These reactions involve at one or

more stages the binding of the base A to the conjugate acid of the base B, forming AHB^+ (reaction 1). Strong



hydrogen bonding of the type illustrated in reaction 1 is, for example, effective in promoting gas phase acid-induced elimination reactions such as the dehydration of alcohols illustrated in reaction 2.^{7,8,10} As indicated



in Table I, the strength of the bond between A and BH^+

Table I. Hydrogen-Bond Strengths in Some Symmetrical Proton Bound Dimers

Process	$-\Delta H$, kcal/mol	Ref
$\text{H}_2\text{O}^+ + \text{H}_2\text{O} \rightarrow (\text{H}_2\text{O})_2\text{H}^+$	32	a, b
$\text{CH}_3\text{OH}_2^+ + \text{CH}_3\text{OH} \rightarrow (\text{CH}_3\text{OH})_2\text{H}^+$	31	c
$\text{NH}_4^+ + \text{NH}_3 \rightarrow (\text{NH}_3)_2\text{H}^+$	25	d
$\text{OH}^- + \text{H}_2\text{O} \rightarrow \text{HOHOH}^-$	24, 36	e, f
$\text{Cl}^- + \text{HCl} \rightarrow \text{ClHCl}^-$	24	e
$\text{F}^- + \text{HF} \rightarrow \text{FHF}^-$	30, 36	e, g

^a M. DePaz, J. J. Levanthal, and L. Friedman, *J. Chem. Phys.*, **51**, 3748 (1969). ^b A. J. Cunningham, J. D. Payzant, and P. Kebarle, *J. Amer. Chem. Soc.*, **94**, 7627 (1972). ^c P. Kebarle, R. N. Haynes, and J. G. Collins, *ibid.*, **89**, 5753 (1967). ^d Reference 11. ^e Reference 14. Considerable uncertainty is attached to these numbers. ^f M. DePaz, A. Guidoni Giardini, and L. Friedman, *J. Chem. Phys.*, **52**, 687 (1970). ^g S. A. Harrell and D. H. McDaniel, *J. Amer. Chem. Soc.*, **92**, 6101 (1970).

(the negative enthalpy change for reaction 1) can be as large as 32 kcal/mol in symmetrical dimers and will be even larger in unsymmetrical dimers if the proton affinity of A is significantly higher than B.¹¹ Thus the

(10) J. L. Beauchamp and R. C. Dunbar, *J. Amer. Chem. Soc.*, **92**, 1477 (1970).

(11) R. Yamdagni and P. Kebarle, *J. Amer. Chem. Soc.*, **95**, 3504 (1973).

(1) (a) National Defense Education Act Predoctoral Fellow; (b) Dreyfus Teacher Scholar.

(2) J. L. Beauchamp, *Annu. Rev. Phys. Chem.*, **22**, 527 (1972).

(3) A preliminary account of this work is given in ref 2 and in D. P. Ridge and J. L. Beauchamp, *J. Amer. Chem. Soc.*, **96**, 637 (1974).

(4) For a discussion of intramolecular interactions of remote functional groups in which strong hydrogen bonding is important, see T. H. Morton and J. L. Beauchamp, *J. Amer. Chem. Soc.*, **94**, 1369 (1972), and D. H. Aue, H. M. Webb, and M. T. Bowers, *ibid.*, **95**, 2699 (1973).

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

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

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

(8) J. L. Beauchamp, *J. Amer. Chem. Soc.*, **91**, 5925 (1969).

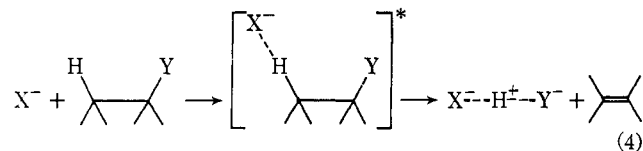
(9) D. P. Ridge and J. L. Beauchamp, *J. Amer. Chem. Soc.*, **93**, 5925 (1971).

postulated intermediate in reaction 2 is chemically activated, with the indicated dehydration process yielding one of the observed decomposition products.

The interaction of the conjugate base of the acid XH with the acid YH, forming XHY⁻ (eq 3), involves the



formation of a strong hydrogen bond with binding energies (Table I) comparable to those observed for process 1.¹²⁻¹⁵ By analogy with reaction 2, we expected the type of strong hydrogen bonding illustrated in eq 3 to participate in the base-induced elimination reaction generalized by reaction 4.



While considerable uncertainty presently exists in the thermochemical data available for specific examples of reaction 3, the data of Kebarle and coworkers¹²⁻¹⁴ can be used to estimate the bond strengths in anionic dimers, and values pertinent to the present work are summarized in Table II. Some trends observed in the

Table II. Bond Strengths in Anionic Dimers^a

X ⁻	HY	D(X ⁻ -HY)	D(XH-Y ⁻) ^e
F ⁻	HOH	23 ^b	44
F ⁻	CH ₃ OH	24 ^d	40
F ⁻	HF	30 ^c	30
F ⁻	HCl	50 ^c	14
Cl ⁻	HOH	13.1 ^b	70.1
Cl ⁻	CH ₃ OH	14.1 ^b	66
Cl ⁻	HCl	24 ^c	24

^a Bond strengths in kcal/mol. ^b Experimentally measured bond strengths from ref 14. ^c Estimated bond strengths from ref 14. Estimates based on trends observed in measured bond strengths. ^d Estimated assuming $D(\text{CH}_3\text{OH-F}^-) - D(\text{HOH-F}^-) \cong D(\text{CH}_3\text{OH-Cl}^-) - D(\text{HOH-Cl}^-)$. ^e These values calculated from $D(X^- - \text{H}^+)$, $D(Y^- - \text{H}^+)$, and $D(X^- - \text{HY})$. Values of $D(X^- - \text{H}^+)$ and $D(Y^- - \text{H}^+)$ were taken from ref 14, except $D(\text{CH}_3\text{O}^- - \text{H}^+)$ which was taken as 385 kcal/mol: D. Holtz, J. L. Beauchamp, and J. R. Eyler, *J. Amer. Chem. Soc.*, **92**, 7045 (1970).

bond strength measurements of Kebarle are also useful in interpreting the results of the present experiments. The bond strength $D(\text{XH-Y}^-)$ was observed to increase with the acidity of XH and decrease with the acidity of YH.¹⁴ These trends imply that if XH has several acidic hydrogen an anion Y⁻ will be most strongly bound to the most acidic site. An obvious example is that F⁻ is expected to form a stronger bond to the hydroxylic hydrogen in methanol than to the methyl hydrogens. A second implication of these trends is that if reaction 5 is exothermic then R₂H is more acidic than R₁H.



(12) M. Arshadi, R. Yamdagni, and P. Kebarle, *J. Phys. Chem.*, **74**, 1475 (1970).

(13) M. Arshadi and P. Kebarle, *J. Phys. Chem.*, **74**, 1483 (1970).

(14) R. Yamdagni and P. Kebarle, *J. Amer. Chem. Soc.*, **93**, 7139 (1971).

(15) Strong hydrogen bonding of the type illustrated in eq 2 has been implicated in gas phase decarbonylation reactions: L. K. Blair, P. C. Isolani, and J. M. Riveros, *J. Amer. Chem. Soc.*, **95**, 1057 (1973).

The enthalpy changes for the removal of HY (Y = F or Cl) from a number of haloethanes are listed in Table III. Comparison of these changes with the bond

Table III. Enthalpy Changes for Removal of HY from RY^a

RY	HY	ΔH^b	Enthalpy change for reaction 4 ^c	
			X ⁻ = CH ₃ O ⁻	X ⁻ = F ⁻
CH ₃ CH ₂ F	HF	8	-32	-22
CH ₃ CHF ₂	HF	25	-15	-5
CH ₃ CF ₃	HF	33	-7	+3
CH ₂ FCHF ₂	HF	14 ^d	-26	-16
CH ₂ FCF ₃	HF	26	-14	-4
CHF ₂ CHF ₂	HF	26	-14	-4
CHF ₂ CF ₃	HF	46	+6	+16
CH ₃ CH ₂ Cl	HCl	17	-49	-33
CH ₃ CCl ₃	HCl	13	-53	-37

^a All data in kcal/mol. ^b Enthalpy change for the 1,2-elimination of HY from RY. Calculated using the heats of formation of the haloethanes (except CHF₂CHF₂, CH₂CF₂, and CF₂CHF from J. R. Skinner and H. A. Lacher, *J. Chem. Soc. A*, 1968, 1034. The heat of formation of CHF₂CHF₂ used is from G. E. Millward, R. Hartig, and E. Tschuikow-Roux, *J. Phys. Chem.*, **75**, 3195 (1971). All other heats of formation used in the calculations are from J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, K. Draxl, and F. H. Field, *Nat. Stand. Ref. Data Ser., Nat. Bur. Stand.*, **26** (1969). ^c Calculated using the bond strengths listed in Table II. ^d Calculated assuming the product is CH₂CF₂. The reaction actually observed is believed to involve formation of CHFCHF (see Discussion), but a reliable heat of formation for CHFCHF is not available.

strengths in Table II suggests that sufficient energy is available from the formation of a bond between an anionic base and the leaving group HY to render reaction 4 exothermic for an appropriate choice of reactants. This is verified for specific cases by the numbers in columns 4 and 5 of Table III. Reaction 4 where RY is ethyl fluoride and X⁻ is F⁻, for example, is predicted to be 22 kcal/mol exothermic. If X⁻ is CH₃O⁻ and RY is ethyl fluoride then reaction 4 is 32 kcal/mol exothermic. Exothermicity may be considered a necessary (but not sufficient) condition for a reaction between thermal energy reactants to proceed. The data in Table III suggest that 1,2-elimination of hydrogen halide may be important in the reactions of basic anions with alkyl halides. Efforts to characterize the elimination process of reaction 4 thus led to the investigation of the reactions of CH₃O⁻, a relatively strong base in the gas phase,^{16,17} with a series of alkyl halide substrates, with particular attention given to the variously substituted fluoroethanes.

Experimental Section

All experiments were performed using a Varian V-5900 (9 in. magnet system) ion cyclotron resonance spectrometer. Trapping voltage modulation was utilized to record negative ion spectra in the adsorption mode.¹⁸

The reactant ion CH₃O⁻ can be generated from CH₃ONO by low-energy electron attachment.^{16,17} The process is probably analogous to that by which ethoxide anion is formed from ethyl nitrite.¹⁹ Methyl-*d*₃ nitrite was also used in the present experiments so that CH₃O⁻ (*m/e* 31) could be distinguished from HNO⁻ (*m/e* 31). In

(16) J. I. Brauman and L. K. Blair, *J. Amer. Chem. Soc.*, **92**, 5986 (1960).

(17) D. Holtz, J. L. Beauchamp, and J. R. Eyler, *J. Amer. Chem. Soc.*, **92**, 7045 (1970).

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

(19) K. Jaeger and A. Henglein, *Z. Naturforsch. A*, **222**, 700 (1967).

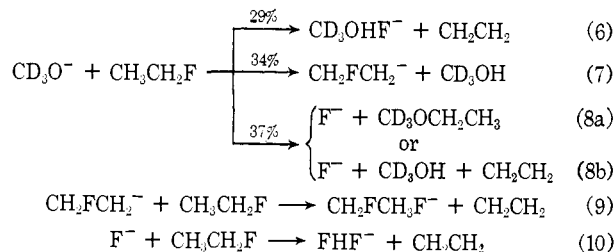
CD_3ONO at 1.75 eV electron energy the major ions are CD_3O^- (m/e 34) and DNO^- (m/e 32). These two species appear in a ratio of 10 to 1. In addition, small peaks at m/e 46 (NO_2^-), 62 ($\text{CD}_2\text{-NO}_2^-$), and 64 (CD_3NO_2^-) are present in the spectrum. CD_3O^- remains the most abundant negative ion at all electron energies, generated by the attachment of scattered electrons which are trapped in the icr cell. The methoxide anion is observed to react slowly with methyl nitrite to form NO_2^- . No other reactions were observed in methyl nitrite alone.

In a typical experiment CD_3ONO is admitted to the analyzer of the ion cyclotron resonance spectrometer at a pressure of 10^{-6} Torr. The alkyl halide is admitted through a second sample inlet so that its pressure could be varied independently. Reactions were identified both by double-resonance experiments and by the variation of relative single-resonance intensities with partial pressure of the alkyl halide.¹ Except where specifically noted in the text, no negative ions were observed in any of the alkyl halides alone. The range of alkyl halide partial pressures was 1 to 20×10^{-6} Torr. Reactions with CD_3ONO neutrals are assumed unimportant under these conditions. Rates were determined from single-resonance intensity vs. pressure data by the method of Marshall and Buttrill.²⁰ The variation of ion abundance with pressure is indicated in figures by normalized plots of single-resonance intensities divided by ion mass, a quality which is approximately equal to ion abundance.^{1,6,20}

CH_3ONO and CD_3ONO were prepared by the method described by Gray²¹ using CD_3OH of 99 atom % purity supplied by Stohler Isotope Chemical Co. The fluoroethanes were obtained from Peninsular Chemresearch with the exception of 1,1-difluoroethane which was supplied by Matheson and 1,1,1,3-tetrafluoroethane which was a gift from Dr. R. F. Hein of the E. I. du Pont de Nemours Co. Ethyl chloride was obtained from Matheson. Samples of *cis*- and *trans*-2-chlorocyclopentanol were generously provided by J. Kim of the University of California at Irvine. $\text{CD}_3\text{CH}_2\text{F}$, prepared by the reaction of $\text{CD}_3\text{CH}_2\text{I}$ with AgF , was supplied by J. Park of the California Institute of Technology. Ethyl bromide, β -chloroethanol and 1,1,1-trichloroethane were supplied by Matheson Coleman and Bell, and β -bromoethanol was obtained from Eastman Kodak. All samples were subjected to freeze-pump-thaw cycles to remove noncondensable gases and were otherwise used as supplied. Purities as determined by mass spectral analysis were acceptable.

Results

Ethyl Fluoride. As ethyl fluoride is added to methyl- d_3 nitrite the CD_3O^- disappears and ions with m/e 19 (F^-), 39 (FHF^-), 47 ($\text{CH}_2\text{FCH}_2^-$), 54 (CD_3OHF^-), and 67 ($\text{CH}_2\text{FCH}_3\text{F}^-$) appear. Double resonance indicates that CD_3O^- reacts to form F^- , $\text{CH}_2\text{FCH}_2^-$, and CD_3OHF^- , that $\text{CH}_2\text{FCH}_2^-$ reacts to form $\text{CH}_2\text{FCH}_3\text{F}^-$, and that F^- reacts to form FHF^- . In $\text{CD}_3\text{CH}_2\text{F}$ the products are F^- , FDF^- , $\text{CH}_2\text{FCD}_2^-$, CD_3ODF^- , and $\text{CH}_2\text{FCD}_3\text{F}^-$. These are the only isotopic products observed. The variation of ion abundances with $\text{CD}_3\text{CH}_2\text{F}$ pressure is illustrated in Figure 1. Double resonance in $\text{CD}_3\text{CH}_2\text{F}$ indicates that CD_3O^- reacts to form F^- , $\text{CH}_2\text{FCD}_2^-$ and CD_3ODF^- , that F^- reacts to form FDF^- , and that $\text{CH}_2\text{FCD}_2^-$ reacts to form $\text{CH}_2\text{FCD}_3\text{F}^-$. These data are consistent with the proposed reactions 6-10 and suggest that the β hydrogen of ethyl fluoride are more acidic than the α hydrogens. In this



(20) A. G. Marshall and S. E. Buttrill, Jr., *J. Chem. Phys.*, **52**, 2752 (1970); computer program courtesy of T. B. McMahon.

(21) P. Gray, *Proc. Roy. Soc., Ser. A*, **232**, 389 (1955).

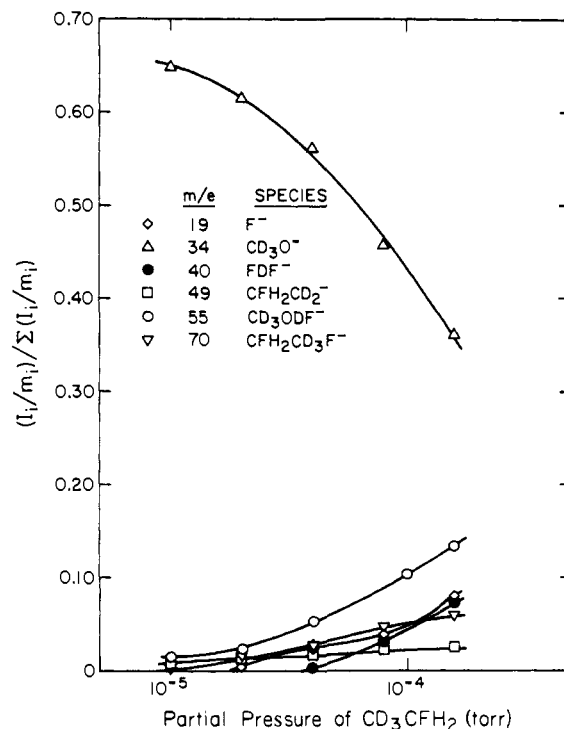
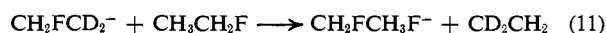


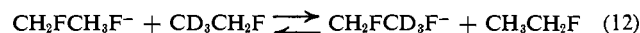
Figure 1. Relative negative ion abundances as a function of the partial pressure of CD_3CFH_2 in a mixture of CD_3CFH_2 and CD_3ONO . The pressure of CD_3ONO is kept constant ($\sim 10^{-6}$ Torr) as the CD_3CFH_2 pressure is varied. Reaction conditions are further detailed in the text.

and subsequent cases the α position of fluoroethane neutrals is taken to be the carbon possessing the greatest number of fluorine substituents.

When a mixture of $\text{CD}_3\text{CH}_2\text{F}$ and $\text{CH}_3\text{CH}_2\text{F}$ is added to CD_3ONO ions of m/e 67 ($\text{CH}_2\text{FCH}_3\text{F}^-$) and 70 ($\text{CH}_2\text{FCD}_3\text{F}^-$) appear, but no ions of m/e 68 ($\text{CH}_2\text{-FCH}_2\text{DF}^-$) and 69 ($\text{CH}_2\text{FCD}_2\text{HF}^-$) are observed. Double resonance indicates that $\text{CH}_2\text{FCH}_2^-$ and $\text{CH}_2\text{-FCD}_2^-$ each react to form both 67 and 70. As indicated in reaction 11 these data show that reaction 9



proceeds by the transfer of F^- from the ion to the neutral rather than by the transfer of DF from the neutral to the ion. Double resonance²² in this mixture indicates that reaction 12 proceeds with $dk/dE < 0$ in both

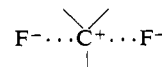


directions indicating that the m/e 67 and 70 ions have a labile fluorine. The labile fluorine is assumed to be attached to one of the acidic β hydrogens rather than the α hydrogen in accordance with the finding of Kebarle, *et al.*,¹⁴ that the strength of the $\text{X}^-\text{-HR}$ bond increases with the acidity of HR .²³

Since they are not directly identified, it is not possible

(22) For a discussion of the significance of the sign of dk/dE , see J. L. Beauchamp and S. E. Buttrill, *J. Chem. Phys.*, **48**, 1783 (1968).

(23) Another possibility is that the structure of the product of reaction 9 is a "trapped" SN_2 transition state in which the structural moiety



is present. Although they present evidence to the contrary, a similar possibility has been considered by J. M. Riveros, A. C. Breda, and L. K. Blair, *J. Amer. Chem. Soc.*, **95**, 4066 (1973).

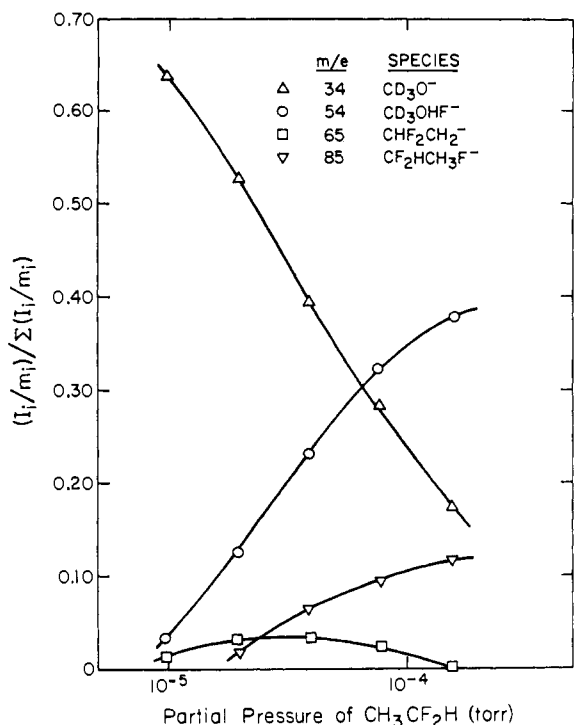
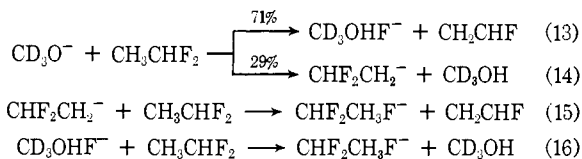


Figure 2. Relative negative ion abundances as a function of the partial pressure of $\text{CH}_3\text{CF}_2\text{H}$ in a mixture of $\text{CH}_3\text{CF}_2\text{H}$ and CD_3ONO .

to distinguish the two possible sets of product neutrals indicated in reaction 8.²⁴ Reactions 8a and 8b are exothermic by 25 and 8 kcal/mol, respectively, thus obviating the possibility of ruling one of the processes out using thermochemical arguments.

1,1-Difluoroethane. Product ions observed when CH_3CHF_2 is added to CD_3ONO have m/e 54 (CD_3OHF^-), 65 ($\text{CHF}_2\text{CH}_2^-$), and 85 ($\text{CHF}_2\text{CH}_3\text{F}^-$). The variation of ion abundance with CH_3CHF_2 pressure is illustrated in Figure 2. Double resonance indicates that CD_3OHF^- and $\text{CHF}_2\text{CH}_2^-$ come from CD_3O^- and that $\text{CHF}_2\text{CH}_3\text{F}^-$ comes from $\text{CHF}_2\text{CH}_2^-$ and CD_3OHF^- . These data are consistent with reactions 13 to 16. At 70 eV a small amount of F^- was observed.



Double resonance gave no indication that it was a reaction product. It disappeared when the electron energy was dropped to 1.75 eV and was therefore assumed to be generated by electron impact directly from CH_3CHF_2 . The m/e 65 ion is written $\text{CHF}_2\text{CH}_2^-$ implying loss of a β hydrogen by analogy with ethyl fluoride. In addition, the β hydrogens of CH_2CHF_2 are found to be the most acidic in solution.^{25,26} The F^-

(24) Reaction 8a is a nucleophilic substitution reaction of the type reported by D. K. Bohme and L. B. Young, *J. Amer. Chem. Soc.*, **92**, 7354 (1970). In the case of reaction 8b a substantial fraction of the product ions from reactions 6 and 7 may retain sufficient internal excitation to dissociate to yield F^- and the appropriate neutral.

(25) M. Hudlicky, "Chemistry of Organic Fluorine Compounds," Macmillan, New York, N. Y., 1962.

(26) J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory," McGraw-Hill, New York, N. Y., 1970, pp 119-121.

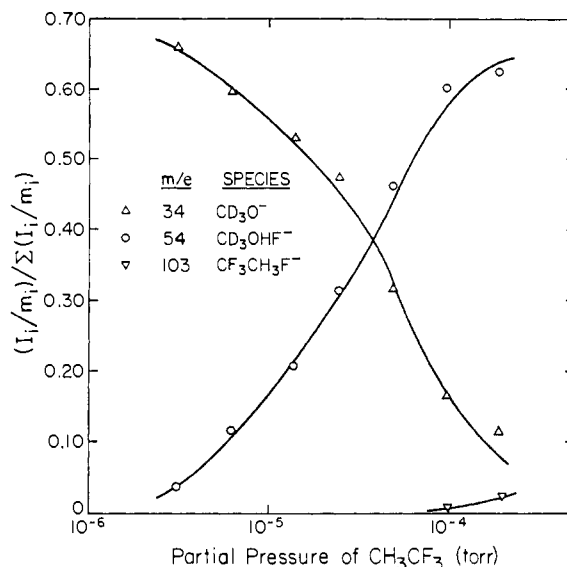
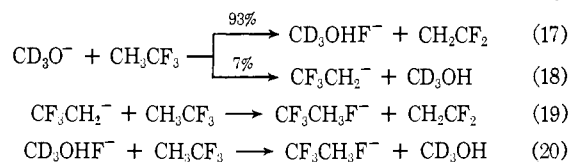


Figure 3. Relative negative ion abundances as a function of the partial pressure of CH_3CF_3 in a mixture of CH_3CF_3 and CD_3ONO . CF_3CH_2^- is observed as a minor ion at pressures in the range of 10^{-6} Torr (see Discussion).

transfer reaction 15 is consistent with the reactant ion possessing labile β fluorine. It is not expected that fluorine bound to the carbanion center would be readily transferred to acidic species. The m/e 85 ion is written $\text{CHF}_2\text{CH}_3\text{F}^-$ also by analogy with ethyl fluoride. The method of Marshall and Buttrill for determining rates is not easily applied in cases where two reactant ions form the same product ion. Reactions 15 and 16 give the same product ion, but it was estimated from the data shown in Figure 2 that reaction 15 is much faster than reaction 16, making it possible to neglect the latter process in calculating rate constants from the data. Reaction rate constants are summarized in Table IV. The large standard deviations reflect the inaccuracy of the capacitance manometer at pressures less than about 2×10^{-5} Torr.

1,1,1-Trifluoroethane. The predominant product that appears when CF_3CH_3 is added to CD_3ONO is the m/e 54 (CD_3OHF^-) ion. At higher pressures an ion of m/e 103 ($\text{CF}_3\text{CH}_3\text{F}^-$) appears. Double resonance indicates that CD_3O^- is the precursor of CD_3OHF^- and that CF_3CH_2^- and CD_3OHF^- are precursors of $\text{CF}_3\text{CH}_3\text{F}^-$. These data are consistent with reactions 17 to 20. The variation of ion concentrations with CH_3CF_3



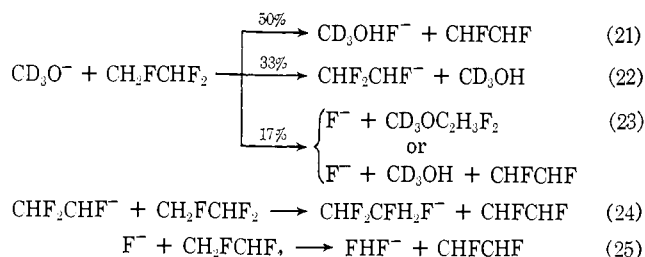
CF_3 partial pressure is illustrated in Figure 3. Reaction 19 is sufficiently fast that the low abundance of the intermediate ion CF_3CH_2^- did not permit accurate intensity measurements for this species. The ion was observed and the rates of (17) to (19) were determined from spectra taken with a higher partial pressure of CD_3ONO (5×10^{-6} Torr) which improved signal to noise at low conversion. As in the case of reaction 16, the rate of reaction 20 was estimated to be relatively slow and was considered to be zero in determining the rate constants summarized in Table IV.

Table IV. Negative Ion Reactions in Fluoroethanes

Reaction	Rate constant, ^a 10 ⁻¹⁰ cm ³ molecule ⁻¹ sec ⁻¹	Reaction no. (text)	
CH ₃ CH ₂ F + CD ₃ O ⁻ →	CD ₃ OHF ⁻ + CH ₂ CH ₂	0.38 ± 0.12	6
	CH ₂ FCH ₂ ⁻ + CD ₃ OH	0.44 ± 0.09	7
	F ⁻ + C ₂ H ₄ + CD ₃ OH ^b	0.47 ± 0.06	8
CH ₃ CH ₂ F + CH ₂ FCH ₂ ⁻ →	CH ₂ FCH ₂ F ⁻ + CH ₂ CH ₂	1.87 ± 0.24	9
CH ₃ CH ₂ F + F ⁻ →	FHF ⁻ + CH ₂ CH ₂	1.32 ± 0.06	10
CH ₃ CHF ₂ + CD ₃ O ⁻ →	CD ₃ OHF ⁻ + CH ₂ CHF	9.0 ± 2.4	13
	CHF ₂ CH ₂ ⁻ + CD ₃ OH	3.6 ± 1.5	14
CH ₃ CHF ₂ + CHF ₂ CH ₂ ⁻ →	CHF ₂ CH ₂ F ⁻ + CH ₂ CHF	1.5 ± 0.4	15
CH ₃ CF ₃ + CD ₃ O ⁻ →	CD ₃ OHF ⁻ + CH ₂ CF ₂	14.4 ± 2.0	17
	CF ₃ CH ₂ ⁻ + CD ₃ OH	1.1 ± 0.4	18
CH ₃ CF ₃ + CF ₃ CH ₂ ⁻ →	CF ₃ CH ₂ F ⁻ + CH ₂ CF ₂	7.9 ± 0.9	19
CHF ₂ CH ₂ F + CD ₃ O ⁻ →	CD ₃ OHF ⁻ + CHFCHF	8.4 ± 1.0	21
	CHF ₂ CHF ⁻ + CD ₃ OH	5.6 ± 0.4	22
	F ⁻ + C ₂ H ₂ F ₂ + CD ₃ OH ^b	2.8 ± 0.3	23
CHF ₂ CH ₂ F + CHF ₂ CHF ⁻ →	CHF ₂ CFH ₂ F ⁻ + CHFCHF	1.5 ± 0.2	24
CHF ₂ CH ₂ F + F ⁻ →	FHF ⁻ + CHFCHF	2.8 ± 1.5	25
CHF ₂ CHF ₂ + CD ₃ O ⁻ →	CD ₃ OHF ⁻ + CF ₂ CHF	15.0 ± 2.0	26
	CHF ₂ CF ₂ ⁻ + CD ₃ OH	1.9 ± 0.5	27
CHF ₂ CHF ₂ + CHF ₂ CF ₂ ⁻ →	CHF ₂ CF ₂ HF ⁻ + CF ₂ CHF	10.7 ± 1.0	29
CH ₂ FCF ₃ + CD ₃ O ⁻ →	CD ₃ OHF ⁻ + CF ₂ CHF	5.4 ± .8	30
	CF ₃ CFH ⁻ + CD ₃ OH	3.4 ± .5	31
CH ₂ FCF ₃ + CF ₃ CFH ⁻ →	CF ₃ CFH ₂ F ⁻ + CF ₂ CHF	1.5 ± .3	32
CF ₃ CF ₂ H + CD ₃ O ⁻ →	CF ₃ CF ₂ ⁻ + CD ₃ OH	19.0 ± 2.0	33

^a Thermal energy rate constants determined using the analysis of A. G. Marshall and S. E. Buttrill, Jr. *J. Chem. Phys.*, **52**, 2752 (1970). All experiments were performed at ambient temperature (295°K). Errors quoted are standard deviations. ^b Neutral products uncertain. See Discussion.

1,1,2-Trifluoroethane. The reactions observed in CH₂FCHF₂ are analogous to those observed in ethyl fluoride. Ions with *m/e* 19 (F⁻), 39 (FHF⁻), 54 (CD₃OHF⁻), 83 (CHF₂CHF⁻), and 103 (CHF₂CFH₂F⁻) appear as the partial pressure of CH₂FCHF₂ is increased. The variation of ion abundances with CH₂FCHF₂ pressure is illustrated in Figure 4. Double resonance indicates that CD₃O⁻ is the precursor of CD₃OHF⁻, CHF₂CHF⁻, and F⁻, that CHF₂CHF⁻ is the precursor of CHF₂CFH₂F⁻, and that F⁻ is the precursor of FHF⁻. These data are consistent with reactions 21 to 25. The β fluorine introduces an ambiguity in



the identities of the products of these reactions. Reactions 21 to 25 are written assuming that the β (CH₂F) hydrogens in CH₂FCHF₂ are more acidic than the α hydrogen and that reactant bases interact only with the β hydrogens. The reactivities of ethyl fluoride and 1,1-difluoroethane suggest this to be the case.

1,1,1,2-Tetrafluoroethane. Product ions that appear when CHF₂CHF₂ is added to CD₃ONO correspond to *m/e* 54 (CD₃OHF⁻), 101 (CHF₂CF₂⁻), and 121 (CHF₂CF₂HF⁻). The variation of ion abundances with CHF₂CHF₂ pressure is illustrated in Figure 5. Double resonance indicates that CD₃O⁻ reacts to form CD₃OHF⁻ and CHF₂CF₂⁻ which both in turn react to form CHF₂CF₂HF⁻. These data are consistent with reactions 26 to 29. The rates given in Table IV for reactions 26, 27, and 29 are calculated assuming the rate of reaction 28 to be negligible.

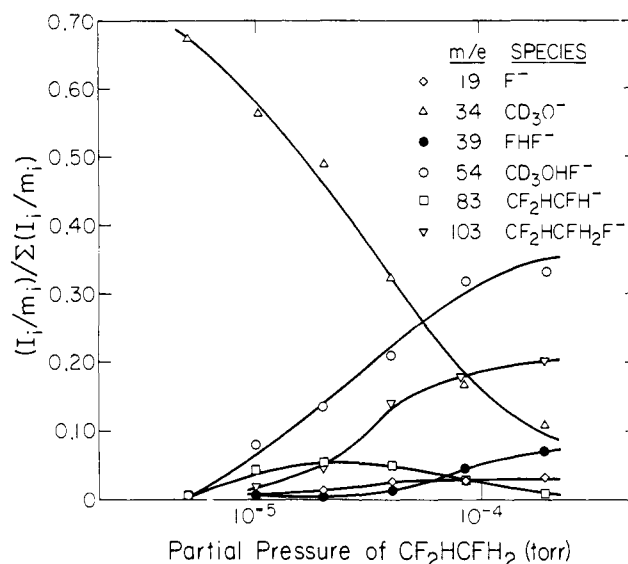
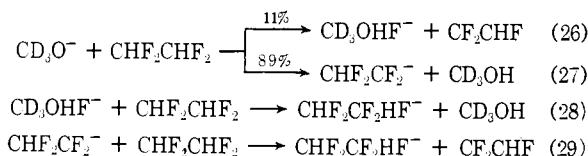


Figure 4. Relative negative ion abundances as a function of the partial pressure of CF₂HCFH₂ in a mixture of CF₂HCFH₂ and CD₃ONO.



1,1,1,2-Tetrafluoroethane. The product ions that appear when CH₂FCF₃ is added to CD₃ONO have *m/e* 54 (CD₃OHF⁻), 101 (CF₃CFH⁻), and 121 (CF₃CFH₂F⁻). The variation of ion abundances with CH₂FCF₃ pressure is illustrated in Figure 6. Double resonance indicates that CD₃O⁻ reacts to form CD₃OHF⁻ and CF₃CFH⁻, the latter product reacting further to form CF₃CFH₂F⁻. These data are consistent with reactions 30–32, the rates for which are summarized in Table IV.

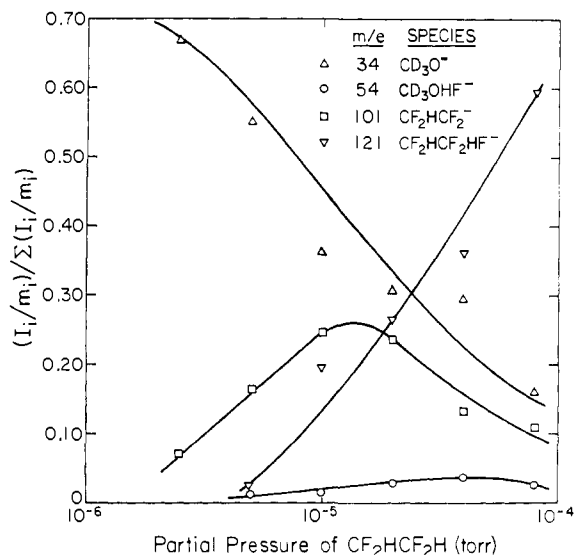
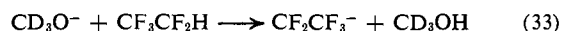
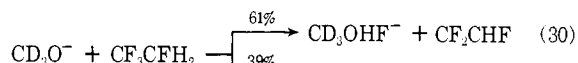


Figure 5. Relative negative ion abundances as a function of the partial pressure of CF₂HCF₂H in a mixture of CF₂HCF₂H and CD₃ONO.

Pentafluoroethane. The only product ion observed when CF₃CF₂H is added to CD₃ONO has *m/e* 119 (C₂F₅⁻). Double resonance confirms reaction 33 as the source of C₂F₅⁻.

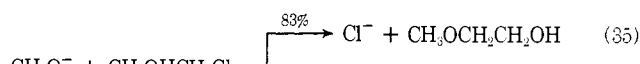


Other Alkyl Halides. The only products observed in mixtures of CH₃ONO, CH₃CH₂Cl, and CH₃CH₂Br are the Cl⁻ and Br⁻ ions, respectively. Double resonance indicates that CH₃O⁻ reacts with the corresponding neutrals to form the halide ions. In a mixture of CH₃ONO and CH₃CCl₃ ions at *m/e* 67 and 69 appear in addition to the Cl⁻ ion. The concentrations of the *m/e* 67 and 69 ions are in a ratio of 3:1 and double resonance indicates that CH₃O⁻ is their precursor. These data suggest that reaction 34 occurs in CH₃CCl₃.



CH₃OHCl⁻ was never greater than 1% of the total ionization.

β-Chloroethanol. Ions of masses 35, 37, 67, and 69 appear as CH₂OHCH₂Cl is added to CH₃ONO. Double resonance indicates that all four ions are formed by reaction of CH₃O⁻ with CH₂OHCH₂Cl. The relative abundances of the mass 35 and 37 ions are in a ratio of 3:1 as are the relative abundances of the 67 and 69 ions. These data are consistent with reactions 35 and 36.



As the product of a simple nucleophilic displacement the β-methoxyethanol is the most likely of the several possible neutral products of reaction 35. Ethylene oxide is similarly the most mechanistically assessible of the several possible neutral products of reaction 36.

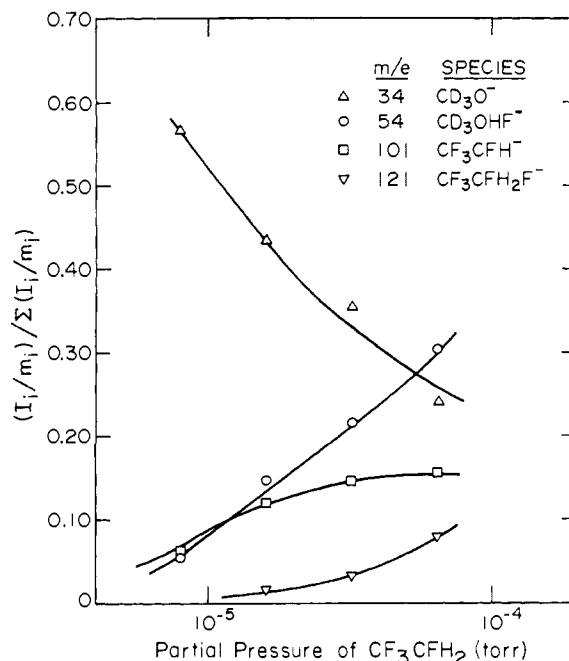


Figure 6. Relative negative ion abundances as a function of the partial pressure of CF₃CFH₂ in a mixture of CF₃CFH₂ and CD₃ONO.

Microwave spectroscopy²⁷ reveals that the hydroxy group is internally hydrogen bonded to the chlorine in β-chloroethanol. This led us to investigate the reactions of CH₃O⁻ with *cis*- and *trans*-2-chlorocyclopentanol to establish the geometrical preferences for the base-induced elimination reaction involving β-chloro alcohols. Surprisingly, neither the *cis* nor the *trans* compounds reacted with methoxide anions. Mixtures of the chloro alcohol with CD₃ONO in a ratio of 10 to 1 were examined at pressures as high as 7 × 10⁻⁴ Torr.

β-Bromoethanol. In a 5 to 1 mixture of CH₂BrCH₂OH and CH₃ONO at 6 × 10⁻⁵ Torr, very small concentrations of negative ions at *m/e* 111 and 113 are observed in addition to ions with *m/e* 31, 79, and 81. The *m/e* 79 and 81 ions are present in CH₂BrCH₂OH by itself and are Br⁻ ions formed by electron attachment. Double resonance on the mixture indicates that Br⁻ is also formed by reaction between CH₃O⁻ and the alcohol. Double resonance also indicates the *m/e* 111 and 113 ions to be products of reaction between CH₃O⁻ and the alcohol. The concentrations of the *m/e* 79 and 81 ions are in a ratio of 1 to 1 as are the concentrations of the *m/e* 111 and 113 ions. These data are consistent with reactions 37 and 38. The product in re-



action 38 was never more than 1% of the total ionization.

Discussion

Summary of Observed Reactions. Reactivity of CD₃O⁻ with the seven fluoroethanes considered in this study is summarized in Table V. Included in Table V

(27) R. G. Azrak and E. B. Wilson, *J. Chem. Phys.*, **52**, 5299 (1970).

Table V. Summary of Results for Reactions of CD_3O^- with Fluoroethanes

Fluoroethane	$\Delta H,^a$ kcal/mol	Total rate constant, 10^{-10} cm^3 $\text{molecule}^{-1} \text{ sec}^{-1}$	Product distribution		
			Base-induced elimination	F^- production	Proton transfer
$\text{CH}_3\text{CH}_2\text{F}$	8	1.3	0.29	0.37	0.34
CH_2FCHF_2	14	16.8	0.50	0.17	0.33
CH_3CHF_2	25	12.6	0.71	0.0	0.29
CHF_2CHF_2	26	16.9	0.11	0.0	0.89
CH_2FCF_3	26	8.8	0.61	0.0	0.39
CH_3CF_3	33	15.5	0.93	0.0	0.07
CHF_2CF_3	46	19.0	0.0	0.0	1.00

^a Enthalpy change for HF elimination from fluoroethane, data from Table III. Table is arranged in order of increasing ΔH .

are the total rate constants and product distributions for the three major reaction channels: (1) base-induced elimination yielding CD_3OHF^- ; (2) generation of F^- ; and (3) proton transfer yielding a fluorine-substituted carbanion. The entries in Table V are in the order of increasing ΔH estimated for HF elimination from the neutral fluoroethane.

Proposed Reaction Mechanism. A discussion of the factors which determine the product distribution among the three reaction channels is necessarily related to assumptions regarding the proposed structure and internal excitation of the reaction intermediate. The reactant base is assumed to interact with the most acidic hydrogen of the fluoroethane, forming a chemically activated intermediate as depicted in reaction 4. This intermediate decomposes in one of two ways, either by cleavage of the C-H component of the strong hydrogen bond (proton transfer) or by elimination of HF. The ionic products of *both* reaction channels may in specific instances retain sufficient internal excitation to decompose further by loss of F^- . Alternatively, loss of F^- may occur directly by cleavage of the C-F bond in the intermediate proposed for reaction 4 or be formed in an independent $\text{S}_{\text{N}}2$ process involving attack of the reactant base at the carbon to which the fluorine is initially bound. If the latter conjecture is correct, then formation of F^- should be exothermic for all of the fluoroethane neutrals.²⁸ With this in mind it is significant that F^- is observed *only* in the two instances where thermochemical estimates indicate that the base-induced elimination and proton-transfer channels are sufficiently exothermic that further decomposition of the ionic products may occur, yielding F^- .

If both the proton-transfer and elimination reactions are exothermic, it is perhaps surprising that elimination can compete with proton transfer to the extent observed, since the frequency factor for the simple proton-transfer process should be much higher. Because of this it is probable that the elimination reaction is not concerted in a temporal sense of bond breaking and forming but rather involves a sequence in which the proton is effectively transferred from carbon to oxygen, followed by F^- transfer from the carbanion to the conjugate acid of the reactant base as the products separate.

Thermochemical Considerations. The least reactive neutral is ethyl fluoride and the most reactive is pentafluoroethane. They probably correspond, respectively, to the least and most acidic of the fluoroethanes.

(28) The reaction $\text{CH}_3\text{O}^- + \text{C}_2\text{H}_5\text{F} \rightarrow \text{C}_2\text{H}_5\text{OCH}_3 + \text{F}^-$ is exothermic by 25 kcal/mol. Further substitution of fluorine may change the exothermicity somewhat but is not likely to render the reaction endothermic.

Pentafluoroethane is also unique in that the only observed reaction channel is proton transfer. This is consistent with thermochemical estimates given in Table II which indicate that the base-induced elimination reaction is 6 kcal/mol endothermic for this species. Furthermore, the observation of HF elimination from CH_3CF_3 implies that $D(\text{CH}_3\text{O}^- - \text{HF})$ is at least 33.4 kcal/mol (see Table III). This is consistent with the estimated value of 40 kcal/mol given in Table II. An interesting extension of the present study is suggested by the observation that F^- is effective in promoting base-induced elimination reactions (reactions 10 and 25). A wide range of values for $D(\text{FH} - \text{F}^-)$ have been reported in the literature,¹⁴ and observation of fluoride-induced elimination of HF would imply limits on the bond strength that would be useful in evaluating the various conflicting measurements and calculations of $D(\text{FH} - \text{F}^-)$. Reaction 25 indicates that $D(\text{FH} - \text{F}^-) \geq 14$ kcal/mol, which is consistent with previous estimates.¹⁴

Proton transfer from the fluoroethanes to CH_3O^- indicates that these species are more acidic than CH_3OH . As discussed in the introduction, the fact that CD_3OHF^- is observed to transfer F^- to several of the fluoroethanes (reactions 16, 20, and 28) is also consistent with these species being more acidic than CH_3OH . Using $D(\text{CH}_3\text{O}^- - \text{H}^+) = 385$ kcal/mol²⁹ and assuming $D(\text{RH}) \cong 98$ kcal/mol,³⁰ it is estimated that the electron affinities of the radicals corresponding to each of the carbanions produced is $\text{EA}(\text{R}\cdot) \geq 1.2$ eV. Fluoride ions were not observed to react by proton transfer in the two instances in which they were observed, which may indicate that the acidities of $\text{CH}_3\text{CH}_2\text{F}$ and $\text{CHF}_2\text{CH}_2\text{F}$ are both between those of F^- and CH_3O^- . These limits on the acidities imply that the electron affinities of CH_2FCH_2 and CHF_2CHF (or CH_2FCF_2) are between 1.2 and 1.9 eV. It should be noted that the lower limit on the acidities (and the upper limit on the electron affinities) is merely suggested and not rigorously established by the observed chemistry. The only fluoroethyl radical for which an electron affinity has been previously estimated is CF_3CF_2 .³¹ The suggested value of 2.1 eV is consistent with the limit obtained above.

Conformational and Stereochemical Considerations. The relative importance of the base-induced elimination reaction increases markedly with increasing α -

(29) D. Holtz, J. L. Beauchamp, and J. R. Eyler, *J. Amer. Chem. Soc.*, **92**, 7045 (1970).

(30) Carbon-hydrogen bond dissociation energies in fluoroethanes may vary somewhat with fluorine substitution. See, for example, J. E. Basset and E. Whittle, *J. Chem. Soc., Faraday Trans. 1*, **68**, 492 (1972), wherein it is reported $D(\text{C}_2\text{F}_5 - \text{H}) = 103.0 \pm 1.0$ kcal/mol.

(31) P. W. Harland and J. C. J. Thynne, *Int. J. Mass Spectrom. Ion Phys.*, **253** (1972).

fluorine substitution. Elimination accounts for 29% of the reaction between CD_3O^- and $\text{CH}_3\text{CH}_2\text{F}$. This fraction increases to 71% in the case of CH_3CHF_2 and 93% in the case of CH_3CF_3 . A probable explanation of this trend is that the elimination requires that the hydrogen and fluorine of the leaving group HF be in a cis configuration as depicted in reaction 4. Increased α -fluorine substitution statistically favors such a configuration. In addition, the direction of the dipole moment relative to the carbon-carbon bond axis changes significantly in this series of fluoroethanes. This may determine the direction of approach of the attacking anion. If a molecule of $\text{CH}_3\text{CH}_2\text{F}$, for example, orients to maximize the attraction between the approaching anion and the carbon-fluorine bond dipole moment,³² then the anion will tend to bind to a proton trans to the fluorine. Since the elimination requires the proton to which the anion is bound and the leaving fluorine to be cis to one another, the elimination will be less probable to the extent that ion-dipole alignment occurs. Similarly, ion-dipole alignment might be expected to reduce the probability of elimination somewhat in CH_3CHF_2 but not to the extent that it does in ethyl fluoride. In CH_3F_3 , on the other hand, ion-dipole alignment would not be expected to reduce the probability of elimination. As a final consideration it is noteworthy that the intermediate suggested in reaction 4 involves a fluoroethyl carbanion as an integral structural entity. Recent quantum mechanical calculations have shown that fluoroethyl carbanions may have large barriers to internal rotation, exhibiting preference for conformations in which the C-F bond is coplanar with the filled p orbital of the carbanion center.³³ While the internal excitation in the intermediate is probably greater than the calculated barriers,^{33,34} such conformational preferences may play a role in determining the observed product distributions.

Base-Induced Elimination Reactions with Substrates Other Than Fluoroethanes. It appears that the probability for elimination of HX increases in the order $\text{HF} > \text{HCl} > \text{HBr}$. This could result from the fact that a fluorine-substituted carbon is less susceptible to nucleophilic attack than a chlorine- or bromine-substituted carbon,³⁵ and nucleophilic substitution is thus less likely to compete with elimination in fluorides. Another important effect could be the acidity of β hydrogens in fluoroethanes, which facilitates the formation of a strong bond between the attacking anion and the fluoroethane substrate. The strength of this bond is the excitation energy of the intermediate complex depicted in reaction 4. Factors which increase the bond strength increase the excitation energy available to effect the elimination.

(32) For a discussion of ion-dipole interactions, see J. V. Dugan and J. L. Magee, *J. Chem. Phys.*, **47**, 3103 (1967).

(33) R. Hoffmann, L. Radom, J. A. Pople, P. v. R. Schleyer, W. O. Hehre, and L. Salem, *J. Amer. Chem. Soc.*, **94**, 6221 (1972).

(34) The barrier to internal rotation predicted for the 2-fluoroethyl carbanion is 9.2 kcal/mol (ref 33).

(35) M. Hudlicky, ref 25, p 200.

In more complex systems the probability of elimination may depend on conformational preferences for stability in the neutral. The elimination of HCl from β -chloroethanol (reaction 36) is an interesting process in that elimination of HX may be assisted by the intramolecular hydrogen bond between the hydroxy proton and the chlorine in β -chloroethanol.

Comparison to Solution Chemistry. Several of the trends observed for gas phase base-induced elimination reactions are consistent with results of studies in solution.³⁶ The process depicted in reaction 4 can be classified formally as a syn-E2H reaction in which the leaving group is in a cis configuration relative to the attacking base. Such processes are known to be promoted in solution by strong bases, poor leaving groups, substituents which acidify the hydrogen subject to base attack, and factors which promote the syn configuration of the intermediate base-substrate complex. There is no evidence for E2 reactions in solution wherein the product is analogous to that observed in reaction 4. Solution E2 reactions invariably involve participation of other molecules in assisting the elimination reaction.

Chemical Consequences of Strong Hydrogen Bonding. This study emphasizes the important role which strong hydrogen bonding plays in chemical transformations resulting from the interaction of ions with neutrals in the gas phase. As is illustrated by the chemistry described, the formation of a strong hydrogen bond involves the release of considerable energy as internal excitation. Since the anionic dimers are formed in the gas phase, this energy is not rapidly dissipated to the solvent and is available to facilitate a variety of chemical changes in the dimer itself. Formation of the strong hydrogen bond is thus a means of chemical activation, and the chemistry that follows the formation of the bond can provide insight into the energetics and mechanisms of a variety of interesting chemical processes, including base-induced elimination reactions. We are currently investigating these processes involving more complex fluoroalkane substrates with a range of reactant bases. In addition to being of intrinsic interest, base-induced elimination reactions provide a bimolecular pathway for generating a variety of strong hydrogen bond species XHY^- that can be the subject of further investigations. Such studies include, for example, dimer equilibria related to base solvation^{14,37} and photodetachment experiments.³⁸

Acknowledgment. This research was supported in part by the United States Atomic Energy Commission under Grant No. AT(04-3) 767-8.

(36) For recent reviews of related processes in solution, see J. F. Bunnett, *Surv. Progr. Chem.*, **5**, 53 (1969); F. G. Bordwell, *Accounts Chem. Res.*, **5**, 374 (1972); A. Fry, *Chem. Soc. Rev.*, **1**, 163 (1972); and H. F. Koch, D. B. Dahlberg, A. G. Toczko, and R. L. Solsky, *J. Amer. Chem. Soc.*, **95**, 2029 (1973).

(37) R. T. McIver, Jr., J. A. Scott, and J. M. Riveros, *J. Amer. Chem. Soc.*, **95**, 2706 (1973).

(38) S. Golub and B. Steiner, *J. Chem. Phys.*, **49**, 5192 (1968).