GAS PHASE INVESTIGATIONS OF THE LEWIS ACID PROPERTIES OF ELECTRON DEFICIENT COMPOUNDS OF BORON, CARBON AND SILICON

Thesis by
Milton Keith Murphy

In Partial Fulfillment of the Requirements
for the Degree of
Doctor of Philosophy

California Institute of Technology
Pasadena, California
1977
(Submitted August 27, 1976)

This thesis is respectfully dedicated to the fond memory of the late Brother Louis Wayne Morton... in his untimely passing, I learned to cherish every moment of life.

"Dear landlord,
Please don't put a price on my soul.
My burden is heavy;
My dreams are beyond control.
When that steamboat whistle blows,
I'm gonna give you all I got to give,
And I do hope you receive it well
Depending on the way you feel that you live.

"Dear landlord,
Please heed these words that I speak.
I know you've suffered much,
But in this you are not so unique.
All of us at times we might work too hard,
Too heavy, too fast and too much,
And anyone can fill his life up with things
He can see but he just can not touch.

"Dear landlord,
Please don't dismiss my case.
I'm not about to argue;
I'm not about to move to no other place.
Now each of us has his own special gift,
And you know this was meant to be true,
And if you don't underestimate me,
I won't underestimate you."

... B. Dylan (1968)

ACKNOWLEDGMENTS[†]

Of the entirety of the written words laid down in this thesis, these lines come the hardest of all. For the four years I have spent here has been, in differing respects, the most wonderous and challenging and difficult period of my life. Ironically, it's now, near the close of my stay at Caltech that I find it so painful to say goodbye.

For teaching me to be a thinking scientist, for his humanly finite patience, and for helping me to love hard work (just a little bit more) I wish to thank my research advisor, Professor Jesse L. Beauchamp. I owe more to Jack than I can ever repay...for friendships are life long debts. Like an expert horseman, Jack seems to have that delicate but sure guiding hand at the reins.

I would also like to express my heartfelt thanks to the entire Beauchamp family. Amanda, Thomas, Melissa, and Diane have all helped make the smiles come so much more frequently. I cannot really imagine how it would have been without the boundless care and love they have shown me.

I have been very fortunate to find so many good friends here at Caltech. Beneath scientific egg shells of Spockian logic, I have found some of the warmest and most down-home folks I have ever known. Dr. Benjamin Sherman Freiser...some know him as Bengie and others simply as B.S....became my very first colleague and probably my

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[†] To the reader: This section is to be processed by the right cranial lobes. Subsequent sections of this thesis are designed for processing by the left side of the brain.

closest friend. My first day at Tech is crystal clear in memory even now, and Ben was there. We have worked and commiserated together many a time, on many a project (a few of scientific nature), during these past years. The friendships of Don McAllister, Mary Jo Johnson, Maura Dwyer, Bill McCurdy, Laura Dagen, Bob Gaul, Dave Dooley, Phil and Barbara Wood, Bob Scott, Phil and Diane Cummins, Carol Jones, Scott Wherland, Paula Clendening, Debbie Levin, Penny Slusser, Cecil Dybowski, Mike Duggan, Valerie Hue, Mel Jones, Jackie Berg, Mark Allen, Tony Pietsch, Harry Finklea, and Ron Rianda have also meant a great deal to me. I hope our paths continue to cross in the future.

For all the things I have had the chance to see and learn at Caltech, I wish to express my appreciation to the faculty members from whom I have taken courses and with whom I have had the opportunity to teach. Special thanks go to Professors Bill Goddard, Norman Davidson, Don Burnett, Harry Gray, Vince McKoy, and Dudley Herschbach.

If it were not for the warmth and encouragement shown by Professor John D. Roberts to a wide-eyed kid from Texas back in January of 1972, I probably would never have tried to get into graduate school at Caltech. I will never forget the extended time he took to talk with me...an upstart from out of the blue. Those few hours totally changed my life. And I am eternally grateful. I never have been able to find out who was on the admissions committee that year, but I will try my best to get even someday.

To the members of the Beauchamp group, past and present, I own a great deal for their inspiration, their help, their unending curiosity and tireless capacity for talking science. But most of all, were it not for their friendship and partying spirits, my stay here would have been unbearable. In particular, Ron Hodges, Frances Houle, Reed Corderman, Sally Sullivan, Dick Woodin, Mike Foster, Ashley Williamson, Mark Swanson, Wayne Berman, Bob Wieting, and the inimitable Frederick Michael Behlen deserve special mention. Dr. Ralph Staley will always occupy a unique place in my memories of Caltech.

To my teammates on the chemistry softball squad and to our staunch rivals on the Hashmarks, I thank you all for many carefree hours of diversion and relaxation. Times spent in practice and play helped so much to balance the fast pace of the lab. Among many others, Bruce Parkinson, John Dwyer, Tom Slankas, Duncan Brown, Don Santilli, Bob Sanner, Jim McArdle, Dave McMillan, Kathy Coyle, Dan Dawson, Neil Schore, Professor John Bercaw, Jim Davis, Tom Orlowski, Bill Jones, and Eric Evitt and the times we have shared will remain with me always.

I would like to especially thank Mrs. Joyce Lundstedt for typing my candidacy report and this thesis. Without her boundless patience and artistry in print, this thesis would not have been possible.

I also wish to express my appreciation to Mrs. Ruth Stratton for the speedy and beautiful job she did in the typing of my research propositions.

I also wish to say "thank you" to several people who made the everyday routine so much more pleasant by their smiles and good humor and their substantial help in times of desperation. I will always remember the kindness accorded me by Adria McMillan, Ernie Moore, Tom Dunn, Fernand Masse, Fred Beal, Charlie Beebie, Elmer Clarke, Jim Olson, Siegfried Jenner, Bill Schuelke, Tony Starke, John Swanson, and last but not least, Pat Ruda.

Many thanks go to Richard Brown of the Athenaeum staff for making lunch a most enjoyable respite. The Earl of Sandwich would have been proud of Rich's epicurian talents.

I am grateful to the late Mr. Jack Rohmar for his words of wisdom and tasty concoctions. The Athenaeum Saloon never has been nor ever will be the same now that Jack is gone.

To my many teachers, colleagues, and friends at the University of Houston, I owe a great deal for providing me the basis from which my graduate studies have evolved. Without the encouragement and help of Professors Jerry Fitzgerald, Claude Veillon, Bob Willcott, Russell Geanangel, and Steve Welch, I would not be here today. Special thanks also go to Drs. Doris Warren, Randy White, John Park, and Jeannie Whileyman for their friendship, love and unending devotion. And to Jim Scheline (Brother Catfish), I will long be indebted for showing me the importance of the whimsical side of any situation.

To Captain Jack E. Rich I am indebted for the opportunity to work my way through undergraduate school. A nicer boss, I will never find.

I am sincerely grateful to the California Institute of Technology, Eastman Kodak, and the Blanche Mowrer Foundation for financial support of my studies. Without that aid I certainly could not have had the opportunity to be here.

Two people in particular have made a very great impression on me this past year. In that short time, I have come to feel closer than if we had known each other a lifetime. To Mary Ann White and Peter Armentrout, my sincerest thanks for your friendship. I hope that we meet again frequently in years to come. We will take that long hike together someday.

Last but most importantly, were it not for my parents and brothers and sister and the love and faith and trust they have given me in abundance all my life, the completion of this thesis would have little meaning for me. To Mom and Dad, Eddie, Dave, Larry, and Valerie...you have made all this worthwhile.

ABSTRACT

Following a brief overview (Chapter I) which is intended to define in very general terms the main direction of this thesis, the results of four distinct but closely interrelated investigations into the gas phase chemistry of a variety of Lewis acids of carbon, boron and silicon are presented.

Chapter II describes photoionization mass spectrometry studies of positive ions generated from the fluoromethylsilanes $(CH_3)_nF_{4-n}Si$ ($n = 1$-4). Results provide accurate adiabatic ionizations of the neutrals and appearance potentials of the parent-minus-methyl fragments generated by photon impact. These data permit the derivation of a variety of thermochemical data describing silicon containing species, including estimates of heats of formation of the ionic species, fluoride affinities (heterolytic bond dissociation energies, $D[R^+{-}F^-]$) of the various siliconium ions $(CH_3)_nF_{3-n}Si^+$ and ionization potentials of the silyl radicals $(CH_3)_nF_{3-n}Si$ ($n = 0$-3).

Chapter III describes ion cyclotron resonance spectroscopy (ICR) studies of fluoride transfer reactions observed to occur between various fluorine and methyl substituted siliconium ions and carbonium ions $(CH_3)_nF_{3-n}M^+$ ($M = C$, Si; $n = 0$-3). These studies provide the first experimental comparisons of the relative stabilities of analogous carbonium and siliconium ions free from the influence of solvation and establish the gas phase ion stability order $F_3Si^+ < CH_3SiF_2^+ < CH_3^+ < CF_3^+ < (CH_3)_2SiF^+ < CH_3CF_2^+ < CH_3CH_2^+ < (CH_3)_3Si^+ < (CH_3)_2CF^+ < (CH_3)_3C^+$ for F^- as reference base. In conjunction with quantitative thermochemical data obtained in the photoionization studies (Chapter II), these studies yield insights into the effects of α methyl and fluorine substitution on carbon and silicon positive ion centers. Comparisons of the present results with available hydride affinity data yield insights into the influence of the nature of the reference species on the strengths of acid-base interactions.

Chapters IV and V describe trapped-anion ICR investigations of the gas phase Lewis acidities of a variety of neutral boranes R_3B and R_2FB (where R = CH_3, C_2H_5, $i\text{-}C_3H_7$, and F) and silanes $(CH_3)_nF_{4-n}Si$ (n = 0-3), respectively, using F^- as the reference Lewis base. Alkyl substituents are observed to decrease the Lewis acidity of both boron and silicon acceptor centers relative to fluorine substituents, but the magnitude of this effect is found to be more pronounced in the case of the silane Lewis acids. For the borane Lewis acids, increasing the size of alkyl groups α to the acceptor center results in increased stability (measured as fluoride affinities, $D[R_3B{-}F^-]$) of the borane-fluoride Lewis adducts. The combined results of these two investigations permit quantification of the observed gas phase ordering of Lewis acidities $BF_3 > SiF_4 > (i\text{-}C_3H_7)_2FB > (i\text{-}C_3H_7)_3B > (C_2H_5)_2FB > (C_2H_5)_3B > CH_3SiF_3 > (CH_3)_2FB > (CH_3)_3B > (CH_3)_2SiF_2 > SF_4 > (CH_3)_3SiF$ for fluoride ion as the reference base. Interesting insights into the variations in stabilities of the pentacoordinate silicon anions $(CH_3)_nF_{5-n}Si^-$ (n = 0-3) are provided by comparisons with available information on the isoelectronic neutral fluoromethylphosphoranes $(CH_3)_nF_{5-n}P$ (n = 0-4).

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CHAPTER I

INTRODUCTION

That portion of chemistry dealing with acid-base properties of molecules encompasses perhaps the most fundamental of phenomena commonly encountered on the macroscopic level and continues to be subject of extensive investigation. Within this field, the Lewis formalism,[1] which defines an acid A as any entity having an accessible low-lying vacant orbital into which it can accept an electron pair from a base B possessing a readily donable electron pair to form a dative covalent bond in adduct AB, is likely the most generally adaptable and certainly among the most enduring of all acid-base theories.

The chemistry of one such acid, the proton H^+ would, at first thought, seem to be the simplest of all chemical phenomena. And yet, in its many and varied roles, ranging from importance in the outer reaches of planetary atmospheres to the currency of energy systems in the biological realm, the proton is inescapably the most important of all acids and as such the most thoroughly investigated.[2-4]

Among the more exotic of Lewis acids are electron deficient compounds of boron.[5, 6] The tricoordinate neutral boranes are typified by molecules such as the parent monomer BH_3, boron trihalides BX_3, and organoboranes BR_3 (R = alkyl, aryl, etc.). With the notable exception of BH_3, which exists normally as the H-bridged dimer B_2H_6, the borane Lewis acids are trigonal-planar monomers utilizing (formally) sp^2 hybridization about the central atom and possessing an empty (or nearly so) $2p_z$ orbital pendicular to the molecular plane defined by the boron and its three substituents. The driving force behind a boranes' Lewis acid character is then, in the view of simple-minded valence bond theory, its propensity to complete an octet of electrons around the central atom. Upon formation of a Lewis acid-base adduct, coordination about boron expands to four accompanied by a change to approximately tetrahedral sp^3 hybridization. Thus the adduct is isoelectronic with neutral tetrahedral carbon compounds.

In as much as the Lewis definition of an acid is charge independent, we may easily by analogy recognize any trigonal planar chemical entity possessing a vacant p orbital perpendicular to the plane defined by the central atom and its substituent groups as a Lewis acid. Examples of note in the present context include tricoordinate cations of carbon[7] and silicon centers, i.e., carbonium and siliconium ions, R_3C^+ and R_3Si^+ (R = H, halogen, alkyl, etc.).

Further, we need not restrict consideration merely to trigonal planar species, so long as there is available a relatively low lying vacant orbital capable of accepting an electron pair from some donor Lewis base for acid-base adduct formation. In this context, numerous examples of tetracoordinate acids exist (to the notable exclusion, with minor exception, of carbon centered compounds) which form pentacoordinate Lewis adducts with suitable donors. Certain tetrahedral silicon compounds,[8] which make use of vacant 3d orbitals in the role of acceptor sights, are known to be capable of undergoing coordinative expansion to trigonal bipyramidal structures. Usual theories of chemical bonding make no special note of stability associated with an electron dectet shell; however, effects of highly electron withdrawing substituents can result in very considerable acceptor strengths of certain silane Lewis acids.

The common thread or focus underlying the various studies which comprise this dissertation is to be the inquiry into Lewis acid properties of electron deficient molecular centers. In particular, the investigations presented herein encompass experimental determinations of acceptor strengths (Lewis acidities) of:

(1) neutral trialkyl- and fluoroalkyl-boranes R_3B and R_2FB ($R = CH_3$, C_2H_5, and $i\text{-}C_3H_7$), and BF_3;

(2) substituted carbonium ions and siliconium ions $(CH_3)_nF_{3-n}M^+$ ($M = C$, Si; $n = 0\text{-}3$); and

(3) neutral fluoromethylsilanes, $(CH_3)_nF_{4-n}Si$ ($n = 0\text{-}3$).

As will be seen, the nature of the substitutional environment at the acceptor center can exercise a profound degree of control over the acceptor strength of the Lewis acid, and numerous comparisons within and among the various types of acceptor species listed above will be made. In order to facilitate concentration on comparative analyses of the three different central atoms (B, C, Si) and further to bring to light similarities and differences in substituent effects at the different centers, a single common reference Lewis base, fluoride ion, is utilized throughout these investigations. The experimental approach utilized is primarily the examination of the preferred direction of fluoride transfer reactions occurring between isolated acid moieties in the gas phase under low pressure conditions, where bimolecular encounters dominate the kinetics of reaction, in the absence of complicating solvation effects. The instrumentation and techniques of ion cyclotron resonance spectroscopy are the principal tools utilized in these investigations. Photoionization mass spectroscopy is used to augment the investigation of the tricoordinate silicon cations.

The first example of a borane Lewis acid-base adduct came as early as 1809 when Gay-Lussac[5] prepared the ammonia-borontrifluoride adduct, H_3NBF_3, and its study shortly thereafter by Davy in 1812. Numerous reviews have dealt primarily with a specific type of borane acceptor and complexes formed by it with various donors. Relatively few studies have been undertaken to study complexes of various acceptors with a specific donor. Two recent reviews[5] provide summaries of quantitative data on adduct strengths of borane Lewis acids, primarily with neutral n-donor bases (e.g., amines, phosphines, oxygen compounds, etc.). Most of the literature data are in the form of equilibrium constants for dissociation of the gaseous adducts, and thus reflect free energies of dissociation rather than enthalpies, which more directly reflect bond strengths between donor and acceptor.

The present work is therefore primarily directed at the quantitative determination of acid-base adduct bond dissociation energies $D[A-B]$. Variations in the magnitudes of these quantities effected by changes in nature of the central atom and by different substituent groups at the acceptor center provide insights into factors governing Lewis acid strength.

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CHAPTER II

PHOTOIONIZATION MASS SPECTROMETRY OF THE FLUOROMETHYLSILANES $(CH_3)_nF_{4-n}Si$ (n = 1-4)[1a]

M. K. Murphy and J. L. Beauchamp[1b]

Abstract

Photoionization efficiency curves for molecular ions P^+ and lowest energy fragments $(P-CH_3)^+$ for the series of methyl and fluoro substituted silanes $(CH_3)_nF_{4-n}Si$ (n = 1-4) are reported for photon energy ranges extending from 1 to 2 eV above the respective parent thresholds. Adiabatic ionization potentials of 9.80 ± 0.03, 10.31 ± 0.04, 11.03 ± 0.03 and 12.48 ± 0.04 eV are determined for $(CH_3)_4Si$, $(CH_3)_3SiF$, $(CH_3)_2SiF_2$ and CH_3SiF_3, respectively, with appearance thresholds of 10.03 ± 0.04, 10.70 ± 0.04, 11.70 ± 0.03 and 13.33 ± 0.04 eV for siliconium ion fragments $(CH_3)_3Si^+$, $(CH_3)_2FSi^+$, $(CH_3)F_2Si^+$ and F_3Si^+ arising from CH_3 loss. These data are interpreted in terms of the thermochemistry of the various ionic and neutral silicon species. Derived heats of formation afford accurate calculation of fluoride affinities (heterolytic bond dissociation energies, $D[R_3Si^+-F^-]$) of 219.5, 237.3, 258.4 and 302.0 kcal/mole for the siliconium ions $(CH_3)_3Si^+$, $(CH_3)_2FSi^+$, $(CH_3)F_2Si^+$ and F_3Si^+, respectively. These values are 30-50 kcal/mole higher than the analogous carbonium ions.

Introduction

The involvement of tricoordinate siliconium ions, as intermediates in organosilicon chemical reactions, has been proposed by numerous investigators.[2, 3] However, many exhaustive experimental attempts to evidence even the existence of R_3Si^+ species in solution have been completely unsuccessful, even under conditions where analogous carbonium ions, R_3C^+, are long-lived.[4, 5] By contrast, R_3Si^+ species are abundant in the mass spectra of a wide variety of organosilicon compounds.[6, 7] Thus, gas phase studies provide a unique opportunity for determinations of chemical properties of these elusive species.

Recent gas phase studies from this laboratory of the positive ion chemistry of fluoromethylsilanes, utilizing ion cyclotron resonance techniques, have provided information regarding the relative stabilities of substituted siliconium ions, $(CH_3)_nF_{3-n}Si^+$ (n = 0-3), in the absence of complicating solvation phenomena. It was shown that methyl- and fluoro-substituents effect variations in siliconium ion stabilities, $F_3Si^+ < (CH_3)F_2Si^+ < (CH_3)_2FSi^+ < (CH_3)_3Si^+$, for fluoride ion as reference base, paralleling trends previously observed in the analogous series of carbonium ions.[8] Further, investigations of fluoride transfer reactions between substituted carbonium and siliconium ions[9] have shown that siliconium ions are substantially less stable than their carbon analogs. The more complete ion stability order (with F^- as the reference base) $F_3Si^+ < (CH_3)F_2Si^+ < CF_3^+ < (CH_3)_2FSi^+ < CH_3CF_2^+ < (CH_3)_3Si^+ < (CH_3)_2FC^+ < (CH_3)_3C^+$, was established.

Accurate carbonium ion heats of formation, obtained principally from high resolution electron and photon impact mass spectrometry,[10-13] have been used to calculate quantitative fluoride affinities of carbonium ions. These values serve to bracket the siliconium ion stabilities within known bounds. A major factor hindering detailed interpretation of these results is the lack of thermochemical data describing ions and neutrals containing silicon. Experimental difficulties involved in calorimetric determinations for silicon containing compounds result in large uncertainties even in neutral heats of formation. Although some thermochemical data describing silicocations are available from electron impact mass spectral studies,[14, 15] associated experimental uncertainties again make comparison with carbonium ions somewhat unreliable. Photoionization mass spectrometry (PIMS) has been shown to afford accurate determinations of appearance potentials for fragmentation processes, much superior to conventional electron impact techniques.[10-13] We have undertaken PIMS studies directed at providing more precise thermochemical information describing ions containing silicon.

In a recent preliminary report,[16] we summarized results of photoionization studies of molecular ions and siliconium ion fragments derived from $(CH_3)_4Si$, $(CH_3)_3SiF$, $(CH_3)_2SiF_2$ and CH_3SiF_3. Tetramethylsilane is the only organosilane previously studied by photoionization.[15c] In the present report, we wish to provide details necessarily omitted from the preliminary account. Photoionization efficiency curves are presented for molecular ions and lowest energy siliconium ion fragments. Factors affecting the interpretation of observed ionization thresholds are discussed. Heats of formation and fluoride affinities of siliconium ions derived from these data allow a detailed evaluation of the effects of methyl- and fluoro-substitution α to carbon and silicon charge centers.[9]

Experimental

The photoionization mass spectrometer utilized in the present studies has been previously described in detail.[17] For these studies the hydrogen molecular spectrum at 1.0 - 1.5 Å FWHM resolution was used as the photon source. Sample pressures were typically $\sim 1 \times 10^{-4}$ torr as measured by an MKS Baratron Model 90H1-E capacitance monometer. Initially, repeller voltages of ~ 0.1 V were used, yielding ion residence times of approximately 50 μsec. In order to minimize ion-molecule reactions in the ion source, measurements were also run at relatively high repeller voltages (~ 10.0 V) resulting in shorter ion residence times of ~ 5.0 μsec. Although higher source repeller fields resulted in considerably poorer ion detection efficiency, both sets of conditions yielded essentially the same threshold energies for ion formation. No attempts were made to correct ion intensities for ^{13}C or ^{29,30}Si isotope contributions. All experiments were performed at ambient temperature (22°C).

Samples of $(CH_3)_3SiF$, $(CH_3)_2SiF_2$, and CH_3SiF_3 (PCR, Inc.) were graciously provided by Professor J. G. Dillard. $(CH_3)_4Si$ was obtained from MCB Chemicals, Inc. All samples were subjected to multiple freeze-pump-thaw cycles to remove non-condensable impurities.

Quoted ionization and appearance potential values are obtained by extrapolation of the linearly rising portion of the appropriate efficiency curves to zero photoionization efficiency. Various considerations relevant to interpretation of observed thresholds are discussed in later sections of this report.

Results

$(CH_3)_4Si$. Photoionization efficiency curves for the molecular ion and lowest energy fragment $(CH_3)_3Si^+$ generated in $(CH_3)_4Si$ for photon energies between 9.4 and 10.8 eV are shown in Figure 1. These are the only ions observed in this energy range. The onset of molecular ion formation occurs at 1265 Å, giving a value of 9.80 ± 0.03 eV for the adiabatic ionization potential of the parent neutral. The ionization efficiency rises with photon energy as higher vibrational levels of the parent ion ground state are populated, peaks at an energy slightly above the onset of the first fragmentation, and declines slightly for higher photon energies. Fragmentation producing $(CH_3)_3Si^+$ by loss of methyl radical from the molecular ion, process 1, exhibits an onset at 1236 Å, corresponding to an appearance potential of 10.03 ± 0.04 eV.

$$(CH_3)_4Si + h\nu \rightarrow (CH_3)_3Si^+ + CH_3 \qquad (1)$$

Observed photoionization thresholds and various ion heats of formation derived therefrom are summarized in Table I. Also included in the table are the heats of formation of neutrals utilized in these calculations.

$(CH_3)_3SiF$. Photoionization efficiency curves for $(CH_3)_3SiF^+$ and $(CH_3)_2SiF^+$ generated in trimethylfluorosilane between 10.0 and 11.4 eV photon energies are shown in Figure 2. The onset of molecular ion formation occurs at 1202 ± 3 Å corresponding to an adiabatic ionization potential of 10.31 ± 0.4 eV. The efficiency curve for the molecular ion exhibits a gradual onset compared with those for all other molecular ions observed in this study. For long ion residence times a rapid ion-molecule reaction ($k = 6.5 \times 10^{-10}$ $cm^3mol^{-1}sec^{-1}$) of $(CH_3)_3SiF^+$ with the parent neutral (reaction 2) yields small amounts

$$(CH_3)_3SiF^+ + (CH_3)_3SiF \rightarrow (CH_3)_3Si^+ + (CH_3)_2SiF_2 + CH_3 \qquad (2)$$

of siliconium ion $(CH_3)_3Si^+$. Reaction 2 is calculated to be ~43 kcal/mole exothermic and has been previously reported in the ion chemistry of $(CH_3)_3SiF$.[8] Not shown in Figure 2, the degree of $(CH_3)_3Si^+$ formation for low repeller voltages closely coincides with the shape of the molecular ion curve (though at only ~20% of the intensity) up to the appearance threshold of $(CH_3)_2SiF^+$, at which point $(CH_3)_3Si^+$ intensity increases in coincidence with the efficiency curve for $(CH_3)_2SiF^+$ due to the occurrence of fluoride transfer

Figure 1

Photoionization efficiency curves for $(CH_3)_4Si^+$ and $(CH_3)_3Si^+$ generated from $(CH_3)_4Si$ in the photon energy range 9.4 - 10.6 eV.

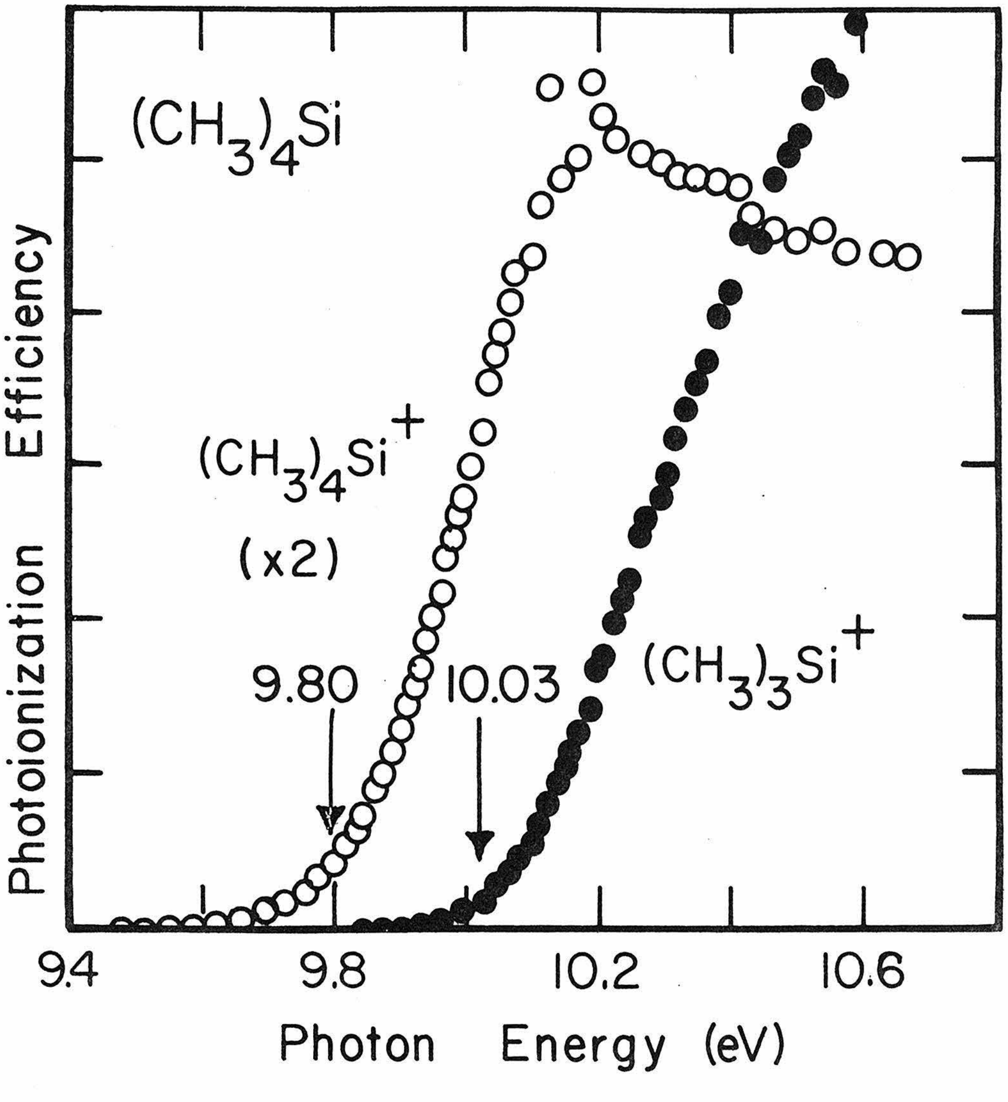
(CH3)4Si
(CH3)4Si+
(x2)
(CH3)3Si+
9.80
10.03
Photoionization Efficiency
9.4
9.8
10.2
10.6
Photon Energy (eV)

Figure 2

Photoionization efficiency curves for $(CH_3)_3SiF^+$ and $(CH_3)_2SiF^+$ generated from $(CH_3)_3SiF$ in the photon energy range 10.0 - 11.2 eV.

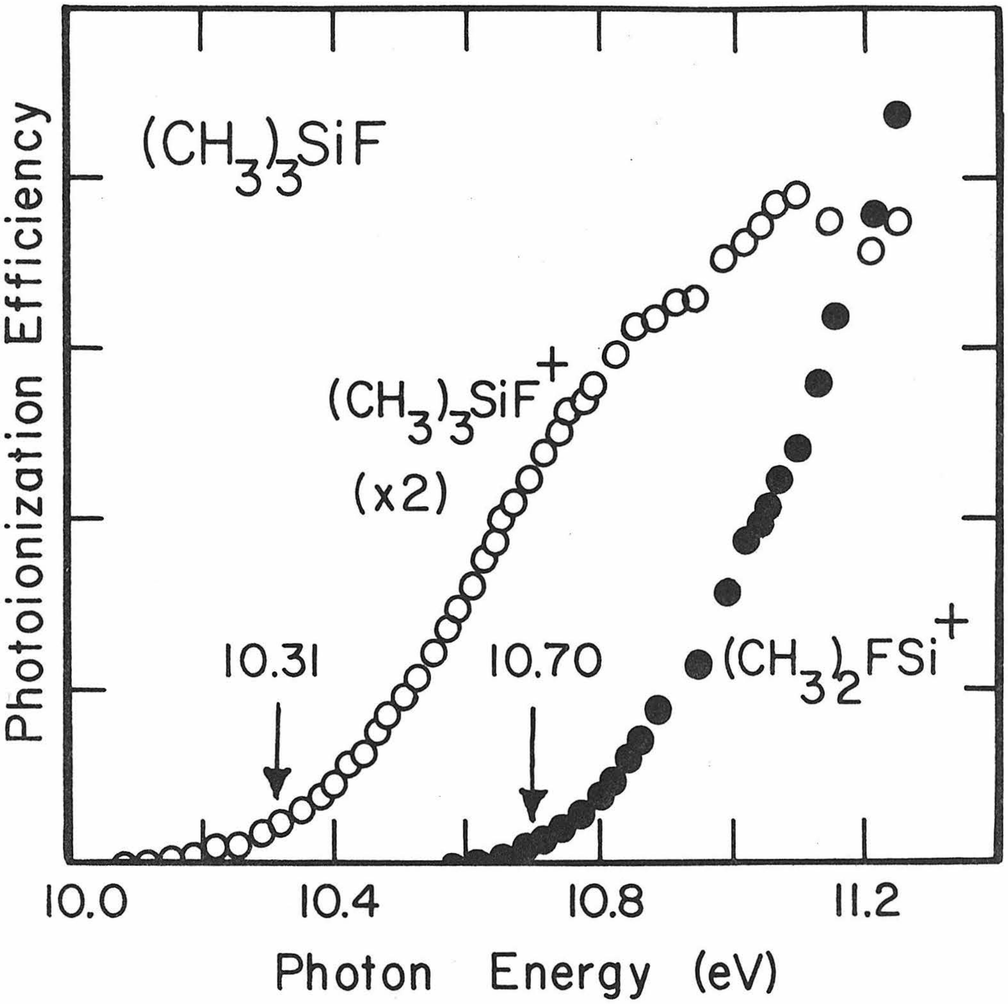
(CH$_3$)$_3$SiF
(CH$_3$)$_3$SiF$^+$
(x2)
(CH$_3$)$_2$FSi$^+$
10.31
10.70
Photoionization Efficiency
10.0
10.4
10.8
11.2
Photon Energy (eV)

TABLE I: Photoionization Data for the Fluoromethysilanes

Molecule	Ion	IP or AP (eV)	$\Delta H^{0}_{f_{298^{\circ}}}$ (kcal/mole)
$(CH_3)_4Si$			-42.4^{f}
	$(CH_3)_4Si^+$	$9.80 \pm 0.03^{a,c,d}$	183.5^{j}
	$(CH_3)_3Si^+$	$10.03 \pm 0.04^{a,c,d}$	154.8^{k}
$(CH_3)_3SiF$			-126.0^{g}
	$(CH_3)_3SiF^+$	$10.31 \pm 0.04^{a,e}$	111.6^{j}
	$(CH_3)_2SiF^+$	$10.70 \pm 0.04^{a,e}$	86.6^{k}
	$(CH_3)_3Si^+$	$9.52,^{l}$ 12.99^{m}	- -
$(CH_3)_2SiF_2$			-212.0^{g}
	$(CH_3)_2SiF_2^+$	11.03 ± 0.03^{a}	42.2^{j}
	$CH_3SiF_2^+$	11.70 ± 0.03^{a}	23.7^{k}
	$(CH_3)_2SiF^+$	$10.30,^{l}$ 13.77^{m}	- -
CH_3SiF_3			$-296.0^{g,h}$
	$CH_3SiF_3^+$	12.48 ± 0.04^{a}	-6.3^{j}
	SiF_3^+	13.33 ± 0.04^{a}	-22.7^{k}
	$CH_3SiF_2^+$	$11.21,^{l}$ 14.68^{m}	- -
SiF_4			-386.0^{i}
	SiF_4^+	15.19^{b}	-35.9^{j}
	SiF_3^+	$13.10,^{l}$ 16.57^{m}	- -

[a] Ionization thresholds determined from this work by extrapolation of the linearly rising portion of the photoionization efficiency curve for the indicated neutral molecule.

[b] Adiabatic IP SiF_4 obtained from photoelectron spectroscopy, vertical IP $SiF_4 = 16.46$ eV, Ref. 26.

[c] Previous literature values: IP $(CH_3)_4Si = 9.98 \pm 0.03$ eV and AP $(CH_3)_3Si^+ = 10.63 \pm 0.13$ eV, determined by RPD electron impact technique, Ref. 14a.

TABLE I: (Continued)

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[d] Previous values: IP $(CH_3)_4Si$ = 9.86 ± 0.02 eV and AP $(CH_3)_3Si^+$ = 10.09 ± 0.02 eV, determined by PIMS, Ref. 15c.

[e] Previous values: IP $(CH_3)_3SiF$ = 10.55 ± 0.06 eV and AP $(CH_3)_2SiF^+$ = 11.11 ± 0.05 eV, determined by RPD electron impact techniaue, Ref. 14a.

[f] Reference 14c.

[g] ΔH_f values determined as specified in the text.

[h] Previous estimate ΔH_f CH_3SiF_3 = -294.6 kcal/mole, Ref. 22.

[i] Reference 22.

[j] Calculated from $\Delta H_f(\text{ion}) = \Delta H_f(\text{neutral}) + \text{IP}(\text{neutral})$.

[k] Calculated from $\Delta H_f(\text{ion}) = \Delta H_f(\text{neutral}) - \text{AP}(\text{ion}) + \Delta H_f(CH_3)$, using $\Delta H_f(CH_3)$ = 34.0 kcal/mole, Ref. 27.

[l] Calculated for the pair processes $R_3SiF \rightarrow R_3Si^+ + F^-$ using fluoride affinities $D[R_3Si^+{-}F^-]$ from Table II.

[m] Calculated threshold for formation of R_3Si^+ by loss of F atom, from data in this table using eq 15, assuming no kinetic shift.

reaction 3 ($k = 3.4 \times 10^{-10}\ cm^3 mol^{-1} sec^{-1}$).[8] $(CH_3)_3Si^+$ production is

$$(CH_3)_2SiF^+ + (CH_3)_3SiF \rightarrow (CH_3)_3Si^+ + (CH_3)_2SiF_2 \qquad (3)$$

eliminated at high source repeller fields, where ion residence times are much reduced.

Fragmentation yielding $(CH_3)_2SiF^+$ by loss of methyl radical (reaction 4) exhibits a much sharper onset than is observed for

$$(CH_3)_3SiF + h\nu \rightarrow (CH_3)_2SiF^+ + CH_3 \qquad (4)$$

molecular ion formation. The threshold for process 4 occurs at 1158 ± 3 Å, yielding an appearance potential of 10.70 ± 0.04 eV. Table I summarizes observed ionization thresholds and derived ion heats of formation.

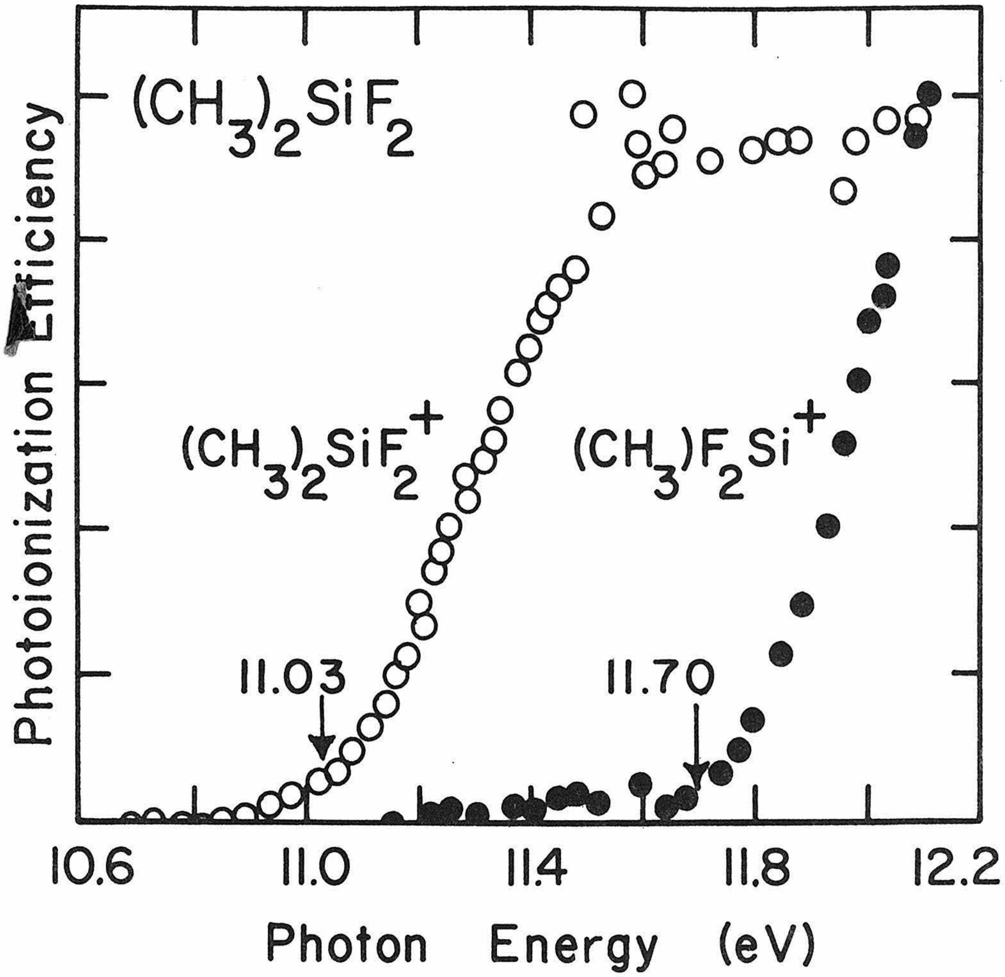
<u>$(CH_3)_2SiF_2$</u>. Photoionization efficiency curves for the molecular ion and lowest energy fragment $CH_3SiF_2^+$ generated from dimethyldifluorosilane in the photon energy range of 10.6 - 12.2 eV are shown in Figure 3. The molecular ion curve exhibits a well-behaved increase with photon energy, reaches a maximum near the onset of the lowest energy fragmentation and remains roughly constant for higher photon energies. The onset of molecular ion formation occurs at 1124 ± 3 Å, corresponding to the adiabatic ionization potential of 11.03 ± 0.03 eV. Process 5, production of $CH_3SiF_2^+$ by loss of CH_3

$$(CH_3)_2SiF_2 + h\nu \rightarrow CH_3SiF_2^+ + CH_3 \qquad (5)$$

from the parent ion, exhibits a sharp onset at 1053 ± 2 Å, yielding an appearance potential of 11.70 ± 0.03 eV. As was found for the

Figure 3

Photoionization efficiency curves for $(CH_3)_2SiF_2^+$ and $CH_3SiF_2^+$ generated from $(CH_3)_2SiF_2$ in the photon energy range 10.6 - 12.2 eV.


$(CH_3)_2SiF_2$
$(CH_3)_2SiF_2^+$
$(CH_3)F_2Si^+$
11.03
11.70
Photoionization Efficiency
10.6
11.0
11.4
11.8
12.2
Photon Energy (eV)

$(CH_3)_3Si^+$ in $(CH_3)_3SiF$, at low repeller voltages the more stable siliconium fragment $(CH_3)_2SiF^+$ derived from dimethyldifluorosilane is observed in low abundance. Its production, not shown in Figure 3, closely matches the variations in efficiency curves for the molecular ion and the low energy fragment, $CH_3SiF_2^+$, in accord with previously reported[8] reactions 6 and 7 ($k = 2.5$ and 3.1×10^{-10} $cm^3 mol^{-1} sec^{-1}$, respectively). $(CH_3)_2SiF^+$ production is eliminated by high repeller

$$(CH_3)_2SiF_2^+ + (CH_3)_2SiF_2 \rightarrow (CH_3)_2SiF^+ + CH_3SiF_3 + CH_3 \qquad (6)$$

$$CH_3SiF_2^+ + (CH_3)_2SiF_2 \rightarrow (CH_3)_2SiF^+ + CH_3SiF_3 \qquad (7)$$

voltages. Observed thresholds and derived ion heats of formation are shown in Table I.

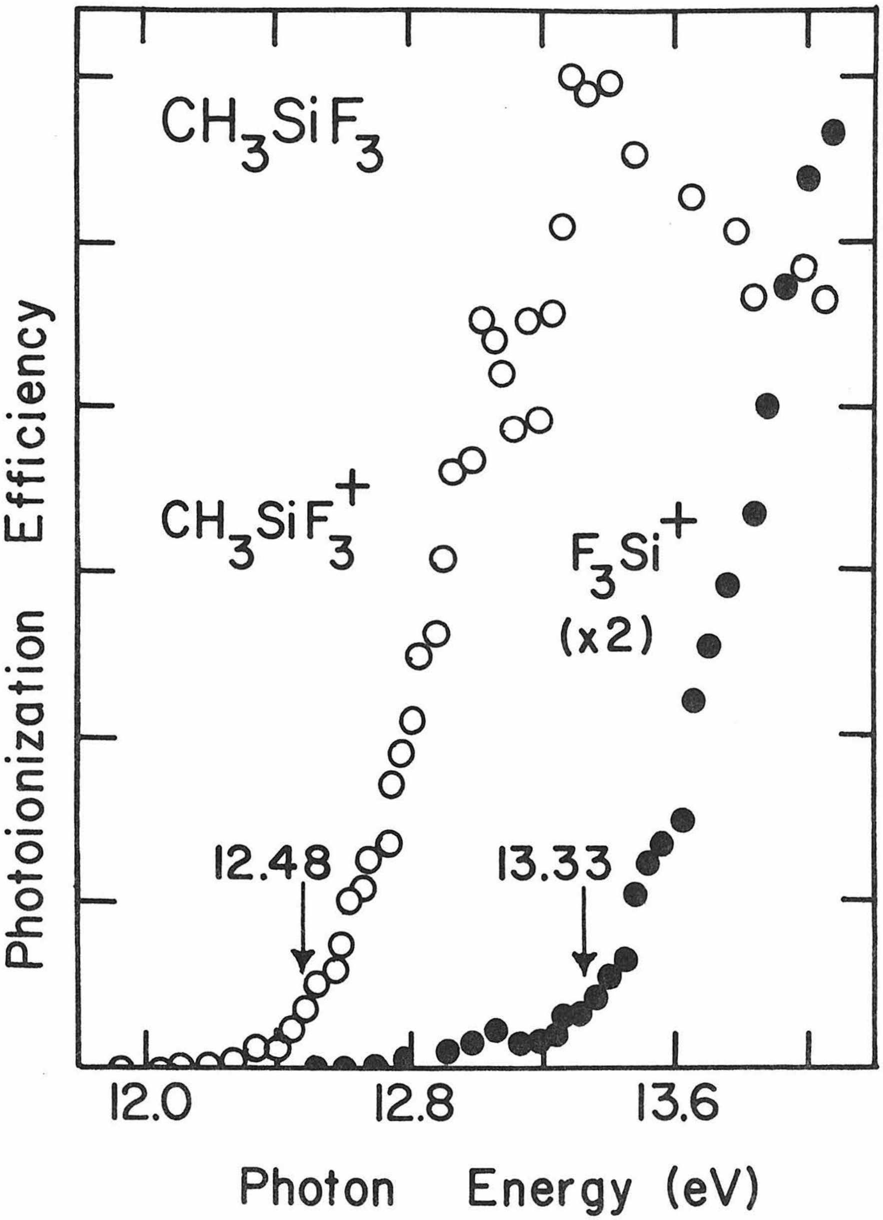
$\underline{CH_3SiF_3}$. Between 12.0 and 14.0 eV photon energies, the only ions formed from direct photon impact on CH_3SiF_3 are the molecular ion and the trifluorosiliconium ion. Photoionization efficiency curves for these ions are shown in Figure 4. The threshold for formation of the molecular ion occurs at 993 ± 3 Å, corresponding to an adiabatic ionization potential of 12.48 ± 0.04 eV. Fragmentation process 8, loss

$$CH_3SiF_3 + h\nu \rightarrow SiF_3^+ + CH_3 \qquad (8)$$

of CH_3 from the parent ion, exhibits an onset at 930 ± 3 Å, yielding 13.33 ± 0.05 eV for the appearance potential of SiF_3^+ from methyltrifluorosilane. The siliconium ion $CH_3SiF_2^+$ is observed in low abundance. Its production under low repeller fields essentially parallels the efficiency curves of $CH_3SiF_3^+$ and SiF_3^+ and is eliminated

Figure 4

Photoionization efficiency curves for $CH_3SiF_3^+$ and SiF_3^+ generated from CH_3SiF_3 in the photon energy range 12.0 - 14.0 eV.


CH$_3$SiF$_3$
CH$_3$SiF$_3^+$
F$_3$Si$^+$
(x2)
12.48
13.33
Photoionization Efficiency
12.0
12.8
13.6
Photon Energy (eV)

with high repeller voltages, consistent with the occurrence of previously reported[8] ion-neutral reactions 9 and 10 (k = 0.67 and 1.9 $\times 10^{-10}$ cm^{3}mol^{-1}sec^{-1}, respectively) observed thresholds and

$$CH_3SiF_3^+ + CH_3SiF_3 \rightarrow CH_3SiF_2^+ + SiF_4 + CH_3 \tag{9}$$

$$SiF_3^+ + CH_3SiF_3 \rightarrow CH_3SiF_2^+ + SiF_4 \tag{10}$$

derived ion heats of formation are summarized in Table I.

Discussion

Theoretical considerations suggest that for molecules, the more favorable threshold law for photoionization results in greater sensitivity at threshold than is observed for electron impact and provides for the precise determination of ionization thresholds. Even so, the interpretation of observed photoionization thresholds requires consideration of the contribution of thermal internal energy of the neutral to dissociation processes as well as the possibility of significant kinetic shifts. These phenomena have been discussed in detail elsewhere.[18-21]

Since these photoionization measurements are conducted at ambient temperatures, the initial thermal energy of the parent neutral contributes to the total internal energy of the molecular ion and convolutes a Maxwellian energy distribution into the observed threshold curve. This results in a low energy tail on the fragment ionization efficiency curve, and causes a shift to lower energy of the apparent threshold by an amount equal to the mean thermal energy content of the parent neutral. Studies of fragmentation processes for the lower alkanes have demonstrated the importance of such effects.[19]

The kinetic shift is a displacement of an apparent fragmentation threshold to higher energy, an effect arising from instrumental limitations of the minimum detectable fragment ion signal. The magnitude of the kinetic shift is equal to the amount of energy, in excess of the true fragmentation threshold, required to raise the dissociation rate to a level sufficient for the production of detectable concentrations of fragment ions.[18-21]

The effects of thermal energy and of kinetic shift are opposite in direction and often comparable in magnitude, and can lead to a fortuitous cancellation of errors. In light of these arguments, we can place reasonable confidence in the observed thresholds, since the fragmentation processes of lowest energy correspond to simple Si—C bond breaking and will not be complicated by significant kinetic shifts. Consistency of the present results with implications of fluoride transfer reactions of the siliconium ions[9, 16] suggest that the measured thresholds are reasonably accurate. Higher energy thresholds (those resulting from loss of F from the molecular ion), where kinetic shifts result from competition with lower energy fragmentation processes, are not utilized in the present study to derive thermochemical data.

Thermochemical Considerations. The observed ionization thresholds (Table I) allow calculation of a variety of ion thermochemical properties, provided that accurate data describing the parent neutral molecules are available. Experimental difficulties associated with calorimetric determinations of heats of formation for compounds of silicon and of fluorine have lead to considerable uncertainties in reported values.[15] Indirect estimations of neutral heats of formation of organosilicon compounds, using the bond interaction term scheme of Allen in conjunction with electron impact appearance potential correlations[14] have met with reasonable success for the methylsilanes. In the present study we take ΔH_f^0 values of the fluoromethylsilanes from an interpolation between those of $(CH_3)_4Si$[14c] at -42.4 and SiF_4[22] at -386 kcal/mole, along with the only available estimate for ΔH_f CH_3SiF_3[22] of -294.6 kcal/mole. The values used (Table I) are fully consistent with limits on siliconium ion fluoride affinities established by direct ICR observations of thermal energy fluoride transfer reactions involving siliconium ions and carbonium ions.[9, 16] Reference thermochemical data on the carbonium ion species involved are known with considerable accuracy from previous investigations.[10-13] The heats of formation of neutral silanes in Table I fit an approximately linear decrease of -85.9 kcal/mole for successive substitution of F for CH_3 throughout the series. Minor positive deviations from this decrease occur for values of ΔH_f of $(CH_3)_3SiF$, $(CH_3)_2SiF_2$ and CH_3SiF_3 (respectively, 1.7, 1.8 and 3.9 kcal). Similar thermochemical correlations are well known and form the basis of Benson's group additivity method[23] and the bond interaction term schemes of Allen.[24] Overall accuracy is conservatively estimated at ± 5 kcal/mole in ΔH_f values, of which only ± 1 kcal/mole is attributable to uncertainties in measured ionization thresholds.

Siliconium Ion Fluoride Affinities. Using the heat of formation data for the siliconium ions fragments R_3Si^+ arising by loss of CH_3 radical from the series of neutrals $(CH_3)_nF_{3-n}SiCH_3$ (where n = 0-3), the relationship 11 is used to calculate the fluoride affinities for all

$$D[R_3Si^+{-}F^-] = \Delta H_f[R_3Si^+] + \Delta H_f[F^-] - \Delta H_f[R_3SiF] \qquad (11)$$

four siliconium ions. The calculated values are summarized in Table II and exhibit a very marked increase with increasing fluorine substitution in place of methyl.

Related Thermochemical Properties. Included in Table II are calculated values for ionization potentials and heats of formation of the various methyl and fluoro substituted silyl radicals and estimates of the excess energies required to fragment the various parent molecular ions, denoted as $D[R_3Si^+{-}X]$ (where $X = CH_3$, F).

Calculation of silyl radical IPs, using appearance potential data for siliconium fragments arising from CH_3 loss (Table I), with eq 12

$$IP[R_3Si\cdot] = AP[R_3Si^+] - D[R_3Si{-}CH_3] \qquad (12)$$

requires knowledge of the $Si{-}CH_3$ bond dissociation energies in the neutral silanes. The only direct measurement in the literature is that of $D[(CH_3)_3Si{-}CH_3] = 78.8 \pm 3$ kcal/mole[25] obtained from the kinetics of thermal decomposition of $(CH_3)_4Si$. In light of the electron withdrawing effects of fluorine substituents and the relatively high polarizability of the methyl group, silicon-methyl homolytic bond dissociation energies might be expected to vary by an as yet unknown

TABLE II: Calculated Thermochemical Quantities

Ion $[R_3Si^+]$	$D[R_3Si^+{-}F^-]$[a, b]	$D[R_3Si^+{-}CH_3]$[a, c]	$D[R_3Si^+{-}F]$[a, d]	IP $[R_3Si]$[e]	$\Delta H_f[R_3Si]$[a, h]
$(CH_3)_3Si^+$	219.5	5.3	58.8	6.61[f]	2.4
$(CH_3)_2FSi^+$	237.3	9.0	63.2	7.23[g]	- 80.1
$(CH_3)F_2Si^+$	258.4	15.4	50.7	8.23[g]	-166.0
F_3Si^+	302.0	19.6	31.8	9.86[g, i]	-250.0

[a] In units of kcal/mole, calculated in each case as described in the text.

[b] Calculated using eq 11 and $\Delta H_f[F^-] = -61.3 \pm 0.1$ kcal/mole taken from Ref. 28.

[c] Calculated using eq 14 and $\Delta H_f[CH_3] = 34.0$ kcal/mole taken from Ref. 27.

[d] Calculated using eq 16 and data in Table I, with $\Delta H_f[F] = 18.7 \pm 1$ kcal/mole taken from Ref. 28.

[e] Radical ionization potentials are in eV.

[f] Calculated using eq 12 with $D[(CH_3)_3Si{-}CH_3] = 78.8 \pm 3$ kcal/mole taken from Ref. 25.

[g] Calculated using eq (12) with estimated $D[R_3Si{-}CH_3] = 80$ kcal/mole.

[h] Calculated using eq 13 and data in Tables I and II.

[i] This value appears to be too high; see text for discussion.

degree with increasing fluoro-substitution on silicon. In Table II, IPs for $(CH_3)_2FSi$, $(CH_3)F_2Si$ and F_3Si are estimated using $D[R_3Si{-}CH_3] = 80$ kcal/mole in each case. This estimate may be questioned, at least for F_3SiCH_3. The calculated IP $[F_3Si\cdot]$ at 9.86 eV is approximately equal to the accurately known value of IP $[CH_3\cdot] =$ 9.84 eV.[10b] From such silimar ionization potentials, one might expect to observe appreciable abundance of CH_3^+ in the mass spectra of CH_3SiF_3. In fact, for electron energies up to 70 eV, essentially no CH_3^+ ($\leq 0.1\%$ of total ionization) is formed, while SiF_3^+ is the base peak from CH_3SiF_3 from the onset of fragmentation to 70 eV.[8] This suggests that IP $[F_3Si\cdot]$ is actually considerably less than 9.84 eV and, assuming the measured AP $[F_3Si^+]$ from CH_3SiF_3 to be correct, requires $D[F_3Si{-}CH_3]$ to be somewhat greater than 80 kcal/mole. Similar uncertainties likely affect the IP values for $(CH_3)_2FSi$ and $(CH_3)F_2Si$ radicals. Even so, the calculated radical IPs show considerable increases with fluoro substitution. Radical heats of formation are calculated from eq 13 and subject to the above considerations

$$\Delta H_f[R_3Si] = D[R_3Si{-}CH_3] - \Delta H_f[CH_3] + \Delta H_f[R_3SiCH_3] \qquad (13)$$

regarding estimates for Si–C bond dissociation energies.

Calculations of excess energies necessary to induce $Si{-}CH_3$ bond breaking in the silane molecular ions (Table II) using eq 14

$$D[R_3Si^+{-}CH_3] = AP[R_3Si^+] - IP[R_3SiCH_3] \qquad (14)$$

require only a knowledge of relative ionization thresholds and do not depend on ΔH_f values of the neutral silanes. The calculated values are small but exhibit substantial increases with fluoro substitution, ranging from 5.3 kcal/mole for $(CH_3)_3Si^+$ to 19.6 kcal/mole for F_3Si^+.

The analogous calculation of $D[R_3Si^+{-}F]$ values is inhibited by a lack of direct measurements of appearance thresholds for siliconium ion fragments arising from F loss. However, approximate APs may be calculated using heat of formation data from Table I in eq 15. These

$$AP[R_3Si^+] = \Delta H_f[R_3Si^+] - \Delta H_f[R_3SiF] + \Delta H_f[F\cdot] \qquad (15)$$

calculated APs are included in Table I and allow calculation of Si–F bond energies in the parent molecular ions from eq 16. It is interesting

$$D[R_3Si^+{-}F] = AP[R_3Si^+] - IP[R_3SiF] \qquad (16)$$

to note that these calculated values of $D[R_3Si^+{-}F)$ (Table II) are considerably larger than those for $D[R_3Si^+{-}CH_3]$ but exhibit an overall decrease with increasing fluoro substitution beyond $(CH_3)_2FSi^+$, in contrast to the consistent increases observed throughout the $D[R_3Si^+{-}CH_3]$ series.

Included in Table I are estimates of the appearance thresholds for the pair processes $R_3SiF \rightarrow R_3Si^+ + F^-$, which in the absence of appreciable kinetic shifts are equal to the fluoride affinities of the siliconium ions R_3Si^+. In contrast to the energy dependence of fragmentation processes involving the loss of neutral species, that for a pair process is typically a resonance phenomena occurring with appreciable cross section only over a relatively narrow energy range. A pair process would appear as a peak in the photoionization efficiency curve. The estimated AP values for ions arising from loss of F and F^- (Table I) lie considerably outside of the photon energy ranges examined for the appropriate silane neutrals in the present study. No systematic attempts were made to detect the pair processes.

Comparisons of thermochemical data for trisubstituted silicon radicals and ions derived in the present study with literature data for the analogous carbon species are shown in Table III. These data represent the first quantitative comparisons available and contribute much to the interpretation of the relative effects of methyl and fluoro substitution at carbon and silicon centers.

Particularly striking from the comparisons in Table II are large but consistent differences in heterolytic bond dissociation energies, $D[R_3M^+-F^-]$ (where M = C, Si). A given siliconium ion is found to bind F^- more strongly by 40 ± 9 kcal/mole than the carbonium ion analog. This result bears significantly on repeated failures to detect siliconium ions in solution, under conditions where analogous carbonium ions are long-lived.[4, 5] While ion solvation can strongly influence ion stabilities in solution, the magnitude of the observed differences in siliconium and carbonium ion fluoride affinities in the gas phase suggests, in addition to effects due to C–Si electronegativity differences, a lack of π backbonding from filled substituent orbitals into the Si 3P orbital as compared with carbonium ions, due to poorer spatial overlap. Detailed discussion of these effects is the subject of a forthcoming report.[9]

TABLE III: Comparison of Thermochemical Properties of Silicon and Carbon Species

R_3M	$\Delta H_f R_3C$[a]	$\Delta H_f R_3Si$[a, c]	IP R_3C[b]	IP R_3Si[b, c]	$\Delta H_f R_3C^+$[a]	$\Delta H_f R_3Si^+$[a, d]	D $[R_3C^+-F^-]$[a]	D $[R_3Si^+-F^-]$[a, c]
$(CH_3)_3M$	6.8[e]	2.4	6.93[e]	6.61	167.0[e]	154.8	182.0[i]	219.5
$(CH_3)_2FM$	- 26.6[f]	- 80.1	7.14[f]	7.23	138.0[f]	86.6	206.5[f]	237.2
$(CH_3)F_2M$	- 73.8[f]	-166.0	7.92[f]	8.23	108.8[f]	23.7	225.7[f]	258.4
F_3M	-112.2[h]	-250.0	9.17[g]	9.86[j]	99.3[g]	-22.7	253.0[i]	302.0

[a] Heats of formation and bond dissociation energies are in units of kcal/mole.

[b] Radical ionization potentials are in units of eV.

[c] Taken from data in Table II.

[d] Taken from data in Table I.

[e] Reference 10.

[f] Reference 12.

[g] Reference 20.

[h] Reference 29.

[i] Reference 30.

[j] This value appears to be too high; see text for discussion.

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CHAPTER III

A QUANTITATIVE COMPARISON OF SILICONIUM AND CARBONIUM ION STABILITIES IN THE GAS PHASE BY ION CYCLOTRON RESONANCE SPECTROSCOPY[1a]

M. K. Murphy and J. L. Beauchamp[1b]

Abstract

The gas phase positive ion chemistry of mixtures of methyl and fluorine substituted methanes and silanes have been investigated using the techniques of ion cyclotron resonance spectroscopy. Fluoride transfer reactions (n, m = 0-3)

$$(CH_3)_nF_{3-n}Si^+ + (CH_3)_mF_{3-m}CF \rightleftharpoons (CH_3)_mF_{3-m}C^+ + (CH_3)_nF_{3-n}SiF$$

are found to proceed to the right whenever $n \leqslant m + 1$. These results serve to establish the ordering of gas phase carbonium and siliconium ion stabilities (expressed as fluoride ion affinities, $D[R^+{-}F^-]$) $SiF_3^+ < CH_3SiF_2^+ < CH_3^+ < CF_3^+ < (CH_3)_2SiF^+ < CH_3CF_2^+ < CH_3CH_2^+ < (CH_3)_3Si^+ < (CH_3)_2CF^+ < (CH_3)_3C^+$. Comparisons with available data for the hydride affinities $D[R^+{-}H^-]$ of the methylsiliconium ions ($R^+ = (CH_3)_nH_{3-n}Si^+$, n = 0-3) and analogous carbonium ions provide insights into the effects of methyl and fluorine substituents α to carbon and silicon cation centers. These observations provide the first direct experimental comparison using F^- as reference base of relative stabilities of

analogous carbonium and siliconium ions free from the influence of solvation. The present results provide insights into solution studies where attempts at observing the elusive siliconium ion species have proven futile.

Introduction

Significant contributions to understanding relationships between chemical structure and reactivity in organic systems have come from investigations of substituent effects on the stabilities of carbonium ions R_3C^+ both in solution and in the gas phase.[2-4] A range of spectroscopic techniques have yielded valuable structural information on long-lived tricoordinate carbocations in solution.[2, 5-8] Various studies indicate that solvent-solute interactions, particularly important for ionic species in solution, can greatly modify "intrinsic" structure-stability-reactivity relationships and result in seemingly anomolous effects.[3] Therefore, it is desirable to obtain information on ionic species in the gas phase. Ion cyclotron resonance (ICR) spectroscopy provides a tool uniquely suited to the detailed examination of ion-molecule processes, which can be used to quantify ion and neutral thermochemical properties, in the gas phase in the absence of complicating solvation phenomena. Recent ICR studies from this laboratory have exploited rapid anion transfer reactions 1 ($X^- = H^-, F^-, Br^-$, etc.) for quantitative deter-

$$R_1^+ + R_2X \rightleftharpoons R_1X + R_2^- \qquad \Delta H \equiv D[R_2^+\!-\!X^-] - D[R_1^+\!-\!X^-] \qquad (1)$$

minations of carbonium ion stabilities (measured as anion affinities, heterolytic bond dissociation energies, $D[R^+\!-\!X^-]$), with accuracies approaching ± 0.1 kcal/mole in favorable cases.[4, 9-13] Precise thermochemical data on carbonium ions is also available from high resolution photoionization and electron impact mass spectrometry.[14-16]

Relatively little detailed information has been available describing analogous tricoordinate cations where the charge center is another Group IVb atom, silicon. Siliconium ions, R_3Si^+, are proposed as intermediates in many organosilicon chemical reactions[17] and are abundant in mass spectra of a variety of organosilicon compounds.[18, 19] Exhaustive experimental attempts to generate even detectable concentrations of siliconium ions in solution, under conditions where analogous carbonium ions are long-lived, have been completely unsuccessful.[20, 21] The factors responsible for the apparently exceedingly low stability of siliconium ions in solution as compared with their carbon analogs have been debated as the "siliconium ion question."[21] Although some thermochemical data describing siliconium ions in the gas phase are available from electron impact mass spectrometry, large experimental uncertainties make stability comparisons with carbonium ions somewhat unreliable.[22, 23] Recently reported from this laboratory, ICR studies[24] of fluoride transfer processes 1, where $X^- = F^-$, yield a qualitative siliconium ion stability order $SiF_3^+ < CH_3SiF_2^+ < (CH_3)_2SiF^+ < (CH_3)_3Si^+$, paralleling trends in substituent effects observed for the analogous carbonium ions.

In the present report, we present a direct comparison of the gas phase stabilities (expressed as heterolytic bond dissociation energies, $D[R^+-F^-]$) of siliconium ions and carbonium ions as determined from

ICR studies of fluoride transfer reactions 1 (where $X^- = F^-$) occurring in mixtures of appropriately substituted methanes and silanes. In conjunction with recent photoionization studies of siliconium ion fragments generated in the fluoromethylsilanes,[25, 26] the present results serve to establish an absolute scale of gas phase ion stabilities with fluoride ion as the reference base and afford a quantitative comparison of factors responsible for the complex and competing effects of methyl and fluorine substituents α to silicon and carbon positive ion centers.

Experimental

All studies reported herein utilize a high-field ICR spectrometer (employing a 15" magnet system) constructed in the Caltech instrument shops. Details of the instrumentation and experimental techniques associated with ICR spectroscopy are described elsewhere.[27] Gas mixtures utilized are prepared directly in the ICR cell by admission of sample components through separate variable leak valves in a parallel inlet manifold. Absolute gas pressures are determined using a Schulz-Phelps ionization gauge, adjacent to the ICR cell, calibrated separately for each component against an MKS Baratron Model 90H1-E capacitance manometer.[10] A linear calibration of Baratron pressure versus ionization gauge current affords pressure determinations over a range of 10^{-7} to 10^{-4} torr. Overall accuracy in pressure measurement for these studies is estimated to be ± 20% and represents the major source of error in reported reaction rate constants. All measurements are performed at ambient temperatures (~22°C). Bimolecular rate constants are determined from the limiting slopes of semi-log plots of trapped-ion abundance versus time, partitioned in accordance with product distributions.

The ionizing voltage utilized throughout this work is nominally 20 eV, with typical electron beam currents of $\sim 3 \times 10^{-7}$ A. Under these conditions, tricoordinate cations (siliconium and carbonium ions) comprise major portions ($\geq 80\%$) of the total ionization, facilitating examination of fluoride transfer processes in detail.

Samples of $(CH_3)_3SiF$, $(CH_3)_2SiF_2$, and CH_3SiF_3 (PCR) were provided through the courtesy of Professor J. G. Dillard. $(CH_3)_2CF_2$ was obtained from Cationics, CH_3CF_3 from PCR, and CH_4, $(CH_3)_3CH$, CF_4, and SiF_4 from Matheson. Non-condensable impurities were removed using multiple freeze-pump-thaw cycles at liquid nitrogen temperatures. Mass spectral analysis of all samples utilized showed no detectable impurities, with the exception of trace amounts of disilylether contaminants in $(CH_3)_2SiF_2$ ($\sim 0.2\%$) and CH_3SiF_3 ($\sim 2\%$).[24] In view of previously reported difficulties encountered in mass spectral studies of organohalosilanes, it is possible that ether impurities arise from reaction with traces of water on inlet manifold surfaces.

Data reported in tables and figures are normalized to monoisotopic abundances (^{12}C, 98.89%; ^{28}Si, 92.21%). Typically, ionic species comprising less than 1% of the total ionization are omitted from the reported data.

Results

The gas phase positive ion chemistries of the fluoromethylsilanes and fluorocarbon compounds individually have been the subject of previous investigations.[9-12, 24, 25, 28, 29] In the present study, positive ion reactions occurring in binary mixtures of methyl- and fluoro-substituted silanes and methanes are examined with the goal of determining relative fluoride affinities of analogous tricoordinate cations $(CH_3)_nF_{3-n}M^+$, (n = 0-3; M = C, Si). Under the experimental conditions employed, fluoride transfer reactions involving carbonium ions and siliconium ions by far dominate the observed chemistry and attention will be focussed on these processes. Reaction rate constants determined in the present study are summarized in Table I. A number of additional ion-molecule reactions are detected in the mixtures examined and are for the most part characteristic of the ion chemistry of the individual components. Detailing of these reactions is omitted except where necessary for clarity of data interpretation regarding the fluoride transfer processes.

CF_4/CH_3SiF_3. Figure 1 illustrates the temporal variation of trapped cation concentrations following a 10 msec electron beam pulse in a 6.9:1 mixture of CH_3SiF_3 and CF_4 at a constant total pressure of 7.9×10^{-6} torr. Previous investigations indicate CF_3^+ to be unreactive with CF_4[29f] and that $CH_3SiF_2^+$ is the more stable siliconium ion arising from CH_3SiF_3.[24-26] Double resonance experiments indicate that fluoride transfer reaction 2 is primarily responsible for the increase

$$CH_3SiF_2^+ + CF_4 \rightarrow CF_3^+ + CH_3SiF_3 \qquad (2)$$

of CF_3^+ abundance with time in Figure 1.

Minor complexity of the ion chemistry of this mixture arises from the presence of a low concentration disilylether impurity, suspected to

Figure 1

Temporal variation of ion abundances following a 10 msec 20 eV electron beam pulse in a 6.9:1 mixture of CH_3SiF_3 and CF_4 at 7.9×10^{-6} torr total pressure.

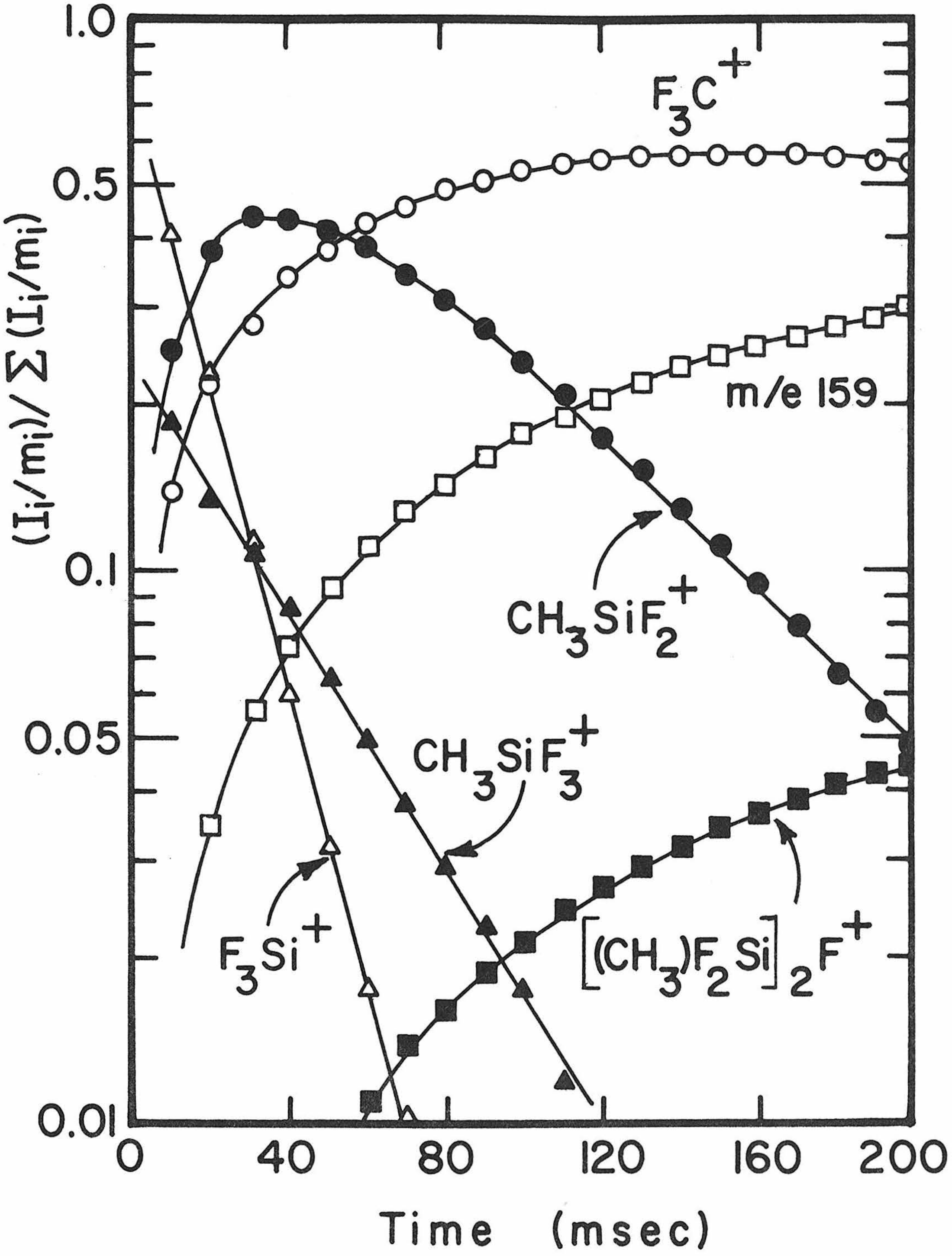

1.0
0.5
0.1
0.05
0.01
$(I_i/m_i)/\sum(I_i/m_i)$
0
40
80
120
160
200
Time (msec)
F_3C^+
m/e 159
$CH_3SiF_2^+$
$CH_3SiF_3^+$
F_3Si^+
$[(CH_3)F_2Si]_2F^+$

Table I. Observed Ion-Molecule Reactions

System	Reaction	Number[a]	Rate Constant, $k^{b,c}$	Thermochemical Implications[d]
CF_4/CH_3SiF_3				
	$CH_3SiF_2^+ + CF_4 \longrightarrow CF_3^+ + CH_3SiF_3$	3	2.8	$D[(CH_3)F_2Si^+-F^-] > D[CF_3^+-F^-]$
CH_3CF_3/CH_3SiF_3				
	$CH_3SiF_2^+ + CH_3CF_3 \longrightarrow CH_3CF_2^+ + CH_3SiF_3$	4	2.9	$D[(CH_3)F_2Si^+-F^-] > D[(CH_3)F_2C^+-F^-]$
$CH_3CF_3/(CH_3)_2SiF_2$				
	$CF_3^+ + (CH_3)_2SiF_2 \longrightarrow (CH_3)_2SiF^+ + CF_4$	5	--[e]	$D[CF_3^+-F^-] > D[(CH_3)_2FSi^+-F^-]$
	$(CH_3)_2SiF^+ + CH_3CF_3 \longrightarrow CH_3CF_2^+ + (CH_3)_2SiF_2$	6	7.8	$D[(CH_3)_2FSi^+-F^-] > D[(CH_3)F_2C^+-F^-]$
$(CH_3)_2CF_2/(CH_3)_2SiF_2$				
	$(CH_3)_2SiF^+ + (CH_3)_2CF_2 \longrightarrow (CH_3)_2CF^+ + (CH_3)_2SiF_2$	7	6.8	$D[(CH_3)_2FSi^+-F^-] > D[(CH_3)_2FC^+-F^-]$
	$CH_3SiF_2^+ + (CH_3)_2CF_2 \longrightarrow (CH_3)_2CF^+ + CH_3SiF_3$	8	--[e]	$D[(CH_3)F_2Si^+-F^-] > D[(CH_3)_2FC^+-F^-]$
$(CH_3)_2CF_2/(CH_3)_3SiF$				
	$CH_3CF_2^+ + (CH_3)_3SiF \longrightarrow (CH_3)_3Si^+ + CH_3CF_3$	9	--[e]	$D[(CH_3)F_2C^+-F^-] > D[(CH_3)_3Si^+-F^-]$
	$(CH_3)_3Si^+ + (CH_3)_2CF_2 \longrightarrow (CH_3)_2CF^+ + (CH_3)_3SiF$	10	3.4	$D[(CH_3)_3Si^+-F^-] > D[(CH_3)_2FC^+-F^-]$
$(CH_3)_3CH/(CH_3)_3SiF$				
	$(CH_3)_2SiF^+ + (CH_3)_3CH \longrightarrow (CH_3)_3C^+ + (CH_3)_2SiFH$	11	--[e]	$D[(CH_3)_2FSi^+-H^-] > D[(CH_3)_3C^+-H^-]$
	$(CH_3)_3Si^+ + (CH_3)_3CH \nrightarrow (CH_3)_3C^+ + (CH_3)_3SiH$	--	$< 0.01^f$	$D[(CH_3)_3Si^+-H^-] < D[(CH_3)_3C^+-H^-]$
	$(CH_3)_3C^+ + (CH_3)_3SiF \nrightarrow (CH_3)_3Si^+ + (CH_3)_3CF$	--	$< 0.01^f$	$D[(CH_3)_3C^+-F^-] < D[(CH_3)_3Si^+-F^-]$
CH_4/CH_3SiF_3				
	$CH_4^+ + CH_3SiF_3 \longrightarrow CH_3SiF_3H^+ + CH_3$	12	Total 3.0	
	$\longrightarrow CH_3SiF_2^+ + HF + CH_3$	13		
	$CH_5^+ + CH_3SiF_3 \longrightarrow CH_3SiF_3H^+ + CH_4$	14	2.4	$PA[CH_3SiF_3] > PA[CH_4]^g$
	$CH_3^+ + CH_3SiF_3 \nrightarrow CH_3SiF_2^+ + CH_3F$	--	$< 0.01^f$	$D[CH_3^+-F^-] < D[(CH_3)F_2Si^+-F^-]$
	$C_2H_5^+ + CH_3SiF_3 \nrightarrow CH_3SiF_2^+ + C_2H_5F$	--	$< 0.01^f$	$D[CH_3CH_2^+-F^-] < D[(CH_3)F_2Si^+-F^-]$
	$SiF_3^+ + CH_4 \nrightarrow CH_3^+ + SiF_3H$	--	$< 0.01^f$	$D[SiF_3^+-H^-] < D[CH_3^+-H^-]$
	$CH_3SiF_2^+ + CH_4 \nrightarrow CH_3^+ + CH_3SiF_2H$	--	$< 0.01^f$	$D[(CH_3)F_2Si^+-H^-] < D[CH_3^+-H^-]$

Table I. (Continued)

System	Reaction	Number[a]	Rate Constant, $k^{b,\,c}$	Thermochemical Implications[d]
$CH_4/(CH_3)_3SiF$				
	$CH_5^+ + (CH_3)_3SiF \rightarrow (CH_3)_3SiFH^+ + CH_4$	15		$PA[(CH_3)_3SiF] > PA[CH_4]^g$
	$\rightarrow (CH_3)_2SiF^+ + 2CH_4$	16	Total 4.3	
	$\rightarrow (CH_3)_3Si^+ + CH_4 + HF$	17		
	$C_2H_5^+ + (CH_3)_3SiF \rightarrow (CH_3)_3SiFH + C_2H_4$	18		$PA[(CH_3)_3SiF] > PA[C_2H_4]^g$
	$\rightarrow (CH_3)_2SiF^+ + CH_4 + C_2H_4$	19	Total 2.0	
	$\rightarrow (CH_3)_3Si^+ + C_2H_5F$	20		$D[C_2H_5^+{-}F^-] > D[(CH_3)_3Si^+{-}F^-]$
	$(CH_3)_2SiF^+ + CH_4 \not\longrightarrow CH_3^+ + (CH_3)_2SiFH$	--	$< 0.01^f$	$D[(CH_3)_2FSi^+{-}H^-] < D[CH_3^+{-}H^-]$
	$(CH_3)_3Si^+ + CH_4 \not\longrightarrow CH_3^+ + (CH_3)_3SiH$	--	$< 0.01^f$	$D[(CH_3)_3Si^+{-}H^-] < D[CH_3^+{-}H^-]$

[a] Reaction numbers refer to reactions specified in the text.

[b] Rate constants determined from the limiting slopes of reactant ion disappearance in semi-log plots of trapped-cation abundance versus time.

[c] Rate constants are in units of 10^{-10} cm^{3}molecule^{-1}sec^{-1}.

[d] Thermochemical limits implied by the preferred direction of ion-molecule reactions, assuming thermal energy reactant ions.

[e] Rate constant not determined.

[f] Reaction not observed, also checked by double resonance and cyclotron ejection experiments.

[g] PA = proton affinity, $PA[B] = \Delta H$ for the reaction $BH^+ \rightarrow B + H^+$.

be $[(CH_3)F_2Si]_2O$. Comprising ~30% total ionization at long times in Figure 1, m/e 159, formulated as $(CH_3)_2F_3Si_2O^+$, has been previously observed in the ion chemistry of CH_3SiF_3 alone.[24] Double resonance indicates that m/e 159 is produced to some small extent by CF_3^+, presumably via fluoride transfer from the neutral ether.

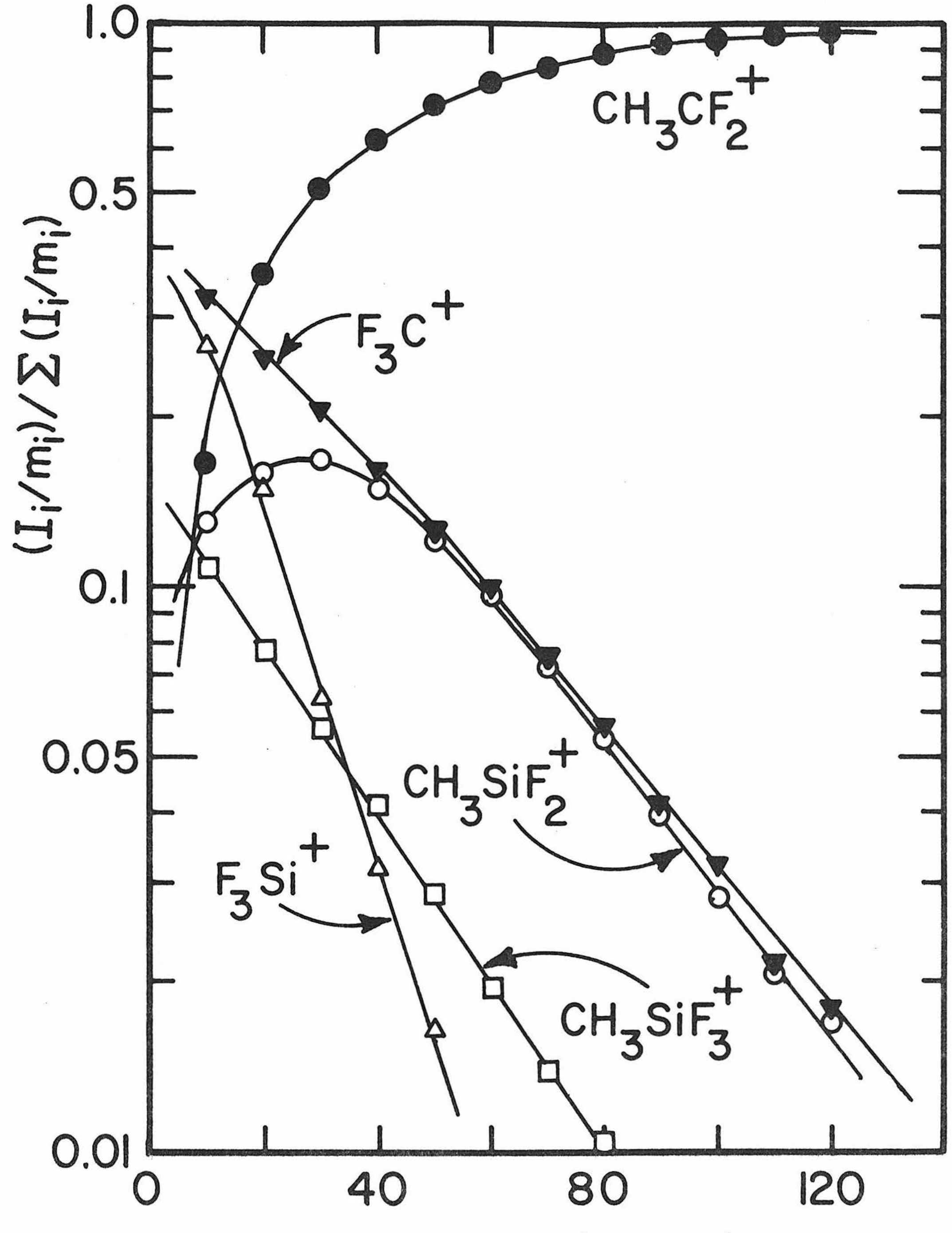
CH_3CF_3/CH_3SiF_3. The temporal variation of ion abundances initiated by a 10 msec electron beam pulse in a 1.5:1 mixture of CH_3SiF_3 and CH_3CF_3 at a constant total pressure of 7.9×10^{-6} torr is displayed in Figure 2. As previously reported,[28b, 30] CF_3^+ reacts by fluoride transfer with CH_3CF_3 to generate the more stable carbonium ion $CH_3CF_2^+$. As shown in Figure 2, $CH_3CF_2^+$ comprises essentially 100% of the total ionization at long times and does not appear to undergo further reaction in this system. From the relative abundances of ions present immediately following the ionization pulse (Figure 2), it is evident that only ~40% of the $CH_3CF_2^+$ can be accounted for by fluoride transfer from CH_3CF_3 to CF_3^+. Double resonance indicates that reaction 3 is responsible for the majority of the observed buildup of $CH_3CF_2^+$.

$$CH_3SiF_2^+ + CH_3CF_3 \rightarrow CH_3CF_2^+ + CH_3SiF_3 \qquad (3)$$

It is interesting to note that, in contrast with observations in CH_3SiF_3 alone[24] and in the CF_4/CH_3SiF_3 mixture described above, m/e 159 is not observed in abundance greater than 1% of total ionization in this mixture. Such behavior would be expected under the present conditions if the fluoride affinity of $(CH_3)_2F_3Si_2O^+$ is intermediate between those of $CH_3CF_2^+$ and CF_3^+.

Figure 2

Temporal variation of ion abundances following a 10 msec 20 eV electron beam pulse in a 1.5:1 mixture of CH_3SiF_3 and CH_3CF_3 at 7.9×10^{-6} torr total pressure.


1.0
0.5
0.1
0.05
0.01
0
40
80
120
$(I_i/m_i)/\sum(I_i/m_i)$
Time (msec)
$CH_3CF_2^+$
F_3C^+
$CH_3SiF_2^+$
F_3Si^+
$CH_3SiF_3^+$

$CH_3CF_3/(CH_3)_2SiF_2$. In a 3.6:1 mixture of $(CH_3)_2SiF_2$ and CH_3CF_3 at 2.7×10^{-6} torr total pressure, a 10 msec electron beam pulse initiates the temporal variation of ion abundances depicted in Figure 3. At short times in the experiment, previously reported fluoride transfer processes result in rapid buildup of $CH_3CF_2^+$[28b, 30] and $(CH_3)_2SiF^+$.[24] Cyclotron ejection experiments indicate that CF_3^+ is responsible in part for the observed increase in $(CH_3)_2SiF^+$ abundance (reaction 4).

$$CF_3^+ + (CH_3)_2SiF_2 \rightarrow (CH_3)_2SiF^+ + CF_4 \tag{4}$$

Present initially at ~15% of the total ionization, CF_3^+ can account for only a small fraction of the overall observed increase in $CH_3CF_2^+$ concentration. As reaction proceeds, $CH_3CF_2^+$ abundance continues to increase at the expense of $(CH_3)_2SiF^+$ via fluoride transfer reaction 5.

$$(CH_3)_2SiF^+ + CH_3CF_3 \rightarrow CH_3CF_2^+ + (CH_3)_2SiF_2 \tag{5}$$

$(CH_3)_2CF_2/(CH_3)_2SiF_2$. Figure 4 illustrates the time evolution of ion abundances observed following the electron beam pulse in a 2:1 mixture of $(CH_3)_2SiF_2$ and $(CH_3)_2CF_2$ at a constant total pressure of 1.7×10^{-6} torr. As previously reported,[15, 30] $(CH_3)_2CF^+$ is the more stable carbonium ion from $(CH_3)_2CF_2$, being produced via fluoride transfer to $CH_3CF_2^+$. $(CH_3)_2CF^+$ exhibits a dramatic increase in concentration in this mixture, comprises ~90% of the total ionization at long reaction times, and is not observed to react further under the present conditions. It is apparent that $CH_3CF_2^+$ can contribute no more than ~30% to the observed increase in $(CH_3)_2CF^+$, while double resonance indicates that a major portion of the observed rise in $(CH_3)_2CF^+$ abundance is the

Figure 3

Temporal variation of ion abundances following a 10 msec 20 eV electron beam pulse in a 3.6:1 mixture of $(CH_3)_2SiF_2$ and CH_3CF_3 at 2.7×10^{-6} torr total pressure.

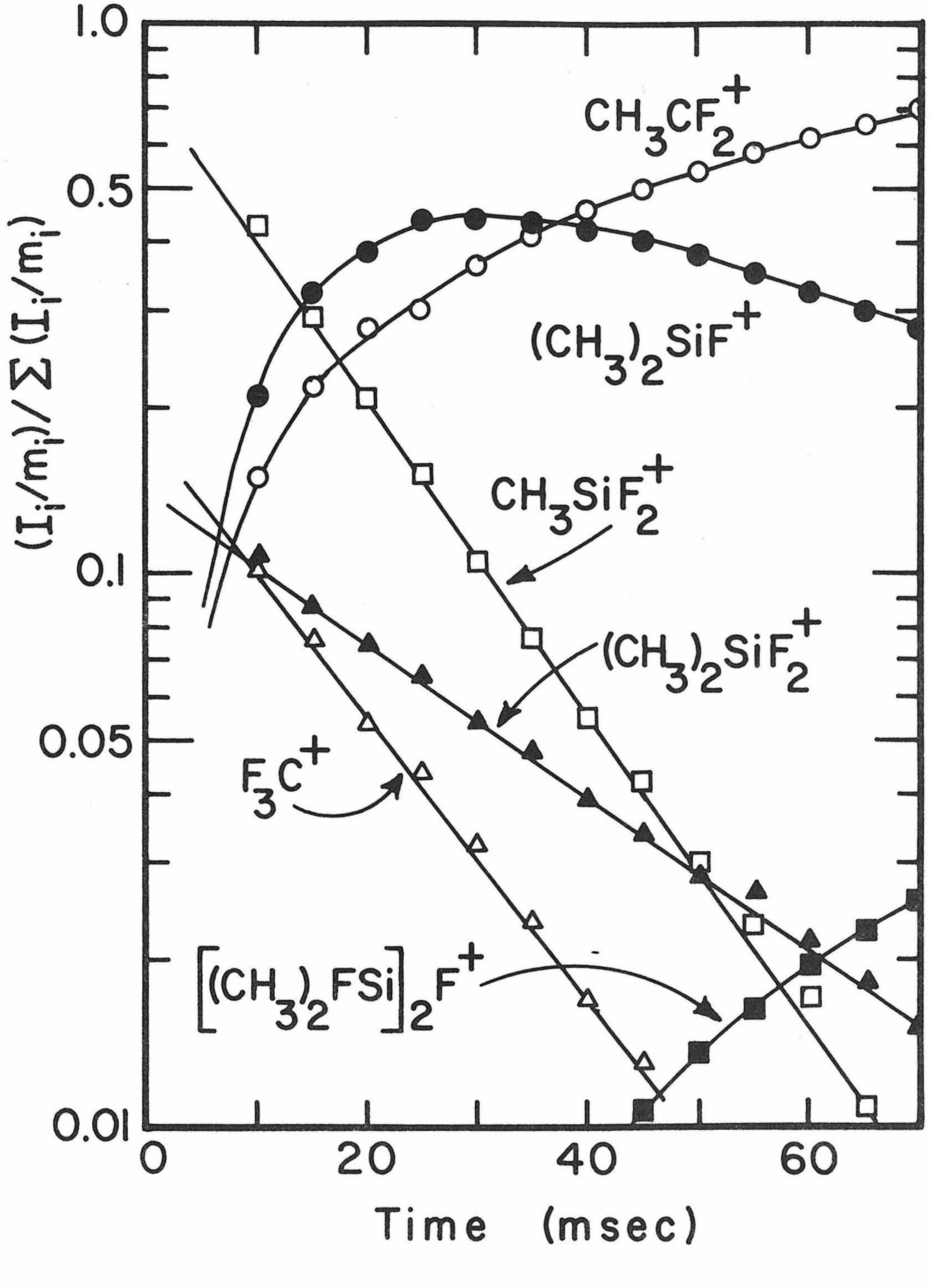
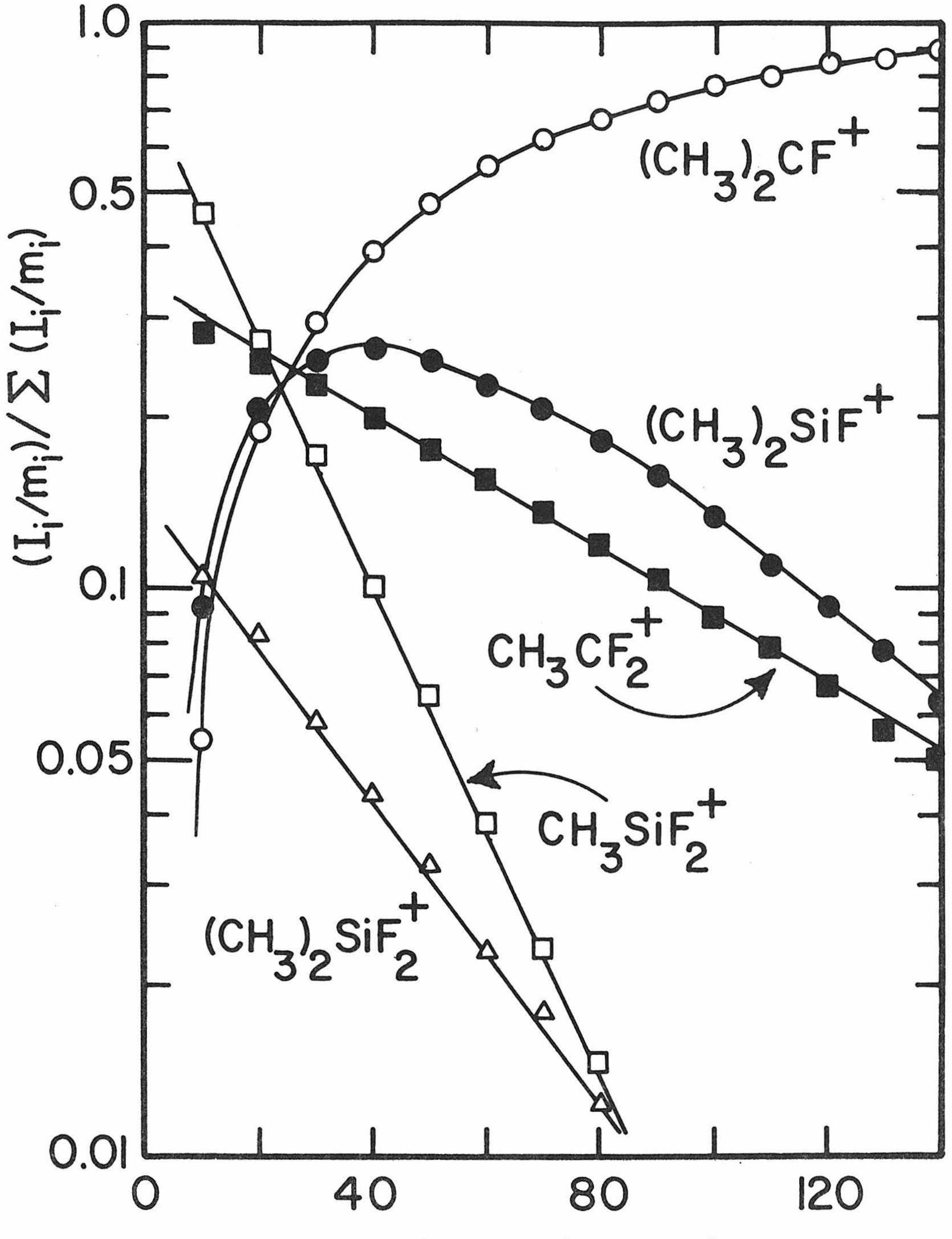

1.0
0.5
0.1
0.05
0.01
0
20
40
60
Time (msec)
$(I_i/m_i)/\sum(I_i/m_i)$
$CH_3CF_2^+$
$(CH_3)_2SiF^+$
$CH_3SiF_2^+$
$(CH_3)_2SiF_2^+$
F_3C^+
$[(CH_3)_2FSi]_2F^+$

Figure 4

Temporal variation of ion abundances following a 10 msec 20 eV electron beam pulse in a 2:1 mixture of $(CH_3)_2SiF_2$ and $(CH_3)_2CF_2$ at 1.7×10^{-6} torr total pressure.


1.0
0.5
0.1
0.05
0.01
0
40
80
120
Time (msec)
$(I_i/m_i)/\sum(I_i/m_i)$
$(CH_3)_2CF^+$
$(CH_3)_2SiF^+$
$CH_3CF_2^+$
$CH_3SiF_2^+$
$(CH_3)_2SiF_2^+$

result of fluoride transfer to $(CH_3)_2SiF^+$ (reaction 6). Cyclotron

$$(CH_3)_2SiF^+ + (CH_3)_2CF_2 \rightarrow (CH_3)_2CF^+ + (CH_3)_2SiF_2 \qquad (6)$$

ejection experiments also indicate that a small fraction (~15%) of the increase in $(CH_3)_2CF^+$ is due to reaction 7 involving fluoride transfer to $CH_3SiF_2^+$.

$$CH_3SiF_2^+ + (CH_3)_2CF_2 \rightarrow (CH_3)_2CF^+ + CH_3SiF_3 \qquad (7)$$

$(CH_3)_2CF_2/(CH_3)_3SiF$. The temporal variation of ion concentrations initiated by the electron beam pulse in an ~1:1 mixture of $(CH_3)_2CF_2$ and $(CH_3)_3SiF$ at a constant total pressure of 2.2×10^{-6} torr in shown in Figure 5. $(CH_3)_2CF^+$ abundance increases rapidly throughout the time span of the experiment, eventually comprising > 90% of total ionization at long times. As previously reported for the ion chemistry of $(CH_3)_3SiF$,[24] fluoride transfer to $(CH_3)_2SiF^+$ generates the more stable trimethylsiliconium ion. From consideration of relative ion concentrations present immediately following the ionizing pulse (Figure 5), it is apparent that reaction of $CH_3CF_2^+$ can account for no more than ~30% of the overall observed increase in $(CH_3)_2CF^+$. Double resonance and cyclotron ejection experiments clearly indicate the occurrence of fluoride transfer reactions 8 and 9, in addition to reaction 7 described

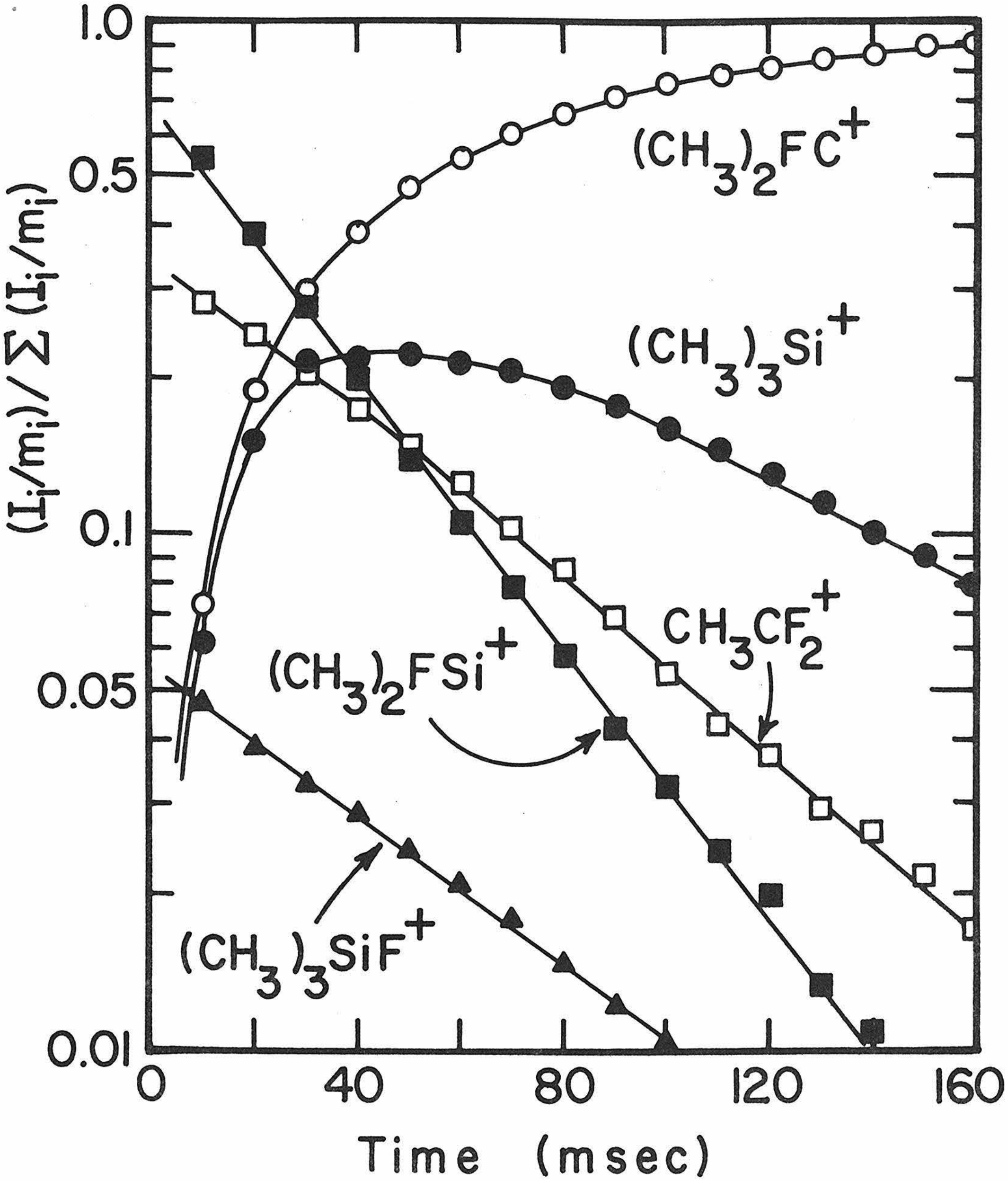
$$CH_3CF_2^+ + (CH_3)_3SiF \rightarrow (CH_3)_3Si^+ + CH_3CF_3 \qquad (8)$$

$$(CH_3)_3Si^+ + (CH_3)_2CF_2 \rightarrow (CH_3)_2CF^+ + (CH_3)_3SiF \qquad (9)$$

above. $(CH_3)_2CF^+$ appears stable to further reaction in this mixture.

Figure 5

Temporal variation of ion abundances following a 10 msec 20 eV electron beam pulse in an ~1:1 mixture of $(CH_3)_2CF_2$ and $(CH_3)_3SiF$ at 2.2×10^{-6} torr total pressure.


1.0
0.5
0.1
0.05
0.01
0
40
80
120
160
Time (msec)
$(I_i/m_i)/\sum(I_i/m_i)$
$(CH_3)_2FC^+$
$(CH_3)_3Si^+$
$CH_3CF_2^+$
$(CH_3)_2FSi^+$
$(CH_3)_3SiF^+$

The previously reported bis-trimethylsilyl fluoronium ion cluster of $(CH_3)_3Si^+$ with $(CH_3)_3SiF$[24] is not observed.

$(CH_3)_3CH/(CH_3)_3SiF$. Figure 6 illustrates the temporal variation of ion abundances initiated by the 18 eV electron beam pulse in a 1.2:1 mixture of $(CH_3)_3SiF$ and $(CH_3)_3CH$ at 1.9×10^{-6} torr constant total pressure. In isobutane, $(CH_3)_3C^+$ is the terminal stable product of ion-molecule processes involving fragments arising from electron impact. In addition to producing $(CH_3)_3Si^+$ by rapid fluoride transfer from $(CH_3)_3SiF$,[24] $(CH_3)_2SiF^+$ reacts in part by hydride transfer with $(CH_3)_3CH$ (reaction 11), as indicated by double resonance. Cyclotron ejection

$$(CH_3)_2SiF^+ + (CH_3)_3CH \rightarrow (CH_3)_3C^+ + (CH_3)_2SiFH \qquad (10)$$

experiments indicate that reaction 10 contributes to ~10% of the overall increase in abundance exhibited by $(CH_3)_3C^+$ in Figure 6. The observed decay of $(CH_3)_3Si^+$ abundance is due entirely to clustering with neutral $(CH_3)_3SiF$ producing $[(CH_3)_3Si]_2F^+$.[24] No further reaction of $(CH_3)_3C^+$ is observed under the present conditions. In particular, hydride transfer from $(CH_3)_3CH$ to $(CH_3)_3Si^+$ is not observed.

CH_4/CH_3SiF_3. Relative fluoride affinities $CH_3SiF_2^+ > CF_3^+$ are indicated by reaction 2 in the CF_4/CH_3SiF_3 system. In order to better define limits on $D[(CH_3)F_2Si^+{-}F^-]$, attempts were made to observe fluoride transfer from CH_3SiF_3 to methyl cation derived from methane. Previous studies show the fluoride affinity of CH_3^+ to be ~ 3 kcal/mole greater than that of CF_3^+.[9, 10] The temporal variation of ion concentrations following the electron beam pulse in a 2.5:1 mixture of CH_3SiF_3 and CH_4 at a total pressure of 2.3×10^{-6} torr is shown in

Figure 6

Temporal variation of ion abundances following a 10 msec 18 eV electron beam pulse in a 1.2:1 mixture of $(CH_3)_3SiF$ and $(CH_3)_3CH$ at 1.9×10^{-6} torr total pressure.

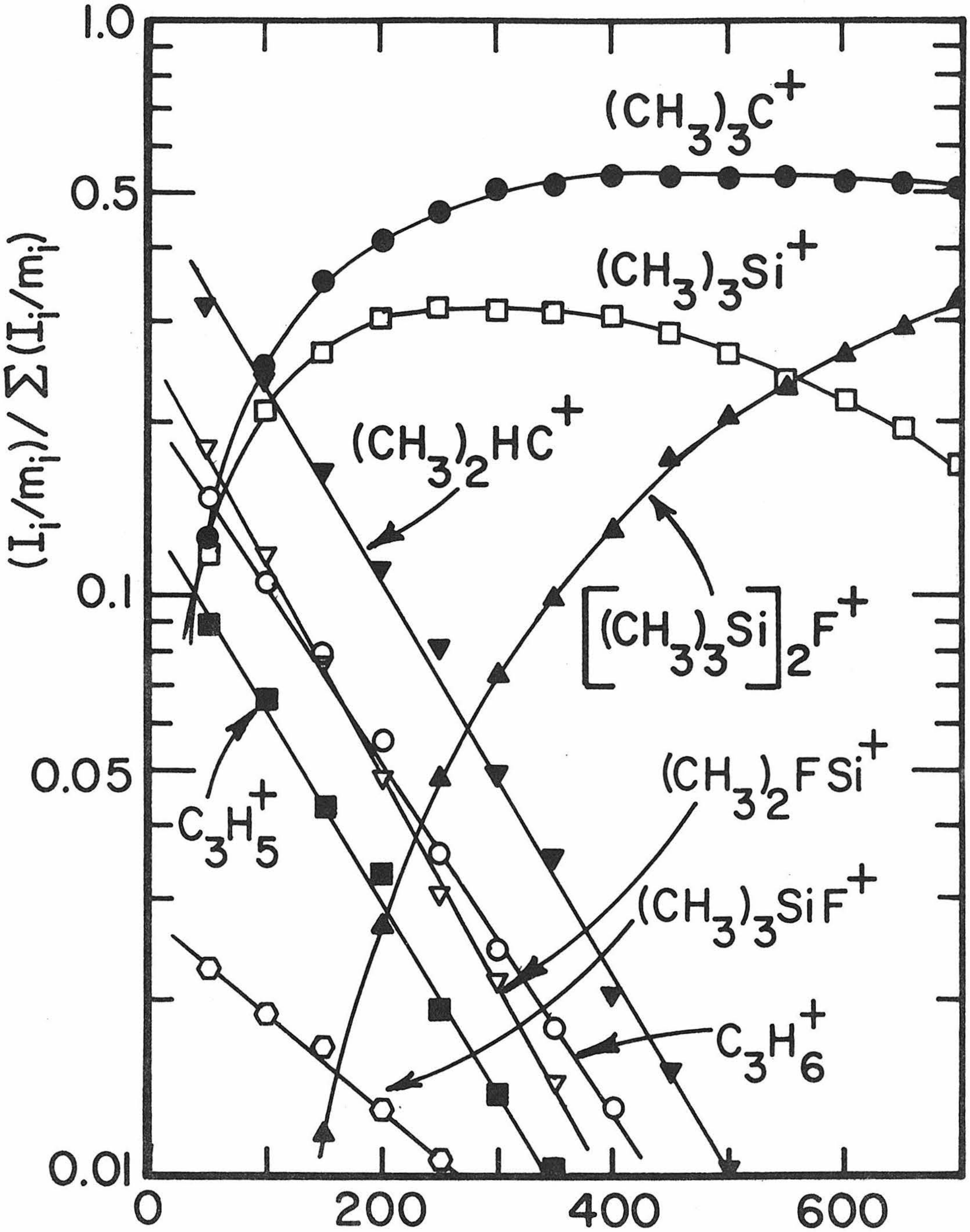

1.0
0.5
0.1
0.05
0.01
0
200
400
600
Time (msec)
$(I_i/m_i)/\sum(I_i/m_i)$
$(CH_3)_3C^+$
$(CH_3)_3Si^+$
$(CH_3)_2HC^+$
$[(CH_3)_3Si]_2F^+$
$(CH_3)_2FSi^+$
$(CH_3)_3SiF^+$
$C_3H_5^+$
$C_3H_6^+$

Figure 7. CH_3^+ and CH_4^+ react rapidly with neutral CH_4 to yield ions $C_2H_5^+$ and CH_5^+, respectively, both of which are stable to further reaction in CH_4 alone. These same reactions are detected in the CH_4/CH_3SiF_3 mixture, however, CH_5^+ abundance decays away at long times in Figure 7 while $C_2H_5^+$ is unreactive. On the time scale of this experiment, ion molecule reactions involving silicon cations[24] contribute only ~3% of the observed 15% increase in $CH_3SiF_2^+$ abundance. (This species is formed by fluoride transfer from CH_3SiF_3 to SiF_3^+). Double resonance experiments reveal no contributions from CH_3^+, CH_4^+, CH_5^+, or $C_2H_5^+$ to SiF_3^+, nor from CH_3^+ or $C_2H_5^+$ to $CH_3SiF_2^+$. In addition, these experiments identify CH_4^+ and CH_5^+ as precursors to $CH_3SiF_3H^+$, and CH_4^+ and $CH_3SiF_3H^+$ as precursors to $CH_3SiF_2^+$. Production of protonated CH_3SiF_3 is not observed in CH_3SiF_3 alone.[24] Processes 11-13 are consistent with the above results and the observed

$$CH_4^+ + CH_3SiF_3 \longrightarrow CH_3SiF_3H^+ + CH_3 \qquad (11)$$

$$CH_4^+ + CH_3SiF_3 \longrightarrow CH_3SiF_2^+ + HF + CH_3 \qquad (12)$$

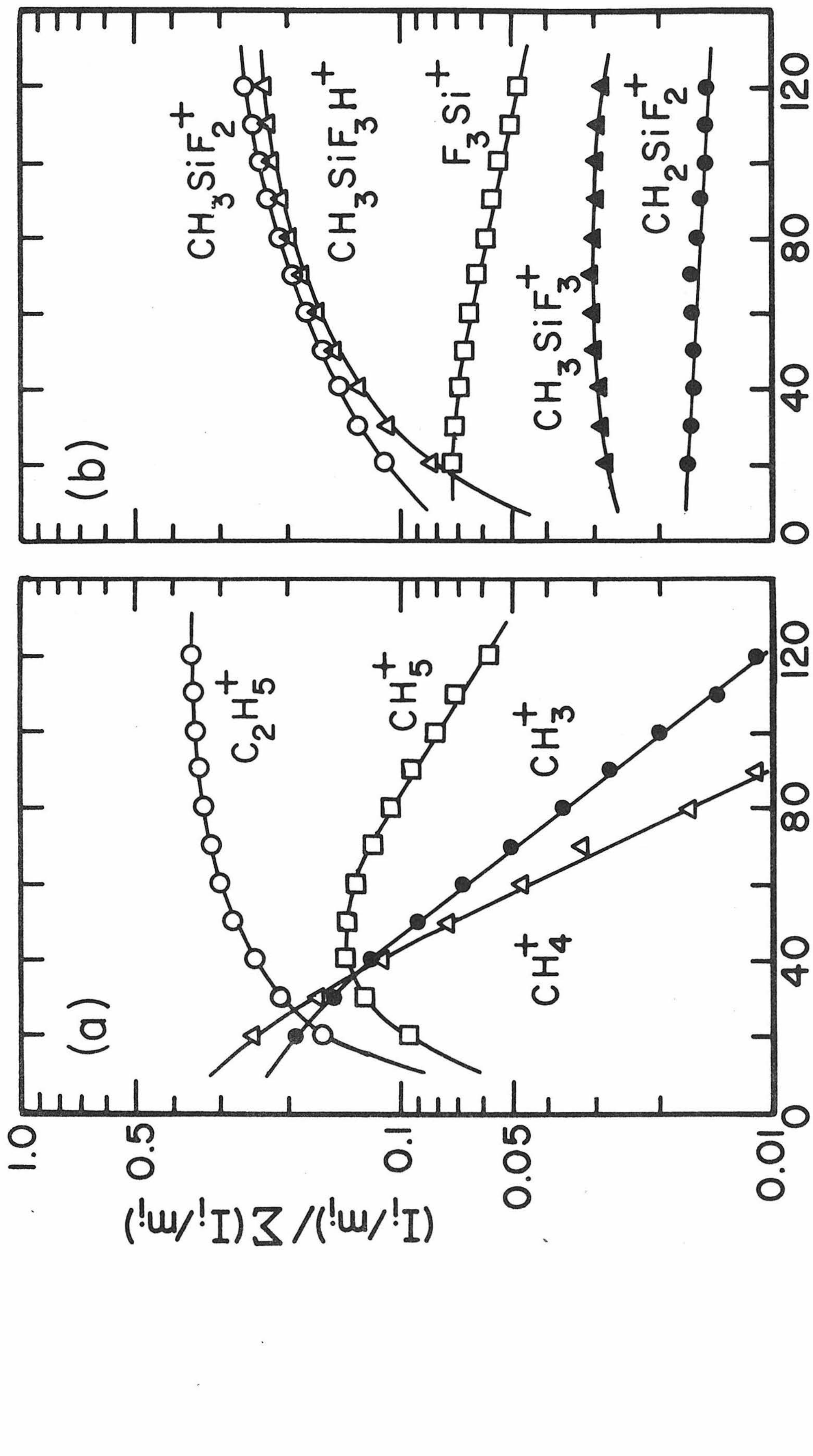
$$CH_5^+ + CH_3SiF_3 \longrightarrow CH_3SiF_3H^+ + CH_4 \qquad (13)$$

variations in ion concentration in Figure 7. No evidence is obtained for the occurrence of reactions of silico-cations with neutral CH_4 under the present conditions.

$CH_4/(CH_3)_3SiF$. Reactions 8 and 9 described above effectively bracket the fluoride affinity of $(CH_3)_3Si^+$ between $CH_3CF_2^+$ and $(CH_3)_2CF^+$, close to the previously reported value for ethylcation.[15] In an

Figure 7

Temporal variation of ion abundances following a 10 msec 20 eV electron beam pulse in a 2.5:1 mixture of CH_3SiF_3 and CH_4 at 2.3×10^{-6} torr total pressure.


(a)
(b)
$C_2H_5^+$
CH_5^+
CH_3^+
CH_4^+
$CH_3SiF_2^+$
$CH_3SiF_3H^+$
F_3Si^+
$CH_3SiF_3^+$
$CH_2SiF_2^+$
Time (msec)
Time (msec)
0
40
80
120
1.0
0.5
0.1
0.05
0.01
$(I_i/m_i)/\Sigma(I_i/m_i)$

attempt to observe fluoride transfer to $C_2H_5^+$ from $(CH_3)_3SiF$, the ion chemistry in a 1.2:1 mixture of $(CH_3)_3SiF$ and CH_4 at 1.1×10^{-6} torr total pressure was examined. Figure 8 illustrates the temporal variation of ion concentrations observed in this mixture. Double resonance indicates that CH_5^+ and $C_2H_5^+$ both react with $(CH_3)_3SiF$ to yield $(CH_3)_3SiFH^+$, $(CH_3)_2SiF^+$ and $(CH_3)_3Si^+$, and that to a very limited extent $(CH_3)_3SiFH^+$ contributes to the production of $(CH_3)_3Si^+$ and $(CH_3)_2SiF^+$ probably by a unimolecular dissociation process. No reactions of silicocations with neutral CH_4 are observed in this system. Processes 14-16 involving CH_5^+ and 17-19 involving $C_2H_5^+$ account for the observed changes in ion abundance with time.

$$CH_5^+ + (CH_3)_3SiF \longrightarrow (CH_3)_3SiFH^+ + CH_4 \tag{14}$$

$$\longrightarrow (CH_3)_2SiF^+ + 2CH_4 \tag{15}$$

$$\longrightarrow (CH_3)_3Si^+ + HF + CH_4 \tag{16}$$

$$C_2H_5^+ + (CH_3)_3SiF \longrightarrow (CH_3)_3SiFH^+ + C_2H_4 \tag{17}$$

$$\longrightarrow (CH_3)_2SiF^+ + C_2H_4 + CH_4 \tag{18}$$

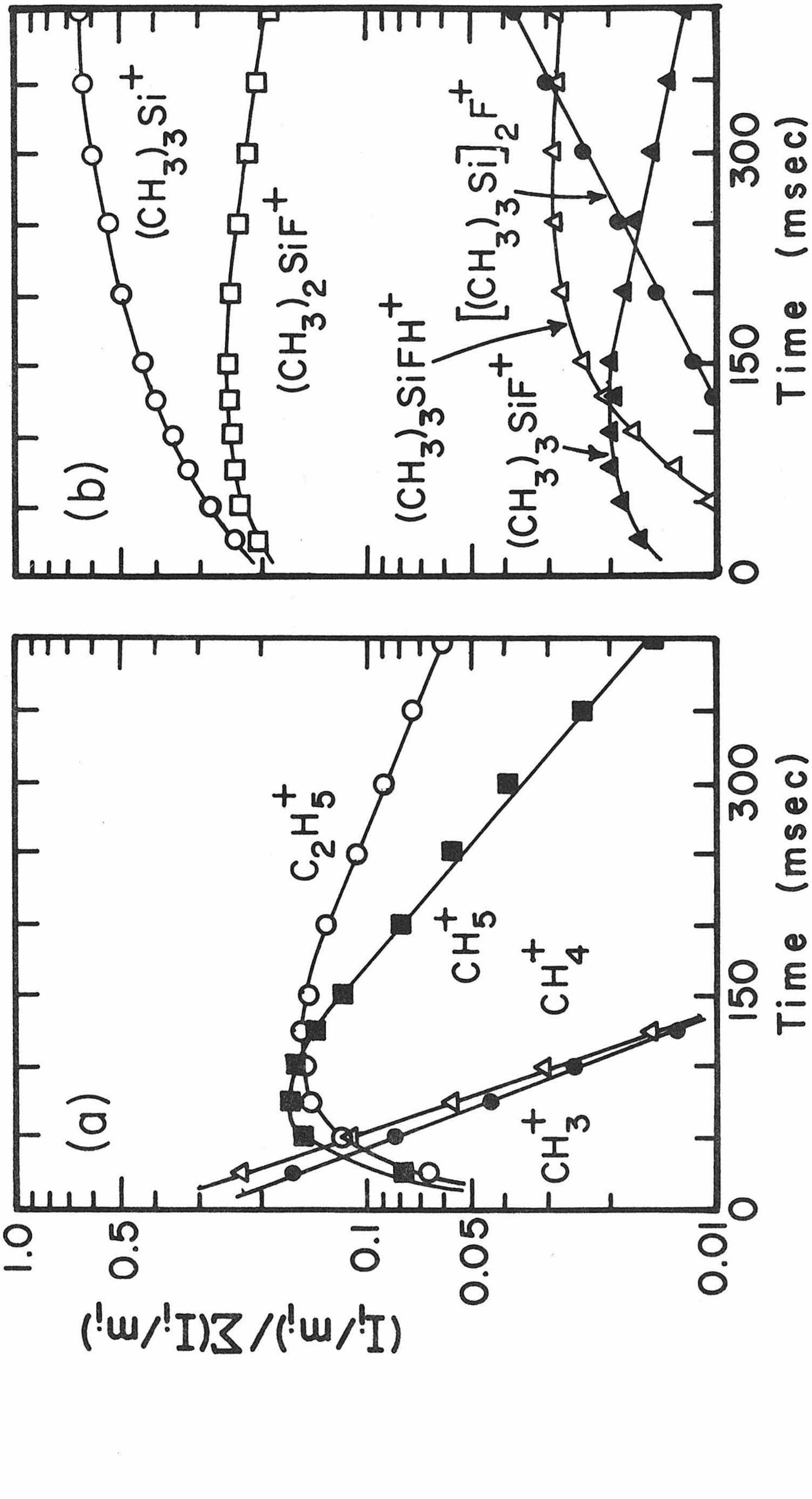
$$\longrightarrow (CH_3)_3Si^+ + C_2H_5F \tag{19}$$

Discussion

Table I summarizes various observed exothermic ion-molecule reactions and measured rate constants obtained in the present work. Under the experimental conditions employed in trapped-ion ICR studies, reactant ion energies are very near thermal. Thus, the observed reactions imply thermochemical limits for properties (such as relative

Figure 8

Temporal variation of ion abundances following a 10 msec 20 eV electron beam pulse in a 1.2:1 mixture of $(CH_3)_3SiF$ and CH_4 at 1.1×10^{-6} torr total pressure.


(a)
(b)
$(I_i/m_i)/\Sigma(I_i/m_i)$
1.0
0.5
0.1
0.05
0.01
0
150
300
Time (msec)
$C_2H_5^+$
CH_5^+
CH_4^+
CH_3^+
$(CH_3)_3Si^+$
$(CH_3)_2SiF^+$
$(CH_3)_3SiFH^+$
$[(CH_3)_3Si]_2F^+$
$(CH_3)_3SiF^+$

fluoride affinities $D[R^+-F^-]$) of ions involved in the cationic chemistry of the various mixtures examined (Table I).

The fluoride transfer processes generalized in (20) (where

$$(CH_3)_nF_{3-n}Si^+ + (CH_3)_mF_{3-m}CF \rightleftharpoons (CH_3)_mF_{3-m}C^+ + (CH_3)_nF_{3-n}SiF \qquad (20)$$

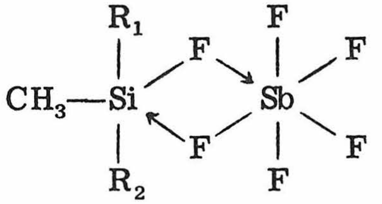
$n = 0\text{-}3$) are found to proceed to the right whenever $n \leqslant m+1$. Along with previously reported information on carbonium ions[9-16, 28, 30] these results yield the qualitative ordering of gas phase carbonium and siliconium ion stabilities using F^- as reference base $F_3Si^+ < CH_3SiF_2^+ < CH_3^+ < CF_3^+ < (CH_3)_2SiF^+ < CH_3CF_2^+ < CH_3CH_2^+ < (CH_3)_3Si^+ < (CH_3)_2CF^+ < (CH_3)_3C^+$. A quantitative comparison is obtained from recent photoionization measurements[26] of the energetics of siliconium ion formation in the fluoromethylsilanes. Collected in Table II are the best available values of heats of formation, hydride affinities $D[R^+-H^-]$ and fluoride affinities $D[R^+-F^-]$ describing analogously substituted carbonium and siliconium ions in the gas phase.

Thermochemical data for various carbon species are known with reasonable accuracy.[9-16, 28, 30] Data describing the fluorine containing silicon species come from the present work and a recent photoionization study of the fluoromethylsilanes.[26] The fluoride affinity of SiH_3^+ and hydride affinity of SiF_3^+, SiH_3^+, $CH_3SiH_2^+$, $(CH_3)_2SiH^+$ and $(CH_3)_3Si^+$ are calculated from the energetics of heterolytic dissociation reactions (processes which have not been experimentally examined) using available estimates for ion and neutral heats of formation[22b, c, 31]

(Table II). Included in Table II are homolytic Si-H and Si-F bond dissociation energies for the various neutral silanes, calculated using available estimates of silyl radical heats of formation.[22b, c, 26, 31]

The anion affinity data are displayed schematically in Figure 9 and provide for the first time a direct comparison of intrinsic stabilities of ions R_3M^+ (where M = C, Si; R = H, CH_3, F) free from the influence of solvation. These data yield insight into factors responsible for the complex and competing effects of α methyl and fluorine substituents on the stabilities of carbonium and siliconium ions.

Consideration of the fluoride affinity data in Table II and Figure 9 reveals that a given siliconium ion is 40 ± 9 kcal/mole less stable toward F^- as a reference base than the analogously substituted carbonium ion. This result immediately illuminates the findings of Olah and Mo from low temperature NMR studies,[20b] that no siliconium ions are formed in low nucleophilicity magic-acid (SbF_5–SO_2ClF) solutions of $(CH_3)_3SiF$, $(CH_3)_2SiF_2$, or CH_3SiF_3, under conditions where analogous carbonium ions are long-lived. Instead, rapidly exchanging donor-acceptor complexes of fluoromethylsilanes with SbF_5, involving pentacoordinate silicon (I-III), are observed. In light of the apparent



I: $R_1 = R_2 = CH_3$
II: $R_1 = F$, $R_2 = CH_3$
III: $R_1 = R_2 = F$

instability of CF_3^+ in solution and difficulties encountered in generation of carbonium ions less stable than $CH_3CF_2^+$[7] in magic-acid media,

Table II. Comparison of the Best Available Estimates of Thermochemical Properties of Carbon and Silicon Species

R	$\Delta H_f[R]^a$	$\Delta H_f[R^+]^a$	$\Delta H_f[RH]^a$	$\Delta H_f[RF]^a$	$IP[R]^b$	$D[R-H]^{c,q}$	$D[R-F]^{c,q}$	$D[R^+-H^-]$	$D[R^+-F^-]$
CH_3	34.0^d	260.9^g	-17.9^k	-55.9^d	9.84^d	104.0	108.6	312.2^j	255.5^j
CH_3CH_2	25.7^d	218.9^f	-20.2^k	-62.9^n	8.38^d	98.0	106.5	272.5^f	220.5^f
$(CH_3)_2CH$	17.6^d	191.7^f	-24.8^k	-69.0^m	7.55^d	94.5	105.3	249.9^f	199.4^f
$(CH_3)_3C$	9.3^e	169.0^h	-32.2^l	-74.1^o	6.93^d	93.6	102.1	234.4^r	181.8^r
$(CH_3)_2CF$	-26.6^f	138.0^f	-69.0^m	-129.8^f	7.14^f	94.5	121.9	240.4^f	206.5^f
CH_3CF_2	-73.8^f	108.8^f	-119.7^n	-178.2^n	7.92^f	98.0	123.1	261.9^f	225.7^f
CF_3	-112.2^d	99.3^i	-166.3^d	-223.0^p	9.17^i	106.2	129.5	292.0^s	253.0^s
SiH_3	45.6^t	238.9^t	8.2^t	-105.0^w	8.39^v	89.5	169.3	263.9^r	282.6^r
CH_3SiH_2	33.0^t	214.5^t	-4.3^t	$--^x$	7.87^v	89.4	$--^x$	252.0^r	$--^x$
$(CH_3)_2SiH$	21.0^t	187.1^t	-16.8^t	$--^x$	7.21^v	89.9	$--^x$	237.1^r	$--^x$
$(CH_3)_3Si$	2.4^u	154.8^u	-29.6^t	-126.0^u	6.61^u	84.1	147.1	217.6^r	219.5^u
$(CH_3)_2SiF$	-80.1^u	86.6^u	$--^x$	-212.0^u	7.23^u	$--^x$	150.6	$--^{x,y}$	237.2^u
CH_3SiF_2	-166.0^u	23.7^u	$--^x$	-296.0^u	8.23^u	$--^x$	148.7	$--^{x,y}$	258.4^u
SiF_3	-250.0^u	-22.7^u	-283.0^w	-386.0^u	$9.86^{u,z}$	85.1	154.7	293.5^r	302.0^u

[a] Heats of formation in kcal/mole at 298°K.

[b] Ionization potentials in eV.

[c] Estimated uncertainties in homolytic bond dissociation energies ± 3 kcal/mole for carbon species and ± 10 kcal/mole for silicon species.

[d] Taken from Ref. 16.

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[f] Taken from Ref. 15.

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[h] Calculated from $\Delta H_f[R^+] = \Delta H_f[R] + IP[R]$ using data in this table.

[i] T. A. Walter, C. Lifschitz, W. A. Chupka, and J. Berkowitz, J. Chem. Phys., 51, 3531 (1969).

[j] Taken from Ref. 10.

Table II. (Continued)

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[q] Calculated from $D[R{-}X] = \Delta H_f[R] + \Delta H_f[X] - \Delta H_f[RX]$ (where X = H, F) using data in this table and $\Delta H_f[H] = 52.1$ kcal/mole and $\Delta H_f[F] = 18.7$ kcal/mole taken from references 33 and 35, respectively.

[r] Calculated from $D[R^+{-}X^-] = \Delta H_f[R^+] + \Delta H_f[X^-] - \Delta H_f[RX]$ (where X = H, F) using data in this table and $\Delta H_f[H] = 33.2$ kcal/mole and $\Delta H_f[F^-] = -61.3 \pm 0.3$ kcal/mole, from references 33 and 34, respectively.

[s] Taken from Ref. 13c.

[t] Taken from Ref. 22c and 31.

[u] Taken from Ref. 26.

[v] Calculated from $IP[R] = \Delta H_f[R] + IP[R]$ using data in this table.

[w] Taken from Ref. 33.

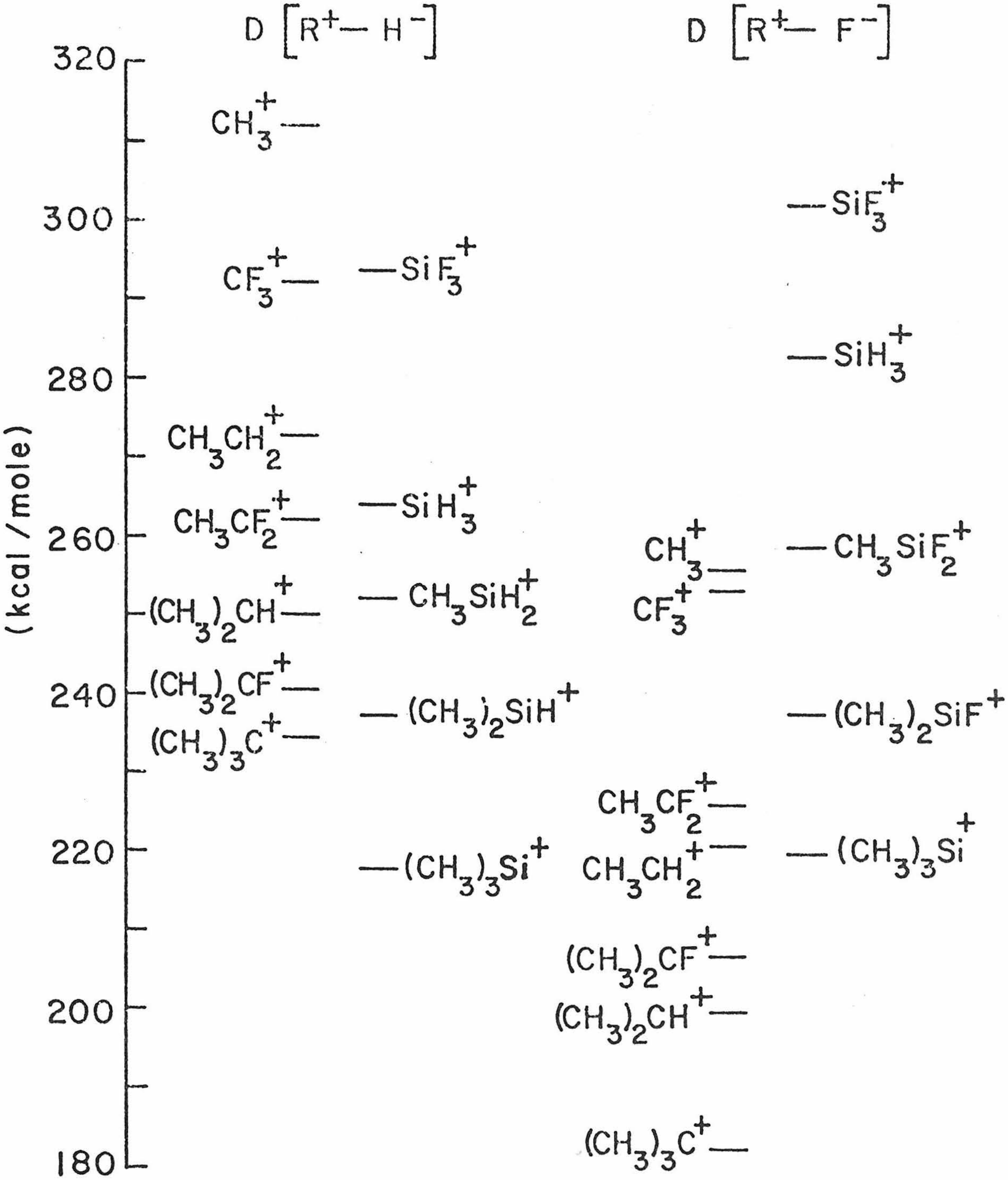
[x] No data available.

[y] From trends observed it is assumed that $D[(CH_3)F_2Si^+{-}H^-] > D[(CH_3)H_2Si^+{-}H^-]$ and that $D[(CH_3)_2FSi^+{-}H^-] > D[(CH_3)_2HSi^+{-}H^-]$, see text for discussion.

[z] This value appears to be somewhat high, see Ref. 26.

Figure 9

Schematic representation of comparisons of hydride affinities $D[R^+-H^-]$ and fluoride affinities $D[R^+-F^-]$ of carbonium ions and siliconium ions.


D [R+— H−]
D [R+— F−]
(kcal / mole)
320
300
280
260
240
220
200
180
CH_3^+
CF_3^+
$CH_3CH_2^+$
$CH_3CF_2^+$
$(CH_3)_2CH^+$
$(CH_3)_2CF^+$
$(CH_3)_3C^+$
SiF_3^+
SiH_3^+
$CH_3SiH_2^+$
$(CH_3)_2SiH^+$
$(CH_3)_3Si^+$
CH_3^+
CF_3^+
$CH_3CF_2^+$
$CH_3CH_2^+$
$(CH_3)_2CF^+$
$(CH_3)_2CH^+$
$(CH_3)_3C^+$
SiF_3^+
SiH_3^+
$CH_3SiF_2^+$
$(CH_3)_2SiF^+$
$(CH_3)_3Si^+$

inability to generate siliconium ions under the similar conditions likely reflects thermochemical limitations imposed by a finite fluoride acceptor strength of SbF_5. Furthermore, recent ICR studies in our laboratory of Lewis acid-base complexes of F^- with the neutral fluoromethylsilanes indicate adduct bond strengths $D[(CH_3)_nF_{4-n}Si-F^-]$ of 50-70 kcal/mole (n = 0-2).[32] Such large fluoride affinities of the silane neutrals thus contribute significantly to stabilization of the silane-SbF_5 complexes reported by Olah and Mo[20b] and provide a reaction path which is energetically more favorable than R_3Si^+ formation.

The present results also afford explanations for the findings of Sommer and co-workers[17d] and Brook and Pannell[20a] that ionization of chloroalkylsilanes and of α-silylcarbinols by reaction with Lewis acids yield α-silylcarbonium ions $R_3Si\overset{+}{C}R_2$ exclusively (reactions 21 and 22, respectively, where R = alkyl, aryl). In neither case was any evidence

$$R_3SiCHClR \xrightarrow{AlCl_3} R_3Si\overset{+}{C}HR \tag{21}$$

$$R_3SiC(OH)R_2 \xrightarrow{BF_3} R_3Si\overset{+}{C}R_2 \tag{22}$$

obtained for the existence of the isomeric siliconium ions in these systems, although hydrogen atom migration from adjacent alkyl groups to give β-silylcarbonium ions $R_3SiCHR\overset{+}{C}R_2$ was observed in each case.[17d, 20a] It seems unlikely that differences in ion solvation alone can account for observed preferential stability of carbonium ions over siliconium ions, even though cation charge density is less for the larger siliconium ions. The instability of siliconium ions is further underscored by the observations that secondary carbonium ions $R_3Si\overset{+}{C}HR$ appear to be considerably more stable than tertiary siliconium ions $(C_6H_5)_2\overset{+}{Si}R$.[20a] Even without taking into account possible differences in solvation of carbonium and siliconium ions, the solution results described above show no inconsistency with the present cation fluoride affinity comparisons displayed in Figure 9 and Table II.

Effects of Substituents and Reference Base on the Apparent Stabilities of Carbonium Ions and Siliconium Ions. From the comparison of fluoride affinity data in Figure 9 it is apparent that methyl substituents stabilize both siliconium and carbonium ions relative to fluorine substituents. Replacement of all three fluorines in F_3M^+ (M = C, Si) by methyl groups effect decreases of 70-80 kcal/mole in values of $D[R_3M^+-F^-]$. The striking feature of the carbon-silicon comparison comes from the fact that there is a consistent shift of ~30-50 kcal/mole between analogously substituted carbon and silicon species with the siliconium ions binding F^- more strongly.

In contrast to the greater stabilities of carbonium ions compared with their siliconium ion analogs for F^- as the reference base, the hydride affinity data in Table II and Figure 9 show a dramatic reversal. With H^- as reference base, carbonium ions are consistently less stable than the substitutionally analogous siliconium ions.

The different ordering of carbonium and siliconium ion stabilities toward fluoride and hydride reference bases can be understood with the aid of the thermochemical cycle of Scheme I described by eq 23. The silyl and alkyl radical ionization potentials are quite comparable for substitutional analogs, therefore the sharp differences in ordering for

$$\begin{tikzcd}
RX \arrow[r, "{D[R^+-X^-]}"] \arrow[d, "{D[R-X]}"'] & R^+ + X^- \\
R + X \arrow[r, "{IP[R]}"] & R^+ + X \arrow[u, "{-EA[X]}"']
\end{tikzcd}$$

Scheme I

$$D[R^+-X^-] = D[R-X] + IP[R] - EA[X] \qquad (23)$$

a particular reference base X^-($X^- = H^-$ or F^-) reflect primarily differences in homolytic C–X and Si–X bond strengths (Table II). That hydride affinities of the various carbonium ions are uniformly larger than those of siliconium ions is reflective of the consistently larger homolytic C–H bond strengths as compared with Si–H bonds. Similarly, the fact that $D[R_3Si^+-F^-]$ values are ~30-50 kcal/mole greater than $D[R_3C^+-F^-]$ values for substitutional analogs is as expected from the differences in Si–F and C–F homolytic bond dissociation energies throughout the two series (Table II). The reversal in carbonium and siliconium ion stability ordering in comparing H^- to F^- is then simply a reflection of the reversal in homolytic M–H and M–F bond dissociation energies in the neutral methanes and silanes.

Various studies indicate that variations in carbonium ion stability effected by methyl and fluorine substitution are the result of σ polarization and π backbonding acting in concert and in competition.[2, 5-13] Methyl groups tend to stabilize the positive charge center at carbon by both σ polarization and π delocalization of electron density (from CH_3 orbitals of π-type symmetry into the formally vacant C^+2p orbital).

Fluorine substituents destabilize carbonium ions by σ polarization due to the greater fluorine electronegativity, but π interaction of formally non-bonded F2p lone pairs with the C^+2p orbital stabilizes the charge center. This later effect accounts for the lower fluoride affinity of CF_3^+ as compared with CH_3^+.[9, 10]

Consider the hydride affinity comparisons in Table II and Figure 9. In the series CH_3^+, $CH_3CH_2^+$, $(CH_3)_2CH^+$, and $(CH_3)_3C^+$, replacement of the first H in CH_3^+ by a methyl group decreases the hydride affinity by ~40 kcal/mole. The introduction of a second CH_3 on carbon in place of H decreases $D[(CH_3)_2HC^+{-}H^-]$ an additional ~23 kcal/mole below $D[CH_3CH_2^+{-}H^-]$. The replacement of the third H by CH_3 reduces $D[(CH_3)_3C^+{-}H^-]$ another ~15 kcal/mole. No such regular attenuation of the methyl stabilizing effect is observed in the siliconium hydride affinities (Figure 9). Furthermore, the incremental decreases in hydride affinities effected by successive methyl substitution appear to be consistently larger for carbonium ions than siliconium ions. For example, $D[CH_3SiH_2^+{-}H^-]$ is ~14 kcal/mole lower than $D[SiH_3^+{-}H^-]$ as compared with the 40 kcal/mole decrease noted above in going from CH_3^+ to $CH_3CH_2^+$.

These differences in methyl substituent effects between carbonium and siliconium ions indicate perhaps that π stabilization of the charge center by methyl groups is relatively more effective for carbon charge centers than for silicon, presumably due to poorer spatial overlap of occupied substituent orbitals with Si^+3p as compared with C^+2p orbital vacancies in the ions. This is consistent with the attenuation effects observed in the series of methyl substituted carbonium ions as compared with the analogous siliconium ions. The methyl effect on carbonium ion stabilities appears to saturate (i.e., π stabilization becomes less and less effective per additional CH_3 substituent) due to what might be described as essentially the filling of the C^+2p vacancy.

If such a difference in π bonding effect of substituents at carbon and silicon cation centers were real, then it should also be apparent for fluorine substituents. An absence of π back-bonding of F lone pairs for siliconium ions would result in a stronger destabilization of fluorosiliconium ions relative to carbon species since the σ polarization of electron density away from the charge center would remain operative. Just such an effect is apparent from comparisons of both hydride and fluoride affinity data in Figure 9 and Table II. In each case CF_3^+ is more stable than CH_3^+ while both the hydride and fluoride affinities of SiF_3^+ greatly exceed values for SiH_3^+.

While data on the hydride affinities of the fluoromethylsiliconium ions are not available, it appears reasonable from the present arguments to expect that $D[(CH_3)F_2Si^+{-}H^-]$ will be somewhat larger than $D[(CH_3)H_2Si^+{-}H^-]$ and similarly that the hydride affinity of $(CH_3)_2FSi^+$ will slightly exceed that of $(CH_3)_2HSi^+$.

Considering siliconium ions as Lewis acids, it should be emphasized that no absolute scale of siliconium ion stabilities exists. As with any acid-base interaction, the scale is dependent on the reference base chosen. The observed reversals of the ordering of hydride and fluoride affinities for selected pairs of siliconium and carbonium ions

(Figure 9 and Table II) have interesting consequences. For example, for a mixture of $(CH_3)_3SiH$ and $(CH_3)_3CF$ the present data predict the occurrence of reactions 24 and 25. The combination these two

$$(CH_3)_3C^+ + (CH_3)_3SiH \rightarrow (CH_3)_3CH + (CH_3)_3Si^+ \qquad (24)$$

$$(CH_3)_3Si^+ + (CH_3)_3CF \rightarrow (CH_3)_3C^+ + (CH_3)_3SiF \qquad (25)$$

processes establish a catalytic cycle for the conversion of t-butylfluoride and trimethylsilane into isobutane and fluorotrimethylsilane via ionic intermediates (reaction 26), the overall process being

$$(CH_3)_3CF + (CH_3)_3SiH \rightarrow (CH_3)_3CH + (CH_3)_3SiF \qquad (26)$$

exothermic by 54.5 kcal/mole! This is but one of many analogous ionic chain reactions suggested by the anion affinity data in Table II and Figure 9. These interesting processes are being further investigated.[36] Similar chain reactions have previously been experimentally observed in the chemistry of certain pairs of carbonium ions.[9-11]

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CHAPTER IV

FLUORINE AND ALKYL SUBSTITUENT EFFECTS ON THE GAS PHASE LEWIS ACIDITIES OF BORANES BY ION CYCLOTRON RESONANCE SPECTROSCOPY[1a]

M. K. Murphy and J. L. Beauchamp[1b]

Abstract

Formation of Lewis acid-base adducts R_3BF^- and R_2FBF^- in reactions of SF_5^- and SF_6^- with neutral boranes R_3B ($R = CH_3$, C_2H_5, $i\text{-}C_3H_7$ and F) are examined using trapped-ion cyclotron resonance techniques. Fluoride transfer reactions observed in binary mixtures of the various boranes (in the presence of traces of SF_6 acting as the source of F^-) establish the Lewis acidity order $BF_3 > (i\text{-}C_3H_7)_2FB > (i\text{-}C_3H_7)_3B > (C_2H_5)_2FB > (C_2H_5)_3B > (CH_3)_2FB > (CH_3)_3B > SF_4$ in the gas phase with F^- as reference base. Quantitative estimates of adduct bond dissociation energies $D[R_3B\text{–}F^-]$ and heats of formation of adducts R_3BF^- are derived. Variations in Lewis acidity resulting from alkyl and fluoro substitution on boron are discussed in terms of properties characteristic of substituents and the anion reference base.

Introduction

The general concepts of electron-pair donor-acceptor chemistry, formalized in the Lewis definition of acids and bases,[2] have contributed much to understanding relationships between molecular structure and chemical reactivity important in organic, inorganic, and organometallic chemistry. Investigations of acid A and base B transfer processes (reactions 1 and 2, respectively) can yield direct measurements of the bond energies D[A–B] and provide a methodology suitable

$$AB_1 + B_2 \rightarrow B_1 + AB_2 \qquad \Delta H = D[B_1{-}A] - D[B_2{-}A] \tag{1}$$

$$A_1B + A_2 \rightarrow A_1 + A_2B \qquad \Delta H = D[A_1{-}B] - D[A_2{-}B] \tag{2}$$

for the study of factors determining the strengths of acid-base interactions.

Ion cyclotron resonance mass spectrometry (ICR) has proven to be a versatile tool for the study of acid-base reactions[3-5] in the gas phase, in the absence of solvation effects, specifically reactions 1 and 2 where species A and/or B are charged. Recent investigations[6-8] of reactions 1, involving cationic Lewis acids (e.g., Li^+,[6] NO^+,[7] cyclo-$C_5H_5Ni^+$[8]) and various neutral organic and inorganic bases, have yielded insight into the factors governing intrinsic n- and π-donor basicity. Transfer reactions such as (2) involving closed shell anionic bases (e.g., H^-, F^-, Br^-) and cations R_3M^+ (where M = C, Si; R = H, alkyl, F) have been exploited for the determination of carbonium and siliconium ion stabilities.[9-11] Recent studies of Lewis acidities of neutral acceptors toward anionic bases (reactions 2) include determinations of relative binding energies of F^- and Cl^- to the hydrogen halides (HX, where X = F, Cl, Br),[12] to a variety of compounds possessing acidic hydrogen (e.g., water, several alcohols and carboxylic acids)[13] and to a variety of inorganic Lewis acids, including BF_3 and BCl_3.[14]

Recent studies from this laboratory[14c] have demonstrated the ability to generate hydride and fluoride adducts [e.g., $(CH_3)_3BH^-$ and $(CH_3)_3BF^-$] in the gas phase under conditions which make possible the examination of anion transfer processes such as (2), thus providing a suitable methodology for the investigation of substituent effects on the Lewis acidity of neutral alkyl-boranes. We wish to present the results of trapped-ion ICR studies of fluoride ion transfer reactions occurring in the trialkylboranes R_3B($R = CH_3, C_2H_5$, i-C_3H_7) and BF_3, both alone and in binary mixtures, in the presence of sulfur hexafluoride as the source of fluoride ion. Quantitative information is obtained describing Lewis acidities of the two homologous series R_3B and R_2FB, expressed as fluoride affinities (adduct bond dissociation energies, defined by eq 3), of the neutral acids. In addition, heats

$$AF^- \rightarrow A + F^- \qquad \Delta H = D[A{-}F^-] \tag{3}$$

of formation of the various boron-containing anions and neutrals are derived.

Experimental

The instrumentation and experimental techniques associated with ICR spectrometry are described in detail elsewhere.[15] All studies reported here utilize a high-field ICR spectrometer, employing a 15" magnet system, constructed in the Caltech instrument shops. Gas mixtures are prepared directly in the ICR cell by admission of the appropriate sample components through separate variable leak valves in a parallel inlet manifold. Absolute gas pressures are determined using a Schulz-Phelps ionization gauge adjacent to the ICR cell, calibrated separately for each sample component against an MKS Baratron Model 90H1-E capacitance manometer. A linear calibration of ionization gauge current versus Baratron pressure (absolute) affords pressure determinations over a range of 10^{-7} to 10^{-4} torr. Overall accuracy in pressure measurements for these studies is estimated to be ± 20%, and represents the major source of error in reported reaction rate constants. Bimolecular rate constants are determined with knowledge of neutral gas pressures from the limiting slopes of semi-log plots of trapped-ion abundance versus time, and by considering product distributions where applicable. All experiments are performed at ambient temperatures (~ 22 °C) as determined using a thermistor located adjacent to the ICR cell. The electron beam energy utilized is 70 eV and emission currents are typically 10^{-8} - 10^{-7} A.

$B(CH_3)_3$ and $B(C_2H_5)_3$ were obtained from Alfa Inorganics, and SF_6 and BF_3 from Matheson. $B(i\text{-}C_3H_7)_3$ was provided through the gracious gift of Professor A. H. Cowley and CH_3SiF_3 through the courtesy of Professor J. G. Dillard. Noncondensable impurities are removed from all samples using multiple freeze-pump-thaw cycles at liquid nitrogen temperatures. Mass spectral analysis of all samples utilized showed no detectable impurities.

Data reported in figures and tables are normalized to monoisotopic abundances (^{12}C, 98.89%; ^{11}B, 80.22%; ^{28}Si, 92.21%; ^{32}S, 95.0%). Typically, ion concentrations comprising less than 1% of the total are not included in the reported data.

Results

Reagent Ion Generation. In all studies reported here, SF_6^- (95%) and SF_5^- (5%) are generated from SF_6 by rapid attachment of near-thermal energy electrons produced in the ICR trapping well by inelastic collisions during the 10 msec electron beam pulse.[12, 16-18] SF_6 is present only in trace concentration ($\sim 10^{-8}$ torr) and the neutral itself does not participate in ion-molecule reactions observed. SF_6^- and SF_5^- serve primarily as sources of fluoride ion and act as reagents for the generation of acid-base adducts (e.g., R_3BF^-) via bimolecular pathways. Under the conditions employed in these studies, boron-containing anions are observed in appreciable concentrations only in the presence of SF_6.

Reactions of anions derived from SF_6 with each of the trialkylboranes R_3B ($R = CH_3, C_2H_5, i\text{-}C_3H_7$) and with BF_3 are presented below. Fluoride transfer processes dominate the observed chemistry via the formation of R_3BF^- species. Reactions observed in binary mixtures of the various boranes are then examined in order to provide direct comparison of fluoride affinities for the two homologous series of Lewis acids, R_3B and R_2BF.

$SF_6/(CH_3)_3B$. Figure 1 illustrates the temporal variation of anion abundances observed following the electron beam pulse in 4.8×10^{-7} torr $(CH_3)_3B$ in the presence of trace amounts of SF_6. Double resonance experiments indicate that reactions 4-6 account for the

$$SF_6^- + (CH_3)_3B \left\{ \begin{array}{ll} \xrightarrow{72\%} SF_5^- + HF + (CH_3)_2BCH_2 & \qquad (4) \\ \\ \xrightarrow{28\%} (CH_3)_2BF_2^- + SF_4 + CH_3 & \qquad (5) \end{array} \right.$$

$$SF_5^- + (CH_3)_3B \longrightarrow (CH_3)_3BF^- + SF_4 \qquad (6)$$

observed changes in anion concentration with time, in agreement with recent results.[14c] Negative ion products of reactions 5 and 6 do not react further in this system. In particular, $(CH_3)_2BF_2^-$ does not transfer fluoride to neutral $(CH_3)_3B$.

$SF_6/(C_2H_5)_3B$. In 4.1×10^{-7} torr $(C_2H_5)_3B$ containing traces of SF_6, the electron beam pulse initiates the temporal variation of ion concentrations shown in Figure 2. Reactions 7-9, analogous with

$$SF_6^- + (C_2H_5)_3B \left\{ \begin{array}{ll} \xrightarrow{76\%} SF_5^- + HF + (C_2H_5)_2BC_2H_4 & \qquad (7) \\ \\ \xrightarrow{24\%} (C_2H_5)_2BF_2^- + SF_4 + C_2H_5 & \qquad (8) \end{array} \right.$$

$$SF_5^- + (C_2H_5)_3B \longrightarrow (C_2H_5)_3BF^- + SF_4 \qquad (9)$$

Figure 1

Temporal variation of trapped-anion abundances initiated by a 10 msec 70 eV electron beam pulse in 4.8×10^{-7} torr $(CH_3)_3B$ in the presence of traces of SF_6.

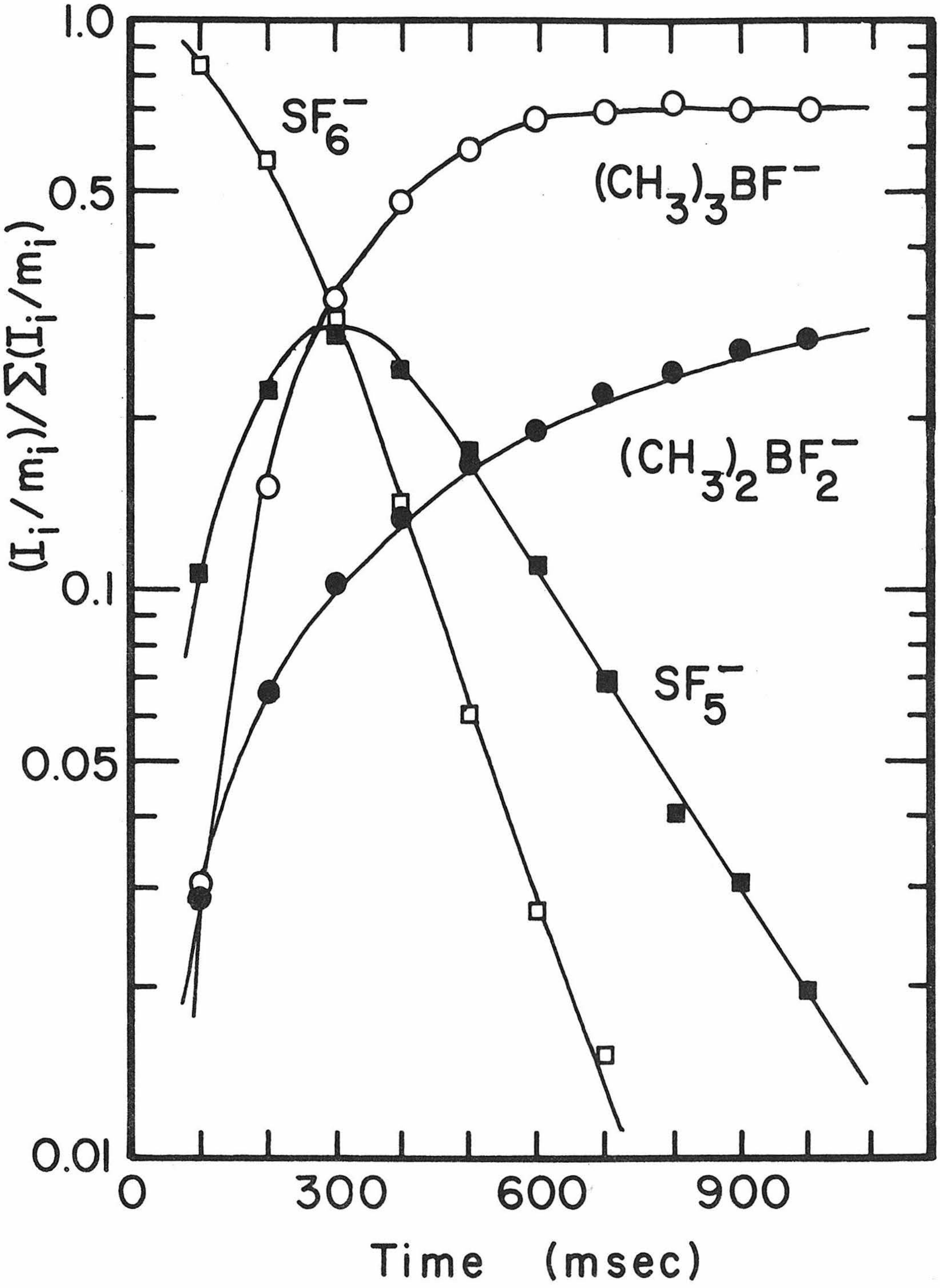
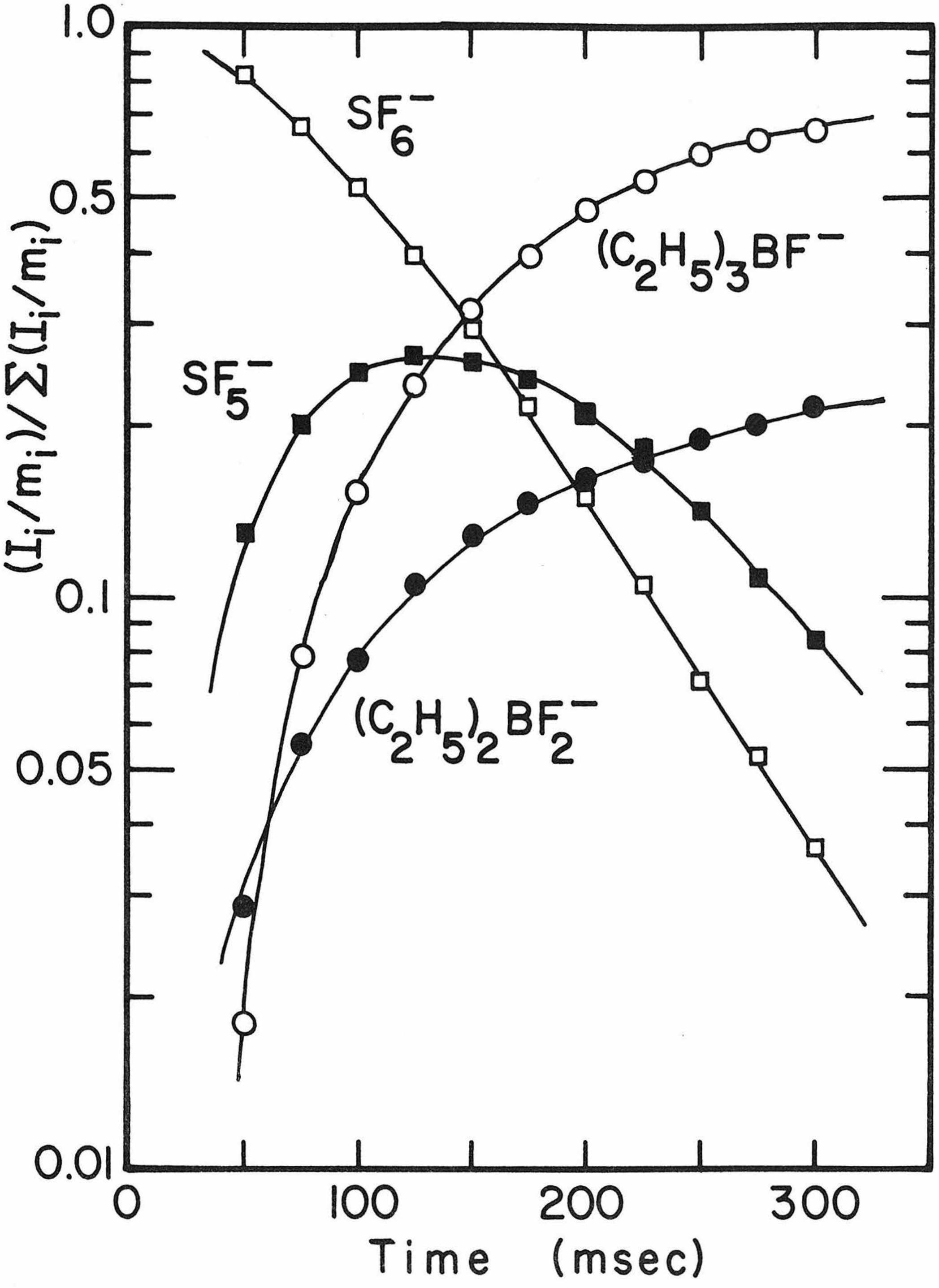

$(I_i/m_i)/\sum(I_i/m_i)$
1.0
0.5
0.1
0.05
0.01
0
300
600
900
Time (msec)
SF_6^-
$(CH_3)_3BF^-$
$(CH_3)_2BF_2^-$
SF_5^-

Figure 2

Temporal variation of trapped-anion abundances initiated by a 10 msec 70 eV electron beam pulse in 1.0×10^{-6} torr $(C_2H_5)_3B$ in the presence of traces of SF_6.


1.0
0.5
0.1
0.05
0.01
0
100
200
300
Time (msec)
$(I_i/m_i)/\sum(I_i/m_i)$
SF_6^-
SF_5^-
$(C_2H_5)_3BF^-$
$(C_2H_5)_2BF_2^-$

processes observed in trimethylborane, lead to the eventual predominance of $(C_2H_5)_3BF^-$ and $(C_2H_5)_2BF_2^-$ at long trapping times. The anion products of reactions 8 and 9 remain stable to further reaction with neutrals present. In particular, fluoride transfer from $(C_2H_5)_2BF_2^-$ to neutral triethylborane is not observed. Analogous with previously reported results for $SF_6/(CH_3)_3B$ mixtures,[14c] cyclotron ejection of SF_5^- results in complete disappearance of $(C_2H_5)_3BF^-$, indicating that $(C_2H_5)_3BF^-$ is produced solely by reaction 9 and not via a bimolecular process involving SF_6^-.

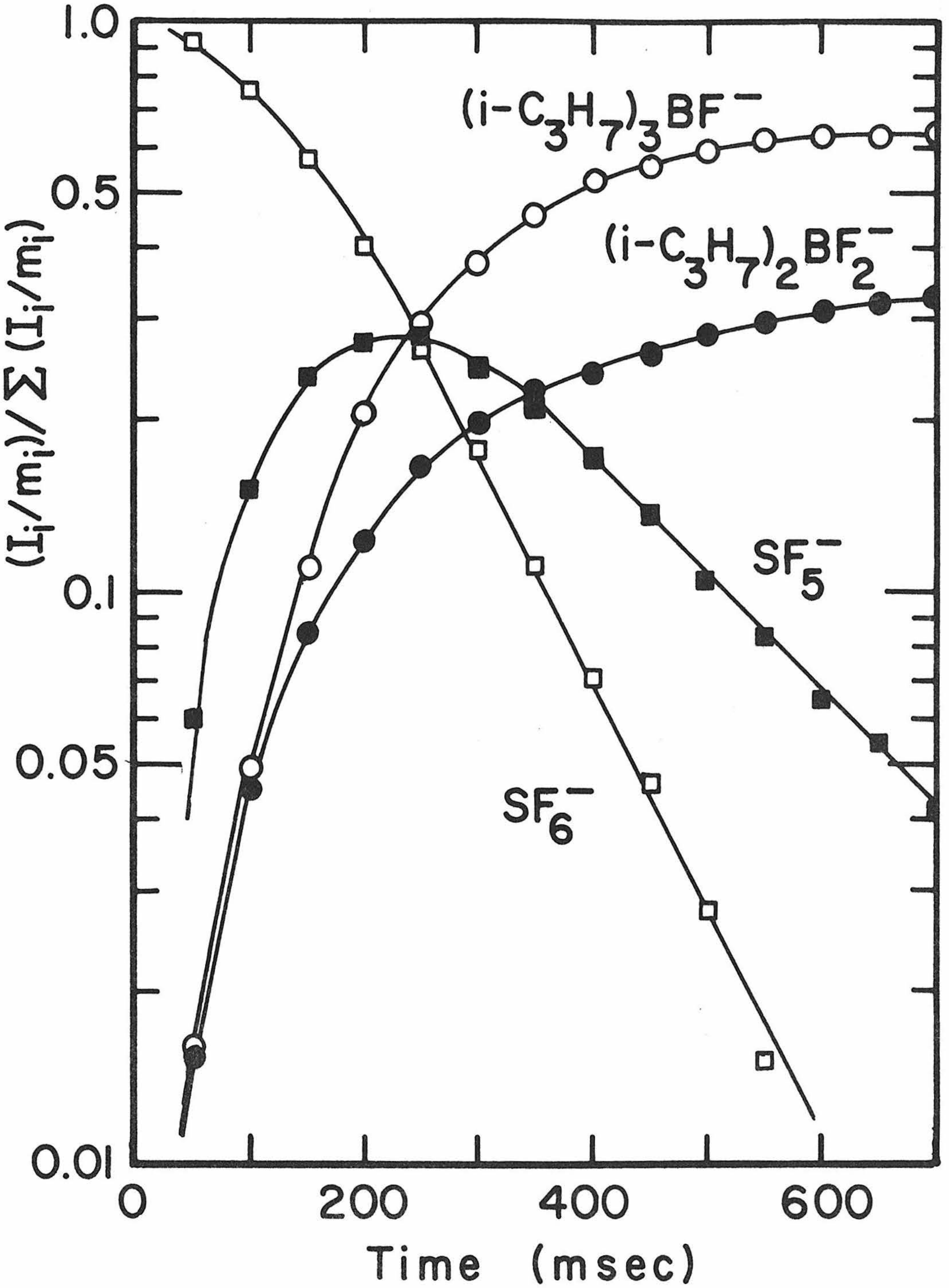
$SF_6/(i\text{-}C_3H_7)_3B$. The temporal variation of trapped-ion abundance observed following the electron beam pulse in 7.1×10^{-7} torr $(i\text{-}C_3H_7)_3B$ in the presence of traces of SF_6 is displayed in Figure 3. Anions generated from SF_6 react with triisopropylborane by reactions 10-12, processes similar to those described above for trimethyl- and triethylborane. SF_6^- does not contribute to a measurable extent to the formation of trialkylborane monofluoride anion $(i\text{-}C_3H_7)_3BF^-$ by direct fluoride transfer. The anionic products of processes 11 and 12 do not react further under the present conditions. Specifically, $(i\text{-}C_3H_7)_2BF_2^-$ is not observed to transfer F^- to $(i\text{-}C_3H_7)_3B$.

$$SF_6^- + (i\text{-}C_3H_7)_3B \begin{cases} \xrightarrow{70\%} SF_5^- + HF + (i\text{-}C_3H_7)_2BC_3H_6 & (10) \\ \xrightarrow{30\%} (i\text{-}C_3H_7)_2BF_2^- + SF_4 + C_3H_7 & (11) \end{cases}$$

$$SF_5^- + (i\text{-}C_3H_7)_3B \longrightarrow (i\text{-}C_3H_7)_3BF^- + SF_4 \qquad (12)$$

Figure 3

Temporal variation of trapped-anion abundances initiated by a 10 msec 70 eV electron beam pulse in 7.1×10^{-7} torr $(i\text{-}C_3H_7)_3B$ in the presence of traces of SF_6.


1.0
0.5
0.1
0.05
0.01
$(I_i/m_i)/\sum(I_i/m_i)$
0
200
400
600
Time (msec)
$(i\text{-}C_3H_7)_3BF^-$
$(i\text{-}C_3H_7)_2BF_2^-$
SF_5^-
SF_6^-

SF_6/BF_3. Figure 4 shows the time evolution of ion abundances initiated by the electron beam pulse in 1.5×10^{-6} torr BF_3 containing SF_6. BF_4^-, the only anion remaining at long reaction times, is generated by fluoride transfer processes 13 and 14. In contrast to the

$$SF_6^- + BF_3 \rightarrow BF_4^- + SF_5 \qquad (13)$$

$$SF_5^- + BF_3 \rightarrow BF_4^- + SF_4 \qquad (14)$$

observed formation of SF_5^- in trialkylborane reactions 4, 7, and 10, SF_5^- is not produced in reactions of SF_6^- with BF_3. Negative ion mass spectrometry studies of BF_3 have shown that negative ions containing boron are formed under certain conditions.[14d] In the present experiments, BF_4^- is generated in appreciable concentrations only in the presence of SF_6.

$SF_6/(CH_3)_3B/(C_2H_5)_3B$. The temporal variation of trapped-ion abundances following the electron beam pulse in a 3:1 mixture of $(CH_3)_3B$ and $(C_2H_5)_3B$ at 9.6×10^{-7} torr total pressure (in the presence of trace amounts of SF_6) is displayed in Figure 5. Initially, reactions 4-9 proceed as described above for the individual components to generate the four boron-containing anions R_3BF^- and $R_2BF_2^-$ ($R = CH_3$, C_2H_5). Double resonance experiments indicate that fluoride transfer reactions 15 and 16 are responsible for the disappearance of $(CH_3)_3BF^-$

$$(CH_3)_3BF^- + (C_2H_5)_3B \rightarrow (C_2H_5)_3BF^- + (CH_3)_3B \qquad (15)$$

$$(CH_3)_2BF_2^- + (C_2H_5)_3B \rightarrow (C_2H_5)_3BF^- + (CH_3)_2BF \qquad (16)$$

Figure 4

Temporal variation of trapped-anion abundances initiated by a 10 msec 70 eV electron beam pulse in 1.5×10^{-6} torr BF_3 in the presence of traces of SF_6.

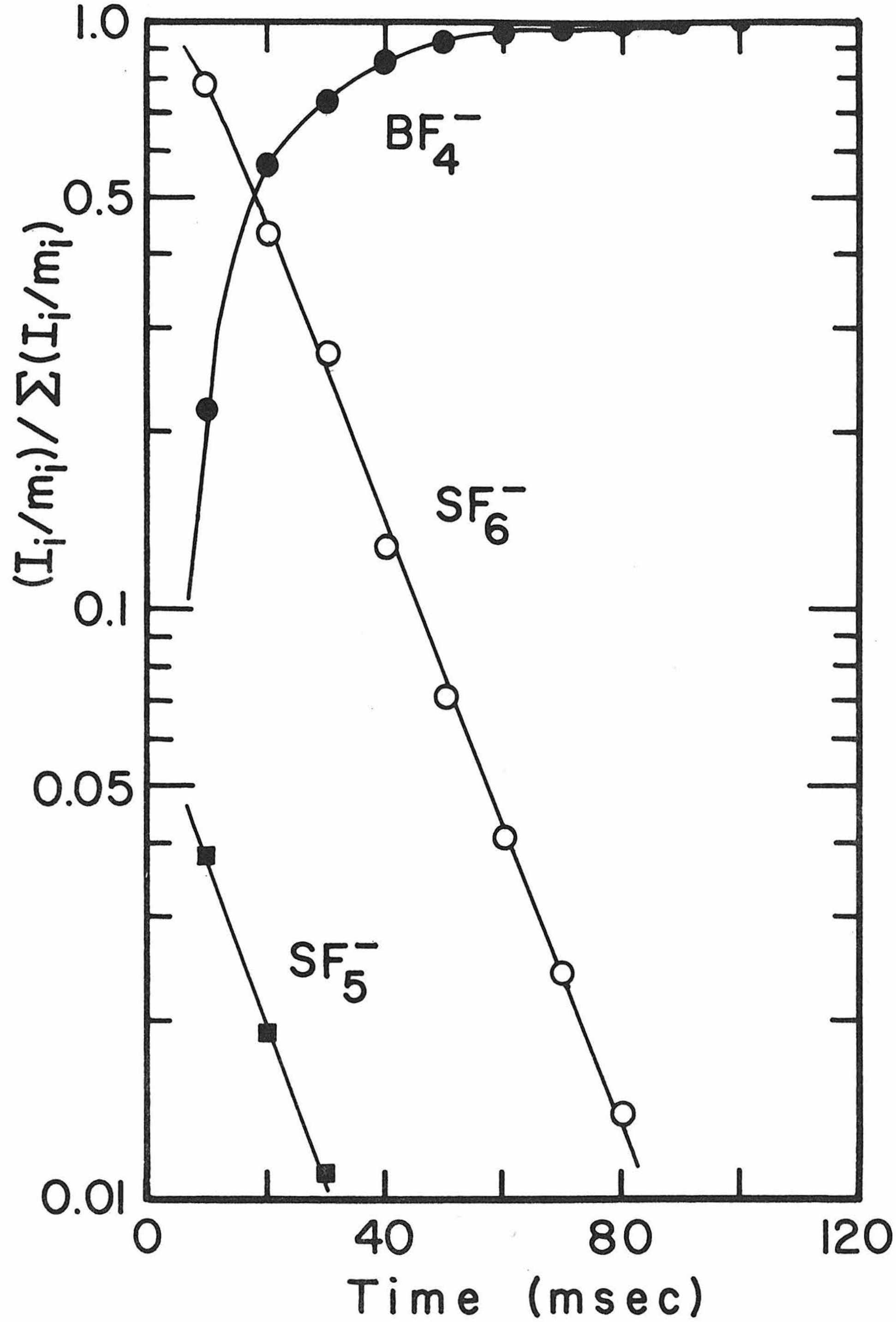
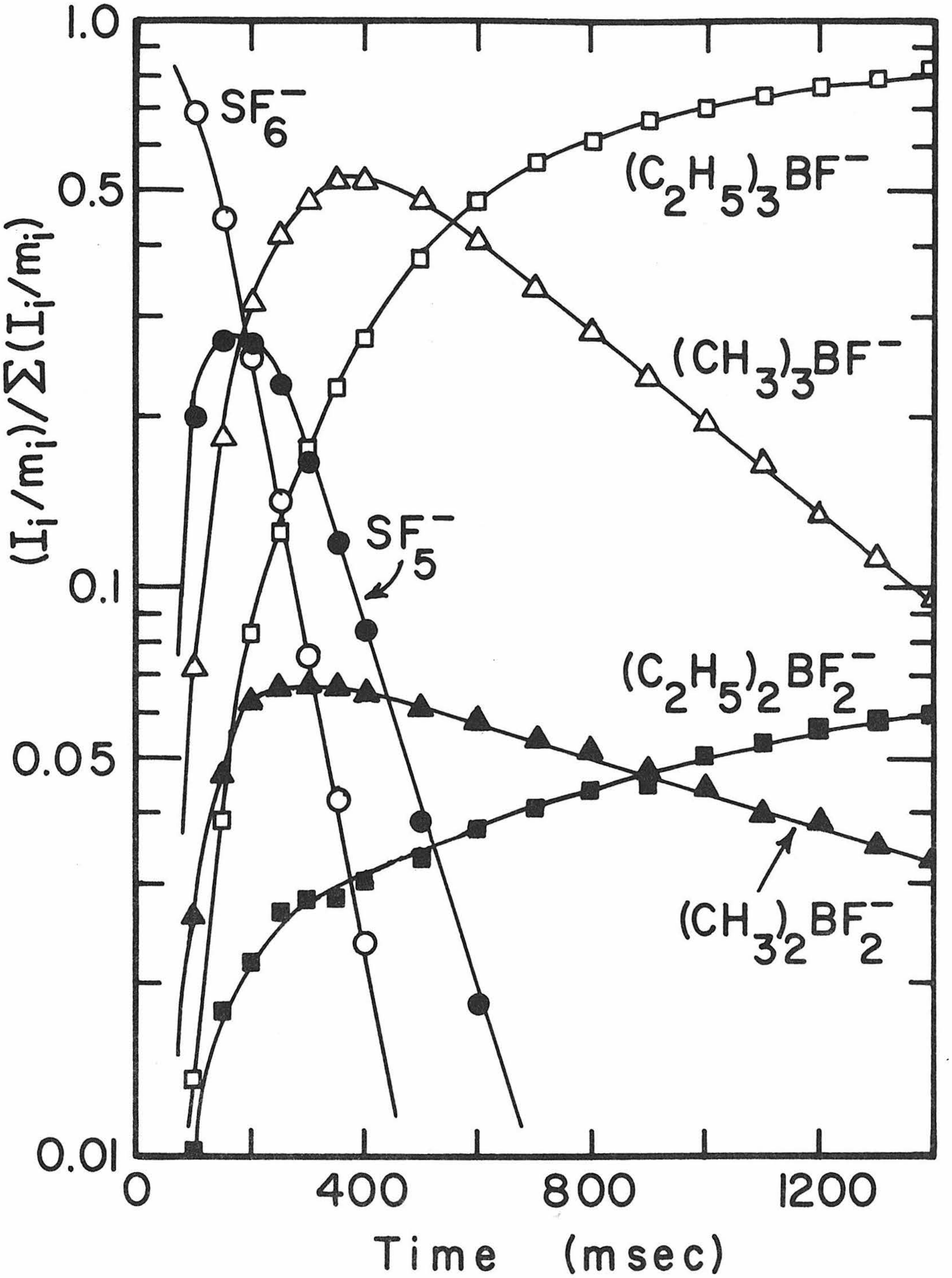

1.0
0.5
0.1
0.05
0.01
0
40
80
120
Time (msec)
$(I_i/m_i)/\sum(I_i/m_i)$
BF_4^-
SF_6^-
SF_5^-

Figure 5

Temporal variation of trapped-anion abundances initiated by a 10 msec 70 eV electron beam pulse in a 3:1 mixture of $(CH_3)_3B$ and $(C_2H_5)_3B$ at 9.6×10^{-7} torr in the presence of traces of SF_6.


1.0
0.5
0.1
0.05
0.01
0
400
800
1200
Time (msec)
$(I_i/m_i)/\sum(I_i/m_i)$
SF_6^-
SF_5^-
$(C_2H_5)_3BF^-$
$(CH_3)_3BF^-$
$(C_2H_5)_2BF_2^-$
$(CH_3)_2BF_2^-$

and $(CH_3)_2BF_2^-$ ions at long times in Figure 5. The ethyl-substituted boron anions $(C_2H_5)_3BF^-$ and $(C_2H_5)_2BF_2^-$ are stable to further reaction in this mixture.

$SF_6/(C_2H_5)_3B/(i\text{-}C_3H_7)_3B$. Figure 6 illustrates the temporal variation of anion concentrations initiated by the electron beam pulse in a 2.2:1 mixture of $(C_2H_5)_3B$ and $(i\text{-}C_3H_7)_3B$ at a pressure of 2.0×10^{-6} torr containing SF_6 in trace concentration. Initially, $(C_2H_5)_3BF^-$, $(C_2H_5)_2BF_2^-$, $(i\text{-}C_3H_7)_3BF^-$ and $(i\text{-}C_3H_7)_2BF_2^-$ ions are produced by reactions 7-12 as described above. Subsequently, the ethyl-substituted boron anions disappear via fluoride transfer reactions 17 and 18. $(i\text{-}C_3H_7)_3BF^-$ and $(i\text{-}C_3H_7)_2BF_2^-$ do not react further under these conditions.

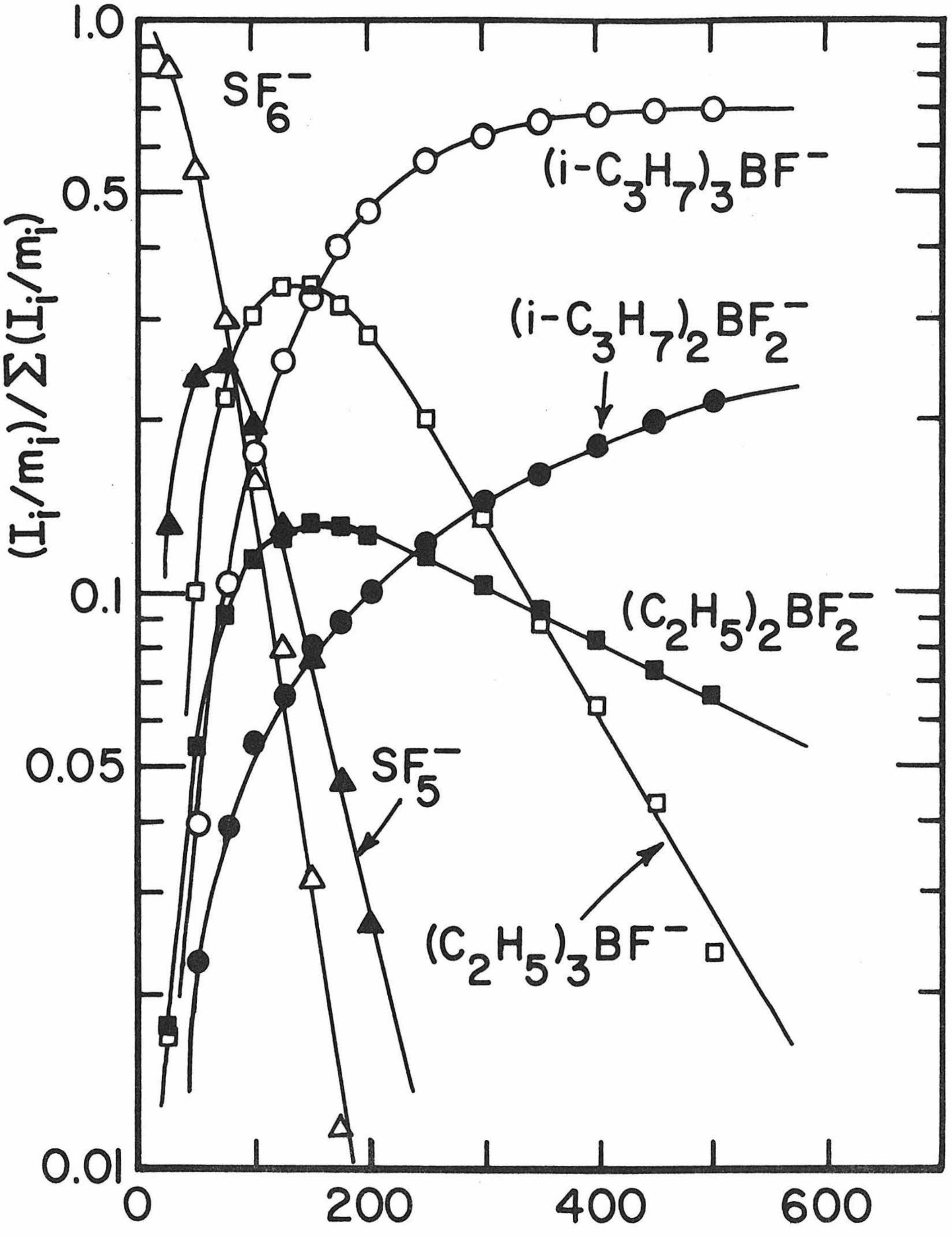
$$(C_2H_5)_3BF^- + (i\text{-}C_3H_7)_3B \rightarrow (i\text{-}C_3H_7)_3BF^- + (C_2H_5)_3B \qquad (17)$$

$$(C_2H_5)_2BF_2^- + (i\text{-}C_3H_7)_3B \rightarrow (i\text{-}C_3H_7)_3BF^- + (C_2H_5)_2BF \qquad (18)$$

$SF_6/BF_3/(i\text{-}C_3H_7)_3B$. In an ~1:1 mixture of BF_3 and $(i\text{-}C_3H_7)_3B$ at $\sim 1 \times 10^{-6}$ torr pressure in the presence of trace SF_6, reactions 10-14 lead initially to the formation of BF_4^-, $(i\text{-}C_3H_7)_3BF^-$ and $(i\text{-}C_3H_7)_2BF_2^-$ as described above. Although experimental difficulties in maintaining stable gas pressures in the mixture (apparently due to sample condensation on leak valve surfaces) inhibit detailed examinations of the reaction kinetics, it is clear that fluoride transfer reactions 19 and 20 proceed rapidly to completion. BF_4^- remains stable to further reaction in the mixture.

Figure 6

Temporal variation of trapped-anion abundances initiated by a 10 msec 70 eV electron beam pulse in a 2.2:1 mixture of $(C_2H_5)_3B$ and $(i\text{-}C_3H_7)_3B$ at 2.0×10^{-6} torr in the presence of traces of SF_6.


$(I_i/m_i)/\Sigma(I_i/m_i)$
1.0
0.5
0.1
0.05
0.01
0
200
400
600
Time (msec)
SF_6^-
$(i\text{-}C_3H_7)_3BF^-$
$(i\text{-}C_3H_7)_2BF_2^-$
$(C_2H_5)_2BF_2^-$
SF_5^-
$(C_2H_5)_3BF^-$ □

$$(i\text{-}C_3H_7)_3BF^- + BF_3 \rightarrow BF_4^- + (i\text{-}C_3H_7)_3B \qquad (19)$$

$$(i\text{-}C_3H_7)_2BF_2^- + BF_3 \rightarrow BF_4^- + (i\text{-}C_3H_7)_2BF \qquad (20)$$

Discussion

SF$_6$/R$_3$B Alone. The negative ion chemistry observed in mixtures of SF$_6$ with a given trialkylborane consists entirely of reactions involving SF$_6^-$ and SF$_5^-$ as generalized in (21)-(23) and terminates in

$$SF_6^- + R_3B \begin{cases} \longrightarrow SF_5^- + \begin{cases} HF + R_2BR' \\ \text{or} \\ RF + R_2B \end{cases} & (21) \\ \longrightarrow R_2BF_2^- + R + SF_4 & (22) \end{cases}$$

$$SF_5^- + R_3B \longrightarrow R_3BF^- + SF_4 \qquad (23)$$

formation of stable borane-fluoride Lewis adducts (where R = CH$_3$, C$_2$H$_5$ and i-C$_3$H$_7$; R′ = R - H). A choice of neutral products accompanying SF$_5^-$ formation in reaction 21 is hindered by lack of thermochemical data on boron-containing radicals. Processes similar to (21) have been observed previously in reactions of SF$_6^-$ with hydrogen halides (HX where X = Cl, Br, I)[12] and with a variety of molecules containing sufficiently reactive hydrogen (RH, e.g., HCO$_2$H, H$_2$S, and (CH$_3$)$_2$SiF$_2$).[14c, 19] Interestingly, reactions analogous to (21) do not occur with H$_2$O, CH$_3$OH, C$_2$H$_5$OH or with simple alkanes.[19]

Processes 22 yield the dialkylfluoroborane-fluoride adducts R$_2$FBF$^-$ resulting (formally) from transfer of F$_2^-$ from SF$_6^-$ accompanied by displacement of an alkyl radical from boron (reactions 5, 8 and 11). In each of the trialkylboranes examined, R_2FBF^- species do not react with the respective neutrals R_3B, indicating that for a given alkyl group R, replacement of R by F results in the significant increase in fluoride affinity of the borane (i.e., $D[R_2FB-F^-] > D[R_3B-F^-]$).

Processes 23 are found to be solely responsible for generation of trialkylborane-monofluoride adducts R_3BF^-, involving fluoride transfer from SF_5^- to the respective neutrals (reactions 6, 9, and 12), as indicated by double resonance and cyclotron ejection experiments. No evidence is obtained for formation of R_3BF^- species (for R = alkyl) via bimolecular encounters with SF_6^-.

In the SF_6/BF_3 system, BF_4^- is produced by fluoride transfer from both SF_6^- and SF_5^-, reactions 13 and 14, respectively, the latter reaction resembling process 23. We cannot experimentally distinguish whether SF_6^- produces BF_4^- by direct F^- transfer or by a more complex process resembling (22) (where R = F).

$SF_6/R_3B, R_3'B$ Mixtures. In addition to processes described above which are characteristic of the anion-molecule chemistry in mixtures of SF_6 and each of the boranes separately, fluoride transfer reactions among the various neutrals, as generalized in (24) and (25), are observed in binary mixtures of the boranes (reactions 15-20). These

$$R_3BF^- + R_3'B \rightarrow R_3'BF^- + R_3B \tag{24}$$

$$R_2FBF^- + R_3'B \rightarrow R_3'BF^- + R_2FB \tag{25}$$

results are summarized in Table I and indicate that the fluoride affinities of the neutral boranes increase with increasing size of the alkyl substituent R and with increasing substitution of F for R on boron. The various observations serve collectively to establish the fluoride affinity (or Lewis acidity) order $BF_3 > (i\text{-}C_3H_7)_2FB > (i\text{-}C_3H_7)_3B > (C_2H_5)_2FB > (C_2H_5)_3B > (CH_3)_2FB > (CH_3)_3B > SF_4$ for isolated species in the gas phase.

Under the experimental conditions usually employed in ICR studies of ion-molecule reactions, ion energies are very near thermal. It is assumed that all reactions observed with appreciable rate constants (see Table I) are exothermic or thermoneutral. While the possible occurrence of reverse of reactions 25 could not be checked without the availability of neutral R_2FB compounds, double resonance experiments are clearly consistent with reactions 16, 18, and 20 being exothermic as written. In all cases, a negative dependence of ion-molecule reaction rate on reactant ion kinetic energy is observed.

Thermochemical Considerations. Quantification of the observed relative order of fluoride affinities of the various borane Lewis acids is hindered by a lack of precise thermochemical data describing ions and neutrals containing boron. Considerations of the energetics of observed exothermic reactions generalized in (21)-(23) infer limiting values for heats of formation of the boron-containing anionic Lewis adducts, $R_2BF_2^-$ and R_3BF^-. Thermochemical data thus obtained are summarized in Table II.

Table I. Ion-Molecule Processes Observed

System	Reaction	Number[a]	Rate Constant, k[b]	Thermochemical Implications
$SF_6/(CH_3)_3B$				
	$SF_6^- + (CH_3)_3B \xrightarrow{72\%} SF_5^- + HF + (CH_3)_2BCH_2$	4	3.7	------
	$\xrightarrow{28\%} (CH_3)_2BF_2^- + SF_4 + CH_3$	5	1.4	------
	$SF_5^- + (CH_3)_3B \longrightarrow (CH_3)_3BF^- + SF_4$	6	2.8	$D[(CH_3)_3B{-}F^-] > D[SF_4{-}F^-]$
	$(CH_3)_2BF_2^- + (CH_3)_3B \not\longrightarrow (CH_3)_3BF^- + (CH_3)_2BF$	--[c]	< 0.01	$D[(CH_3)_2FB{-}F^-] > D[(CH_3)_3B{-}F^-]$
$SF_6/(C_2H_5)_3B$				
	$SF_6^- + (C_2H_5)_3B \xrightarrow{76\%} SF_5^- + HF + (C_2H_5)_2BCHCH_3$	7	3.2	------
	$\xrightarrow{24\%} (C_2H_5)_2BF_2^- + SF_4 + C_2H_5$	8	1.1	------
	$SF_5^- + (C_2H_5)_3B \longrightarrow (C_2H_5)_3BF^- + SF_4$	9	2.7	$D[(C_2H_5)_3B{-}F^-] > D[SF_4{-}F^-]$
	$(C_2H_5)_2BF_2^- + (C_2H_5)_3B \not\longrightarrow (C_2H_5)_3BF^- + (C_2H_5)_2BF$	--[c]	< 0.01	$D[(C_2H_5)_2FB{-}F^-] > D[(C_2H_5)_3B{-}F^-]$
$SF_6/(i\text{-}C_3H_7)_3B$				
	$SF_6^- + (i\text{-}C_3H_7)_3B \xrightarrow{70\%} SF_5^- + HF + (i\text{-}C_3H_7)_2BC(CH_3)_2$	10	2.5	------
	$\xrightarrow{30\%} (i\text{-}C_3H_7)_2BF_2^- + SF_4 + i\text{-}C_3H_7$	11	1.2	------
	$SF_5^- + (i\text{-}C_3H_7)_3B \longrightarrow (i\text{-}C_3H_7)_3BF^- + SF_4$	12	3.8	$D[(i\text{-}C_3H_7)_3B{-}F^-] > D[SF_4{-}F^-]$
	$(i\text{-}C_3H_7)_2BF_2^- + (i\text{-}C_3H_7)_3B \not\longrightarrow (i\text{-}C_3H_7)_3BF^- + (i\text{-}C_3H_7)_2BF$	--[c]	< 0.01	$D[(i\text{-}C_3H_7)_2FB{-}F^-] > D[(i\text{-}C_3H_7)_3B{-}F^-]$
SF_5/BF_3				
	$SF_6^- + BF_3 \longrightarrow BF_4^- + SF_5$	13	11.8	$D[BF_3{-}F^-] > D[SF_5{-}F^-]$
	$SF_5^- + BF_3 \longrightarrow BF_4^- + SF_4$	14	12.9	$D[BF_3{-}F^-] > D[SF_4{-}F^-]$

Table I. (Continued)

System	Reaction	Number[a]	Rate Constant, k[b]	Thermochemical Implications
$SF_6/(CH_3)_3B/(C_2H_5)_3$				
	$(CH_3)_3BF^- + (C_2H_5)_3B \longrightarrow (C_2H_5)_3BF^- + (CH_3)_3B$	15	2.4	$D[(C_2H_5)_3B{-}F^-] > D[(CH_3)_3B{-}F^-]$ $\Delta G \leqslant -1.9^e$
	$(CH_3)_2BF_2^- + (C_2H_5)_3B \longrightarrow (C_2H_5)_3BF^- + (CH_3)_2BF$	16	0.9	$D[(C_2H_5)_3B{-}F^-] > D[(CH_3)_2BF{-}F^-]$
$SF_6/(C_2H_5)_3B/(i\text{-}C_3H_7)_3B$				
	$(C_2H_5)_3BF^- + (i\text{-}C_3H_7)_3B \longrightarrow (i\text{-}C_3H_7)_3BF^- + (C_2H_5)_3B$	17	3.7	$D[(i\text{-}C_3H_7)_3B{-}F^-] > D[(C_2H_5)_3B{-}F^-]$ $\Delta G \leqslant -2.4^e$
	$(C_2H_5)_2BF_2^- + (i\text{-}C_3H_7)_3B \longrightarrow (i\text{-}C_3H_7)_3BF^- + (C_2H_5)_2BF$	18	1.1	$D[(i\text{-}C_3H_7)_3B{-}F^-] > D[(C_2H_5)_2FB{-}F^-]$
$SF_5/(i\text{-}C_3H_7)_3B/BF_3$				
	$(i\text{-}C_3H_7)_3BF^- + BF_3 \longrightarrow BF_4^- + (i\text{-}C_3H_7)_3B$	19	--[d]	$D[BF_3{-}F^-] > D[(i\text{-}C_3H_7)_3B{-}F^-]$ $\Delta G \leqslant -2.3^e$
	$(i\text{-}C_3H_7)_2BF_2^- + BF_3 \longrightarrow BF_4^- + (i\text{-}C_3H_7)_2BF$	20	--[d]	$D[BF_3{-}F^-] > D[(i\text{-}C_3H_7)_2FB{-}F^-]$

[a] Reaction numbers refer to reactions specified in the text.

[b] Rate constants in units of 10^{-10} $cm^3 molecule^{-1} sec^{-1}$, determined from limiting slopes of trapped-ion disappearance versus time data for the respective systems, taking into account product distributions where applicable.

[c] Reaction not observed.

[d] Rate constants not determined.

[e] Upper limits on free energy changes calculated from eqs 26 and 28 using ion abundance ratios at the longest reaction times shown in the respective systems.

Table II. Thermochemical Limitations[a] Imposed by Reactions Observed

R	$\Delta H_f\ R_3B$[b]	$\Delta H_f\ R_2BF_2^-$[c]	$\Delta H_f\ R_3BF^-$[d]
CH_3	-29.3	$\leqslant$ -184.7	$\leqslant$ -144.3
C_2H_5	-36.0	$\leqslant$ -183.1	$\leqslant$ -151.0
i-C_3H_7	-56.3	$\leqslant$ -195.3	$\leqslant$ -171.3

[a] All ΔH_f values in units of kcal/mole at 298°K.

[b] Values taken from Table III, see text for discussion.

[c] Calculated by considering reactions 5, 8, and 11 as generalized in 22, using $\Delta H_f\ R_2BF_2^- \leqslant \Delta H_f\ SF_6^- + \Delta H_f\ R_3B - \Delta H_f\ SF_4 - \Delta H_f\ R$ and data in Table III.

[d] Calculated by considering reactions 6, 9, and 12 as generalized in (23), using $\Delta H_F\ R_3BF^- \leqslant \Delta H_f\ SF_5^- + \Delta H_f\ R_3B - \Delta H_f\ SF_4$ and data in Table III.

Table III. Thermochemical Quantities Used in Calculations[a]

	ΔH_f
$(CH_3)_3B$	$-29.3 \pm 5.5^{b,c}$
$(C_2H_5)_3B$	$-36.0 \pm 3.0^{b,c}$
$(i\text{-}C_3H_7)_3B$	$-56.3 \pm 3.0^{b,c}$
SF_6^-	-304.4 ± 3.5^{d}
SF_5^-	-298 ± 6^{d}
SF_4	-183 ± 6^{d}
CH_3	34.0^{e}
C_2H_5	25.7^{e}
$i\text{-}C_3H_7$	17.6^{e}
F^-	-61.3 ± 0.1^{d}
BF_3	-271.7^{f}
BF_4^-	-404.0^{g}

[a] All ΔH_f values in units of kcal/mole at 298°K.

[b] ΔH_f values for the trialkylboranes calculated using Bensons Benson's group additivity method, Ref. 21, see text.

[c] ΔH_f values of -29.3 ± 5.5, -36.5 ± 1.2, and -60.1 ± 3.0 kcal/mole were determined by static bomb calorimetry, and taken from a critical compilation, Ref. 20, see text.

[d] Taken from Ref. 12.

[e] Taken from Ref. 29.

[f] Taken from Refs. 21 and 30.

[g] Calculated from $\Delta H_f\ BF_4^- = \Delta H_f\ BF_3 + \Delta H_f\ F^- - D[BF_3\text{–}F^-]$ using values quoted in this table and $D[BF_3\text{–}F^-] = 71$ kcal/mole, taken from Ref. 14a.

Static bomb calorimetry measurements yield heats of formation of the trialkylboranes $(CH_3)_3B$, $(C_2H_5)_3B$, and $(i\text{-}C_3H_7)_3B$ of -29.3 ± 5.5, -36.5 ± 1.2, and -60.1 ± 3.0 kcal/mole,[20] respectively. Using the group additivity method of Benson,[21] ΔH_f values of -29.3, -36.0, and -56.3 kcal/mole, respectively, are calculated (with uncertainty estimates of ± 3 kcal/mole). These calculated values do not include corrections for neighboring group interactions, which would, if included, lead to small positive corrections to the values indicated above. In view of the difficulties typically encountered in making accurate calorimetric measurements of boron compounds, it seems likely that the experimental values are somewhat low. Both sets of ΔH_f values are within the quoted uncertainties. In lieu of more precise experimental determinations, ΔH_f values of the boranes (Table II) obtained from the group methods are preferred and utilized in all calculations herein.

Previously reported values of $D[BF_3{-}F^-] = 71$[14a] and $D[SF_4{-}F^-] = 54 \pm 12$ kcal/mole[12] serve to bracket the relative fluoride affinities of the various R_3B and R_2FB neutral Lewis acids within this 17 kcal range. Reactions 15, 17, and 19, involving direct fluoride transfer between $(CH_3)_3B$, $(C_2H_5)_3B$, $(i\text{-}C_3H_7)_3$, and BF_3 (generalized in 24), all proceed rapidly toward completion. Double resonance experiments provide no evidence for the respective reverse reactions. As apparent in Figures 4 and 5 for $(CH_3)_3B/(C_2H_5)_3B$ and $(C_2H_5)_3B/(i\text{-}C_3H_7)_3B$ mixtures, reactions 15 and 17 do not appear to approach equilibrium. The equilibrium constant K_{eq}, defined as in (26), is related to the free energy change for fluoride transfer, $\Delta G = -RT \ln K_{eq}$. The data in

$$A_1F^- + A_2 \rightleftharpoons A_2F^- + A_1; \quad K_{eq} = \frac{[A_2F^-][A_1]}{[A_1F^-][A_2]} \tag{26}$$

Figures 4 and 5 and neutral pressure ratios place limits on equilibrium constants and free energy changes for reactions 15 and 17. Limiting values obtained are $K_{eq}(15) \geq 25.8$ and $K_{eq}(17) \geq 58.8$ and corresponding free energy changes accompanying fluoride transfer of $\Delta G \leq -1.9$ and $\Delta G \leq -2.4$ kcal/mole, respectively. Trapped-ion ICR techniques are generally able to provide accurate determinations of similar ion transfer equilibria and associated free energy changes up to values of ~3 kcal/mole. Larger free energy changes yield equilibrium constants (and forward and reverse rate constants) exceeding the dynamic range of the technique.

The results of a recent study[22] of pentacoordinate Lewis adducts of F^- with fluoromethylsilanes, where the trialkylboranes and BF_3 were used as reference Lewis acids, provide additional insight into further quantification of the Lewis acidities of the boranes examined in the present study. Using the same methodology, the fluoride transfer equilibrium (27) is observed involving $(C_2H_5)_3B$ and CH_3SiF_3. The measured equilibrium constant $K_{eq} = 2.3$ corresponds to a ΔG of -0.5 ± 0.1 kcal/mole favoring F^- transfer to the right as written.

$$CH_3SiF_4^- + (C_2H_5)_3B \rightleftharpoons (C_2H_5)_3BF^- + CH_3SiF_3 \tag{27}$$

A quantity more relevant to discussion of adduct bond energies is the enthalpy, which is related to free energy by eq 28. The entropy

$$\Delta G = \Delta H - T\Delta S = -RT \ln K_{eq} \tag{28}$$

change accompanying reaction 27 is estimated to be $\Delta S \sim 0$,[22] using the statistical mechanical formalism of Searles and Kebarle.[23] Thus $\Delta H \cong 0.5$ kcal/mole is estimated for transfer F^- from CH_3SiF_3 to $(C_2H_5)_3B$.

In the same study,[22] reaction 29 is observed only in the forward direction, while reaction 30 does not occur. Limits obtained for

$$(CH_3)_3BF^- + CH_3SiF_3 \rightarrow CH_3SiF_4^- + (CH_3)_3B \tag{29}$$

$$(CH_3)_2FBF^- + CH_3SiF_3 \not\rightarrow CH_3SiF_4^- + (CH_3)_2FB \tag{30}$$

reaction 29 are $K_{eq} \geqslant 50.8$ and $\Delta G \leqslant -2.3$ kcal/mole. Taken along with results from the present study, these observations suggest the fluoride affinity ordering $(CH_3)_3B < CH_3SiF_3 < (CH_3)_2FB < (C_2H_5)_3B$ for F^- reference base, with CH_3SiF_3 and $(C_2H_5)_3B$ separated by ~ 0.5 kcal/mole. In addition, F^- transfer reactions 31-34 proceed rapidly

$$(CH_3)_2SiF_3^- + (CH_3)_3B \rightarrow (CH_3)_3BF^- + (CH_3)_2SiF_2 \tag{31}$$

$$(i\text{-}C_3H_7)_3BF^- + SiF_4 \rightarrow SiF_5^- + (i\text{-}C_3H_7)_3B \tag{32}$$

$$(i\text{-}C_3H_7)_2BF_2^- + SiF_4 \rightarrow SiF_5^- + (i\text{-}C_3H_7)_2BF \tag{33}$$

$$SiF_5^- + BF_3 \rightarrow BF_4^- + SiF_4 \tag{34}$$

(with rate constants in the range of 10^{-10} to 10^{-9} $cm^3 mol^{-1} sec^{-1}$) toward completion.[22] With the exception of reaction 33, it should have been possible to detect the reverse reactions; none were observed. Limiting values of equilibrium constants obtained are $K_{eq} \geqslant 34.9$, 18.9, and

49.0 with corresponding free energy changes of $\Delta G \leqslant -2.1$, -1.7, and -2.3 kcal/mole for reactions 31, 32, and 34, respectively.

Evaluation of the results of the present work along with the quoted silane-borane study, assuming a minimum of 3 kcal/mole separation in cases where no reverse reactions were evidenced, affords a quantitative scale of fluoride affinities for both the boranes and silanes,[22] fully consistent with all available data. Table IV summarizes values of borane-fluoride dissociation energies $D[A-F^-]$. Values of $D[R_2FB-F^-]$ are simply chosen intermediate between bracketing species,[22] since the neutrals R_2FB were not present thus precluding opportunity of observing equilibria. Included in Table IV are heats of formation, derived from the quantitative estimates of fluoride affinities. These data describe the anionic adducts R_3BF^- and R_2BFB^- and the neutrals R_2FB, species for which no literature data are available for comparison.

Lewis Acidities: Effects of Substituents and Reference Base. Lewis acid properties of boranes have long been the subject of extensive investigations, however, essentially all such studies have dealt with the formation of neutral adducts between a given trisubstituted borane R_3B (R = H, alkyl or halogen) and various n-donor bases (e.g., amines, phosphines).[24] Adducts of $(CH_3)_3B$, the only trialkylborane studied extensively, have been examined primarily as a means of investigating steric effects originating in the base. Very few studies have dealt with effects in the acid, that is by holding the base constant and varying substituents on the acid moiety.

Table IV. Best Estimates of Thermochemical Data[a] for Borane Lewis Acids

Acid, A	$D[A-F^-]$[b]	$\Delta H_f\ AF^-$	$\Delta H_f\ A$
$(CH_3)_3B$	58.5	-148.8[c]	- 29.3[d]
$(CH_3)_2FB$	61.8	$\leqslant$ -184.7[d]	$\leqslant$ - 61.9[e]
$(C_2H_5)_3B$	62.0	-159.0[c]	- 36.0[d]
$(C_2H_5)_2FB$	64.0	$\leqslant$ -183.1[d]	$\leqslant$ - 58.1[f]
$(i\text{-}C_3H_7)_3B$	65.0	-182.3[c]	- 56.3[d]
$(i\text{-}C_3H_7)_2FB$	66.5	$\leqslant$ -195.3[d]	$\leqslant$ - 67.5[g]
F_3B	71.0[h]	-404.0[i]	-271.7[i]

[a] All data in units of kcal/mole at 298°K.

[b] Fluoride affinities estimated as discussed in the text, see also Ref. 22.

[c] Calculated from $\Delta H_f\ R_3BF^- = \Delta H_r - \Delta H_f\ SF_4 + \Delta H_f\ SF_5^- + \Delta H_f\ R_3B$ using data in Table III, where $\Delta H_r = D[SF_4-F^-] - D[R_3B-F^-]$ using $D[SF_4-F^-] = 54$ kcal/mole and values in this table.

[d] Taken from Table II.

[e] Calculated from $\Delta H_f\ R_2BF \leqslant \Delta H_r - \Delta H_f\ R_3'BF^- + \Delta H_f\ R_3'B + \Delta H_f\ R_2BF_2^-$, where $\Delta H_r = D[R_2FB-F^-] - D[R_3'B-F]$ for $R = CH_3$, $R' = C_2H_5$ using data in this table.

[f] Calculated as in e for $R = C_2H_5$ and $R' = i\text{-}C_3H_7$.

[g] Calculated as in e for $R = i\text{-}C_3H_7$ and $R' = F$ using data in this table.

[h] Taken from Ref. 14a.

[i] Taken from Table III.

BH_3 and BF_3 are considerably stronger acids toward nitrogen bases than is $(CH_3)_3B$. Adduct bond strengths, measured as gas phase enthalpies of dissociation obtained from measurements of equilibrium dissociation pressures, typically span a narrow range of 14 to 20 kcal/mole for the acid $(CH_3)_3B$, while for BH_3 and BF_3 bond strengths toward these same bases range from 30 to 45 kcal/mole.[25]

In as much as the fluoride affinity ordering obtained in the present study is among the very few to explore substituent effects in the Lewis acid, comparison with the limited data available proves of interest. Using $(CH_3)_3N$ as the common reference base, ΔH_{diss} values for the gas phase dissociation $(CH_3)_3N:BR_3 \rightleftharpoons (CH_3)_3N + BR_3$ comprise the only extended comparison available. ΔH_{diss} values (in kcal/mole) have been measured for BF_3 (30.9), CH_3BF_2 (23.1), $(CH_3)_2BF$ (18.3), $(CH_3)_3B$ (17.6),[24b] $(CH_3)_2BH$ (23.4), and BH_3 (31.5).[26] No data was obtained for CH_3BH_2, but the enthalpy change for dissociation of its adduct with $(CH_3)_3N$ is estimated to be around 27.5 kcal/mole.

Apparent from a comparison of adduct dissociation energies with both reference bases, replacement of alkyl substituents by fluorine on boron results in increases in the Lewis acidity of the neutral boranes, principally a reflection of the higher electronegativity of F. The overall increases in acidity in going from $(CH_3)_3B$ to BF_3 are approximately the same ~16 kcal/mole for both reference bases, however bond strengths toward F^- are 30-40 kcal/mole larger than toward $(CH_3)_3N$.

Previous studies have shown that the strengths of acid-base interactions can be strongly influenced by the nature of the reference species.[27] Two principal effects are likely responsible for the large differences in adduct strengths toward these two reference bases: differences in electrostatic interactions in the adducts and differences in the steric requirements of the reference bases.

First, the presence of the negative charge in the fluoride adducts results in increased dissociation energies via favorable polarization effects, principally charge-induced dipole interactions ($R \leftarrow\!\!\!+ BF^-$). Such effects are even more favorable in the larger, more polarizable ethyl and isopropyl substituents on boron. Polarization effects in the polar amine-borane neutral adducts, dipole-induced dipole interactions, are likely to be of much smaller magnitude.

Second, the small size of F^- as compared with the much bulkier $(CH_3)_3N$ contributes to the marked preference of the borane Lewis acids for fluoride ion. The importance of steric repulsions in substituted amine-borane Lewis adducts has been extensively discussed by Brown and co-workers.[28] Several effects are discernible, including B-strain, back-side repulsions among substituents groups on the polyatomic base, and F-strain, frontal interactions between substituent groups on both acid and base across the donor-acceptor bond. In addition, the energy required to rehybridize the polyatomic reference base upon formation of the new adduct bond acts to lower the acidity toward $(CH_3)_3N$. These effects are absent with monoatomic F^- reference base, however, repulsions among the bulky alkyl groups on the acid moiety (analogous to B-strain for the base) might be expected to decrease adduct strengths, particularly for $(C_2H_5)_3B$ and $(i\text{-}C_3H_7)_3B$.

Apparently such repulsions in the acid are more than offset by the increased polarization stabilization of the larger alkyl groups. Similar alkyl substituent effects on boron are also operative with hydride ion as the reference base. Recent ICR studies, show that $(C_2H_5)_3B$ binds hydride more strongly than does $(CH_3)_3B$.[31] Quantitative information on borane Lewis acidities toward H^- as a reference base may be useful to understanding the highly selective reductions of functional groups effected by organoborane-hydride reagents in organic synthesis.[32]

Acknowledgments. This work was supported in part by the Energy Research and Development Administration under Grant No. E(04-3)767-8 and the National Science Foundation under Grant No. NSF-GP-18383.

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CHAPTER V

METHYL AND FLUORINE SUBSTITUENT EFFECTS ON THE GAS PHASE LEWIS ACIDITIES OF SILANES BY ION CYCLOTRON RESONANCE SPECTROSCOPY[1a]

M. K. Murphy and J. L. Beauchamp[1b]

Abstract

Formation of gas phase Lewis acid-base adducts $(CH_3)_nF_{4-n}SiF^-$ (n = 0-2) in reactions of SF_6^- and SF_5^- with neutral fluoromethylsilanes are examined using trapped-anion ion cyclotron resonance spectroscopy. Fluoride transfer reactions observed in binary mixtures of the silanes and of silanes with borane Lewis acids R_3B (R = CH_3, C_2H_5, i-C_3H_7, F), in the presence of trace amounts of SF_6 as the fluoride source, establish the Lewis acidity order $BF_3 > SiF_4 > (i\text{-}C_3H_7)_2FB > (i\text{-}C_3H_7)_3B > (C_2H_5)_2FB > (C_2H_5)_3B > (CH_3)_2FB > CH_3SiF_3 > (CH_3)_3B > (CH_3)_2SiF_2 > SF_4 > (CH_3)_3SiF$ in the gas phase for F^- as reference base. Quantitative estimates of adduct bond dissociation energies $D[(CH_3)_nF_{4-n}Si{-}F^-]$ (n = 0-2) and heats of formation of adducts $(CH_3)_nF_{4-n}SiF^-$ are derived. Variations in adduct bond strengths are discussed in terms of the effects of methyl and fluorine substitution on silicon. Analogies are drawn to similar substituent effects observed in the isoelectronic neutral fluoromethylphosphoranes.

Introduction

Electron-pair dative bond formation between acceptor species A, which possess low-lying vacant orbitals, and donors B, which have accessible lone pairs (phenomena most generally described by the Lewis theory of acid-base interactions[2]), encompass chemical behavior common to much of the periodic table. Among the more familiar Lewis acids are the Group IIIb acceptors (compounds of B, Al, Ga, etc.) and many metal cations (from Groups Ia, IIa and compounds of the transition metals).[3,4] Studies of dissociation equilibria 1 and displacement reactions 2, employing a common reference base B, have

$$AB \rightleftharpoons A + B \qquad \Delta H \equiv D[A\text{-}B] \tag{1}$$

$$A_1B + A_2 \rightleftharpoons A_1 + A_2B \tag{2}$$

provided information on adduct bond dissociation energies and insight into relationships between molecular structure and chemical reactivity for a wide variety of polyatomic Lewis acids, both in solution and in the gas phase.[3,4]

By comparison, much less is known about Lewis acid properties of neutral Group IVb acceptors R_4M (M = C, Sn, Ge, etc.), where formation of acid-base adducts requires coordinative expansion of nominally closed-shell (electron-octet) systems. Under the influence of higher effective nuclear charge and with the availability of lower energy vacant d orbitals, the tendency for dative bonding is increased for the heavier members of the group (e.g., Ge, Sn, Pb).[5] For carbon systems, Dougherty has reported several anionic halide adducts

{CH_3XY^- (where X, Y = Cl, Br, I),[6] $H_nCl_{4-n}CCl^-$ (n = 0-3)[7] and $R_3CBr_2^-$ (where R = H, alkyl)[8]} in the gas phase using high pressure mass spectrometry. Only in the case of CCl_5^-, however, is the involvement of pentacoordinate carbon without controversy. Yamdagni and Kebarle[9] have attributed the stability of the chloride adduct with chloroform to strong hydrogen bonding of the type $[Cl_3C\cdots H\cdots Cl]^-$. From studies of the temperature dependence of equilibria such as (1) where B = Cl^-, bond dissociation energies $D[Cl_4C{-}Cl^-] = 14.2 \pm 0.7$ kcal/mol,[7] and $D[Cl_3HC{-}Cl^-] = 15.2$ kcal/mol[9] have been determined.

A number of theoretical calculations[10-18] have examined adducts involving pentacoordinate carbon and silicon, with the primary interest being in the investigation of potential energy surfaces for bimolecular nucleophilic substitution (Sn2) reactions. Relevant to the present study are comparisons of the relative energies of separated reactants and transition states of the Sn2 surfaces (i.e., the reaction complexes corresponding to pentacoordinate adducts). Various calculations[10-14] show that for carbon and silicon systems, the most stable adduct geometries are of D_{3h} symmetry (trigonal bipyramidal). Recently, large basis set <u>ab initio</u> calculations by Baybutt[10] have compared the adducts $H\cdots CH_3\cdots H^-$, $F\cdots CH_3\cdots F^-$, $H\cdots SiH_3\cdots H^-$, and $F\cdots SiH_3\cdots F^-$. CH_5^- and $CH_3F_2^-$ were found to be less stable than the separated reactants by 61.2 and 2.1 kcal/mol, respectively, while SiH_5^- and $SiH_3F_2^-$ adducts were calculated to be more stable by 18.6 and 52.1 kcal/mol, respectively.[10] It was found that while d orbitals are not entirely responsible for the stability of the silicon adducts, their inclusion in the basis functions do increase the stabilities of SiH_5^- and $SiH_3F_2^-$ substantially (by ~10 kcal/mol).[10]

A number of pentacoordinate silicon adducts have been experimentally observed. Pentacoordinate amine adducts $(CH_3)_3NSiF_4$,[19] $(CH_3)_3NSiHF_3$,[20] and $(CH_3)_3NSi(CH_3)F_3$[21] have been observed in the gas phase. From measurements of dissociation equilibria of these complexes it is found that adduct stability decreases sharply with replacement of F by H on silicon and even more so with replacement of F by CH_3.[22] SiF_5^- was first reported as a salt $\{[(C_2H_5)_3P]_2PtCl(CO)\}^+SiF_5^-$, the unexpected product of heating C_2F_4 and $[(C_2H_5)_3P]_2PtHCl$ in a silica vessel.[23] NMR studies of SiF_5^-, $RSiF_4^-$, and $R'_2SiF_3^-$ species (R = alkyl, aryl; R′ = aryl) indicate trigonal-bipyramidal structures below -60°C in solvents of low polarity.[24] Recent gas phase studies using ion cyclotron resonance spectroscopy (ICR) and high pressure mass spectrometry (HPMS) have examined the formation of anions containing pentacoordinate silicon. MacNeil and Thynne[25] report the formation of SiF_5^- by a rapid fluoride transfer reaction ($k = 2.2 \times 10^{-10}$ cm^3 $mol^{-1}sec^{-1}$) from SiF_3^-, generated by electron impact, in SiF_4. Dillard[26] has recently measured cross sections for anion transfer reactions 3 (where n = 1-3) for reactant ion energies as low as 0.5 eV

$$SF_6^- + (CH_3)_nF_{4-n}Si \rightarrow (CH_3)_nF_{4-n}SiF^- + SF_5 \tag{3}$$

using HPMS. Reaction cross sections were observed to decrease rapidly with successive substitution of CH_3 for F on silicon; the fluoride adduct of $(CH_3)_3SiF$ was barely detectable. McDaniel[27] has reported an ICR study of fluoride transfer reactions (analogous to process 2) among a variety of inorganic Lewis acids. The observed relative Lewis acidity order $SF_4 < HCl < SiF_4 < BF_3$ served to establish the limits[27, 28] $54 \leqslant D[F_4Si{-}F^-] < 71$ kcal/mole in the gas phase.

Recent ICR studies from this laboratory[20] of fluoride transfer reactions (analogous to processes 2 and 3) in mixtures of trialkylboranes and BF_3 indicate that the fluoride affinities $D[A{-}F^-]$ of acids R_3B and R_2FB ($R = CH_3$, C_2H_5, i-C_3H_7) all lie intermediate between SF_4 and BF_3. In the present report, we wish to describe results of trapped-anion ICR investigations of gas phase fluoride transfer reactions occurring in the fluoromethylsilanes $(CH_3)_nF_{4-n}Si$ ($n = 0$-3), both alone and in binary mixtures, in the presence of SF_6 as the fluoride source. In addition, fluoride transfer reactions observed in mixtures of these silanes with the alkylboranes and BF_3 afford quantitative estimates of silane Lewis acidities, for F^- as reference base.

Experimental

All studies reported herein utilize a high-field ICR spectrometer (employing a 15" magnet system) constructed in the Caltech instrument shops. Details of the instrumentation and experimental techniques associated with ICR spectrometry are described elsewhere.[30] Gas mixtures utilized are prepared directly in the ICR cell by admission of appropriate sample components through separate variable leak valves in a parallel inlet manifold. Absolute gas pressures are determined using a Schulz-Phelps ionization gauge, adjacent to the ICR cell, calibrated separately for each component against an MKS Baratron capacitance manometer (Model 90H1-E).[30c] A linear calibration of Baratron pressure (absolute) versus ionization gauge current affords pressure determinations over a range of 10^{-7} to 10^{-4} torr. Overall accuracy in pressure measurement for these studies is estimated to be ± 20%, and represents the major source of error in reported reaction rate constants. All measurements are performed at ambient temperature (~ 22 °C). Bimolecular reaction rate constants are determined with knowledge of neutral gas pressures from the limiting slopes of semi-log plots of trapped-ion abundance versus time and by considering product distributions where applicable.

$(CH_3)_3B$ and $(C_2H_5)_3B$ were purchased from Alfa Inorganics and SF_6, SiF_4, BF_3, and SO_2 from Matheson. Samples of $(CH_3)_3SiF$, $(CH_3)_2SiF_2$, and CH_3SiF_3 were provided through the courtesy of Professor J. G. Dillard, and that of $(i\text{-}C_3H_7)_3B$ from Professor A. H. Cowley. Noncondensable impurities are removed from all samples by multiple freeze-pump-thaw cycles at liquid nitrogen temperatures, mass spectral analyses showed no detectable impurities in the samples utilized.

In all studies reported here, SF_6 is utilized as the source of fluoride ion. SF_6^- (~ 95%) and SF_5^- (~ 5%) are generated from neutral SF_6, typically present at ~ 10^{-8} torr pressure, by rapid attachment of near-thermal energy electrons produced in the ICR trapping well by inelastic collisions with neutrals present during the 10 msec electron beam pulse.[31-33] In mixtures containing $(CH_3)_3SiF$, SO_2F^- (generated by fluoride transfer from SF_6^- to SO_2[27, 28a]) was also tried as a source of F^-. The electron beam energy utilized is nominally 70 eV for emission currents of $\sim 10^{-7}$ A.

Data reported in tables and figures are normalized to mono-isotopic abundances (^{12}C, 98.89%; ^{11}B, 80.22%; ^{28}Si, 92.21%; ^{32}S, 95.0%). Typically, ion concentrations comprising less than 1% of the total are not included in the reported data.

Results

Observed ion-molecule reactions between SF_6^- and each of the silanes $(CH_3)_nF_{4-n}Si$ (n = 0-3) are described below. Fluoride ion transfer reactions dominate the anion chemistry of these systems and ultimately yield stable pentacoordinate silane-fluoride adducts $(CH_3)_nF_{4-n}SiF^-$ (n = 0-2). Then reactions initiated by SF_6^- in binary mixtures of the silanes are examined to determine relative fluoride affinities (Lewis acidities) of the neutrals. Finally, in attempts to quantify the fluoride affinities of the silanes, studies of mixtures of the silanes with various borane Lewis acids R_3B (where R = CH_3, C_2H_5, i-C_3H_7, and F) are described. The gas phase fluoride affinities of these boranes are available from recent studies[29] and provide reference points for quantitative comparisons. Experimentally determined reaction rate constants are summarized in Table I.

SF_6/SiF_4. In a sample of SiF_4 at 9.7×10^{-7} torr pressure containing trace amounts of SF_6 ($\sim 10^{-8}$ torr), production of SiF_5^- via reaction 4 involving fluoride transfer from SF_6^- is in agreement with

Table I. Ion-Molecule Processes Observed

System	Reaction	Number[a]	Rate Constant[b]	Thermochemical Implications
SF_6/SiF_4				
	$SF_6^- + SiF_4 \longrightarrow SiF_5^- + SF_5$	4	4.2	$D[SiF_4-F^-] > D[SF_5-F^-]$
	$SF_5^- + SiF_4 \longrightarrow SiF_5^- + SF_4$	5	6.8	$D[SiF_4-F^-] > D[SF_4-F^-]$
SF_6/CH_3SiF_3				
	$SF_5^- + CH_3SiF_3 \longrightarrow CH_3SiF_4^- + SF_5$	6	1.5	$D[(CH_3)F_3Si-F^-] > D[SF_5-F^-]$
	$SF_5^- + CH_3SiF_3 \longrightarrow CH_3SiF_4^- + SF_4$	7	2.6	$D[(CH_3)F_3Si-F^-] > D[SF_4-F^-]$
$SF_6/(CH_3)_2SiF_2$				
	$SF_6^- + (CH_3)_2SiF_2 \xrightarrow{90\%} (CH_3)_2SiF_3^- + SF_5$	8	1.3[d]	$D[(CH_3)_2F_2Si-F^-] > D[SF_5-F]$
	$\xrightarrow{10\%} SF_5^- + HF + (CH_3)F_2CH_2$ or $CH_3F + (CH_3)F_2Si$	9	0.1[d]	$\Delta H_f[(CH_3)F_2SiCH_2] \leqslant -157.1$ $\Delta H = -3.5$[f]
	$SF_5^- + (CH_3)_2SiF_2 \longrightarrow (CH_3)_2SiF_3^- + SF_4$	10	0.3	$D[(CH_3)_2F_2Si] > D[SF_4-F^-]$
$SF_6/(CH_3)_3SiF$				
	$SF_6^- + (CH_3)_3SiF \not\longrightarrow (CH_3)_3SiF_2^- + SF_5$	--[c]	< 0.01	$D[(CH_3)_3FSi-F^-] > D[SF_5-F^-]$
	$SF_5^- + (CH_3)_3SiF \not\longrightarrow (CH_3)_3SiF_2^- + SF_5$	--[c]	< 0.01	$D[(CH_3)_3FSi-F^-] < D[SF_4-F^-]$
$SF_6/(CH_3)_3SiF/SO_2$				
	$SO_2F^- + (CH_3)_3SiF \not\longrightarrow (CH_3)_3SiF_2^- + SO_2$	11[c]	< 0.01	$D[(CH_3)_3FSi-F^-] < D[SO_2-F^-]$
	$SO_2F_2^- + (CH_3)_3SiF \not\longrightarrow (CH_3)_3SiF_2^- + SO_2F$	12[c]	< 0.01	$D[(CH_3)_3FSi-F^-] < D[SO_2F-F^-]$
$SF_6/(CH_3)_3SiF/(CH_3)_2SiF_2$				
	$(CH_3)_2SiF_3^- + (CH_3)_3SiF \longrightarrow (CH_3)_3SiF_2^- + (CH_3)_2SiF_2$	13[c]	< 0.01	$D[(CH_3)_3FSi-F^-] < D[(CH_3)_2F_2Si-F^-]$
$SF_6/(CH_3)_2SiF_2/CH_3SiF_3$				
	$(CH_3)_2SiF_3^- + CH_3SiF_3 \longrightarrow CH_3SiF_4^- + (CH_3)_2SiF_2$	14	2.2	$D[(CH_3)F_3Si-F^-] > D[(CH_3)_2F_2Si-F^-]$ $\Delta G < -2.6$[g]
$SF_6/CH_3SiF_3/SiF_4$				
	$CH_3SiF_4^- + SiF_4 \longrightarrow SiF_5^- + CH_3SiF_3$	15	~3[e]	$D[F_4Si-F^-] > D[(CH_3)F_3Si-F^-]$
$SF_6/(CH_3)_3B/(CH_3)_2SiF_2$				
	$(CH_3)_2SiF_3^- + (CH_3)_3B \longrightarrow (CH_3)_3BF^- + (CH_3)_2SiF_2$	19	3.4	$D[(CH_3)_3B-F^-] > D[(CH_3)_2F_2Si-F^-]$ $\Delta G < -21.$[g]
	$(CH_3)_2BF_2^- + (CH_3)_2SiF_2 \not\longrightarrow (CH_3)_2SiF_3^- + (CH_3)_2FB$	--[c]	< 0.01	$D[(CH_3)_2F_2Si-F^-] < D[(CH_3)_2FB-F^-]$

Table I. (Continued)

System	Reaction	Number	Rate Constant[b]	Thermochemical Implications
$SF_6/(CH_3)_3B/CH_3SiF_3$				
	$(CH_3)_3BF^- + CH_3SiF_3 \longrightarrow CH_3SiF_4^- + (CH_3)_3B$	20	9.5	$D[(CH_3)F_3Si\text{–}F^-] > D[(CH_3)_3B\text{–}F^-]$
	$(CH_3)_2BF_2^- + CH_3SiF_3 \not\longrightarrow CH_3SiF_4^- + (CH_3)_2FB$	--[c]	< 0.01	$D[(CH_3)F_3Si\text{–}F^-] < D[(CH_3)_2FB\text{–}F^-]$
$SF_6/(C_2H_5)_3B/CH_3SiF_3$				
	$CH_3SiF_4^- + (C_2H_5)_3B \rightleftharpoons (C_2H_5)_3BF^- + CH_3SiF3$	24	$K_{eq} = 2.3^h$	$D[(C_2H_5)_3B\text{–}F^-] > D[(CH_3)F_3Si\text{–}F^-]$ $\Delta G = 0.5 \pm 0.1^g$
	$(C_2H_5)_2BF_2^- + CH_3SiF_3 \not\longrightarrow CH_3SiF_4^- + (C_2H_5)_2FB$	--[c]	< 0.01	$D[(CH_3)F_3Si\text{–}F^-] < D[(C_2H_5)_2FB\text{–}F^-]$
$SF_6/(C_2H_5)_3B/SiF_4$				
	$(C_2H_5)_3BF^- + SiF_4 \longrightarrow SiF_5^- + (C_2H_5)_3B$	25	2.8	$D[F_4Si\text{–}F^-] > D[(C_2H_5)_3B\text{–}F^-]$
	$(C_2H_5)_2BF_2^- + SiF_4 \longrightarrow SiF_5^- + (C_2H_5)_2FB$	26	2.0	$D[F_4Si\text{–}F^-] > D[(C_2H_5)_2FB\text{–}F^-]$
$SF_6/(i\text{-}C_3H_7)_3B/SiF_4$				
	$(i\text{-}C_3H_7)_3BF^- + SiF_4 \longrightarrow SiF_5^- + (i\text{-}C_3H_7)_3B$	30	2.2	$D[F_4Si\text{–}F^-] > D[(i\text{-}C_3H_7)_3B\text{–}F^-]$ $\Delta G < -1.7^g$
	$(i\text{-}C_3H_7)_2BF_2^- + SiF_4 \longrightarrow SiF_5^- + (i\text{-}C_3H_7)_3B$	31	1.5	$D[F_4Si\text{–}F^-] > D[(i\text{-}C_3H_7)_2FB\text{–}F^-]$
$SF_6/BF_3/CH_3SiF_3$				
	$CH_3SiF_4^- + BF_3 \longrightarrow BF_4^- + CH_3SiF_3$	34	2.1	$D[F_3B\text{–}F^-] > D[(CH_3)F_3Si\text{–}F^-]$
$SF_6/BF_3/SiF_4$				
	$SiF_5^- + BF_3 \longrightarrow BF_4^- + SiF_4$	35	~3[e]	$D[F_3B\text{–}F^-] > D[F_4Si\text{–}F^-]$

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[a] Reaction numbers refer to reactions specified in the text.

[b] Rate constants are in units of × 10^{-10} $cm^3 molecule^{-1} sec^{-1}$, determined from the limiting slopes of reactant ion disappearance, considering product distributions where applicable.

[c] Reactions not observed by double resonance, see text for discussions.

[d] Total disappearance rate constant for reaction of SF_6^- with $(CH_3)_2SiF_2$; product distributions determined in cyclotron ejection experiments.

[e] Rate constants estimated though quantitative data were not obtained, see text for discussion.

[f] Calculated using data in Table II.

[g] Free energy changes in units of kcal/mole, determined as specified in the text.

[h] Equilibrium constant for reaction 24, determined as specified in the text.

$$SF_6^- + SiF_4 \rightarrow SiF_5^- + SF_5 \qquad (4)$$

previous reports.[27, 34] SF_5^- produced by dissociative electron capture in SF_6 also generates SiF_5^- via fluoride transfer reaction 5. SiF_5^-

$$SF_5^- + SiF_4 \rightarrow SiF_5^- + SF_4 \qquad (5)$$

appears stable to further reaction under these conditions.

SF_6/CH_3SiF_3. The temporal variation of ion abundances initiated by the electron beam pulse in 2.8×10^{-6} torr CH_3SiF_3 in the presence of trace amounts of SF_6 is displayed in Figure 1. Fluoride transfer reactions 6 and 7, yielding $CH_3SiF_4^-$, are detected by double resonance.

$$SF_6^- + CH_3SiF_3 \rightarrow CH_3SiF_4^- + SF_5 \qquad (6)$$

$$SF_5^- + CH_3SiF_3 \rightarrow CH_3SiF_4^- + SF_4 \qquad (7)$$

In contrast to processes described below in the $SF_6/(CH_3)_2SiF_2$ system, SF_5^- is not produced by reaction of SF_6^- with CH_3SiF_3. $CH_3SiF_4^-$ produced by reactions 6 and 7 does not react further under the present conditions.

$SF_6/(CH_3)_2SiF_2$. Electron impact in a sample of $(CH_3)_2SiF_2$ at 1.6×10^{-6} torr containing trace amounts of SF_6 results in the temporal variation of trapped anion abundances shown in Figure 2. The pentacoordinate $(CH_3)_2SiF_3^-$ anion is formed by fluoride transfer reactions 8 and 10, analogous to processes observed in SiF_4 and CH_3SiF_3. In addition, double resonance indicates reaction 9 to be responsible for the initial increase in SF_5^- shown in Figure 2. Generation of SF_5^- has

Figure 1

The temporal variation of trapped-anion abundances following a 10 msec 70 eV electron beam pulse in 2.8×10^{-6} torr CH_3SiF_3 in the presence of trace amounts of SF_6.

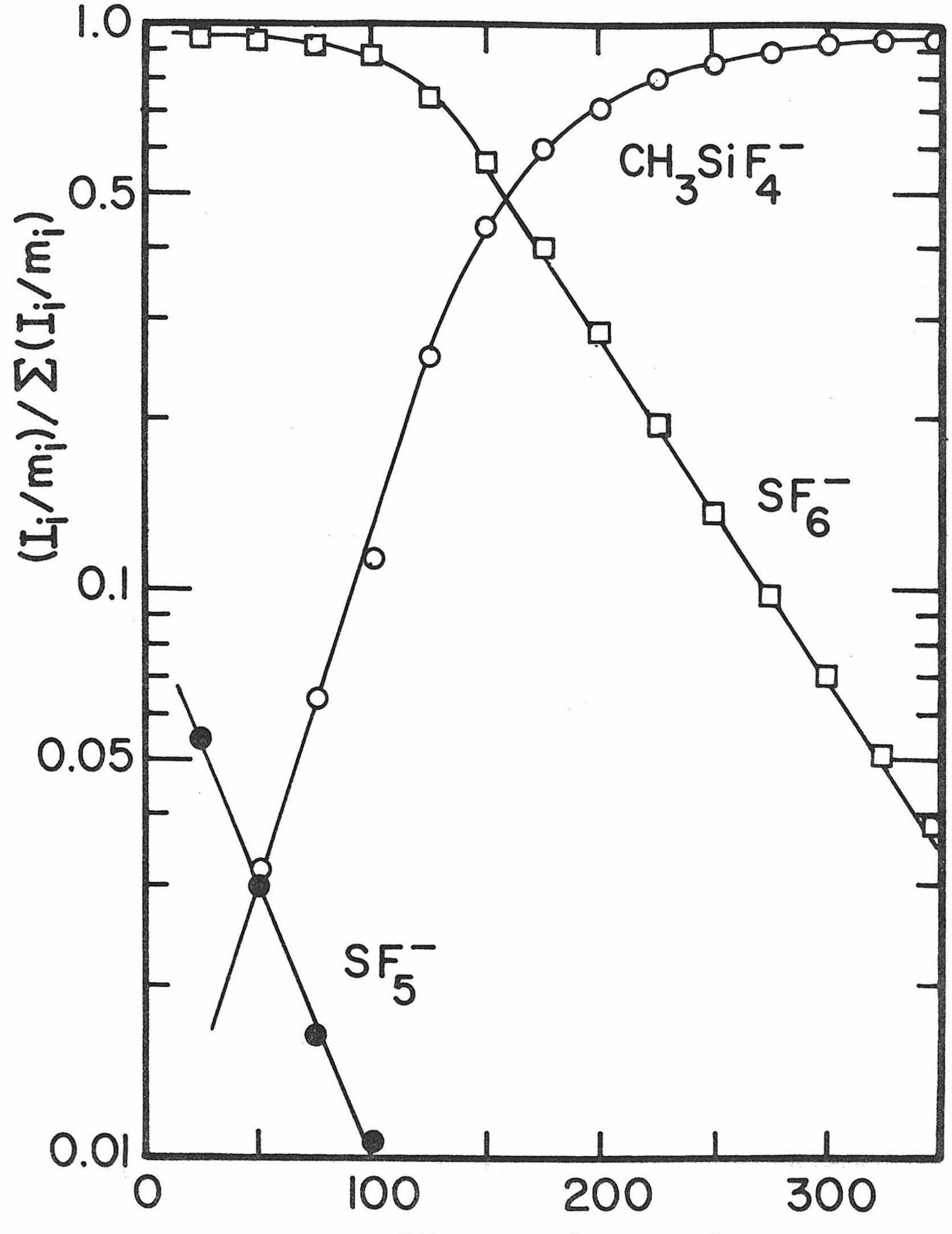
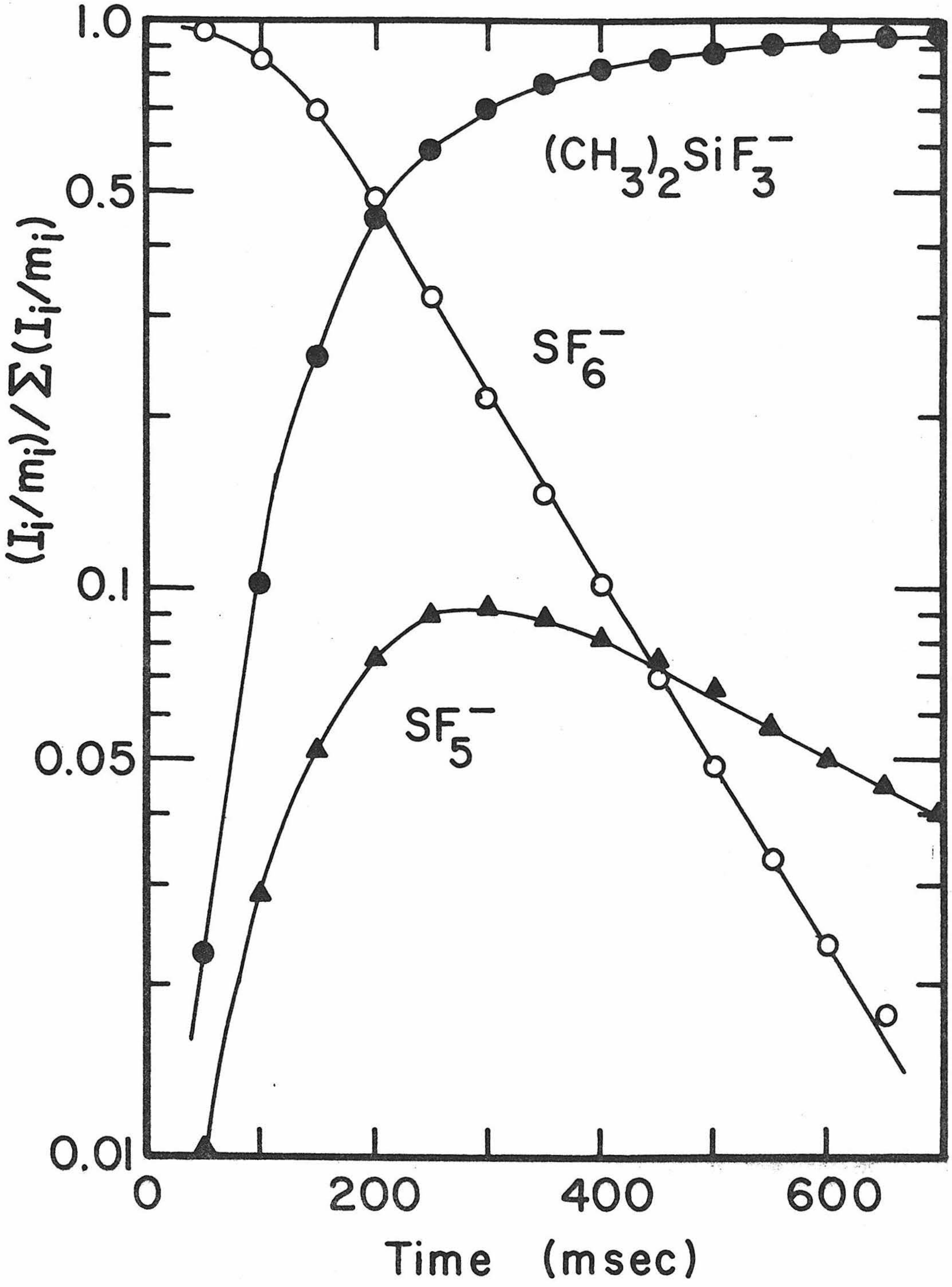

1.0
0.5
0.1
0.05
0.01
0
100
200
300
Time (msec)
$(I_i/m_i)/\sum(I_i/m_i)$
$CH_3SiF_4^-$
SF_6^-
SF_5^-

Figure 2

The temporal variation of trapped-anion abundances following a 10 msec 70 eV electron beam pulse in 1.6×10^{-6} torr $(CH_3)_2SiF_2$ in the presence of trace amounts of SF_6.


1.0
0.5
0.1
0.05
0.01
0
200
400
600
Time (msec)
$(I_i/m_i)/\sum(I_i/m_i)$
$(CH_3)_2SiF_3^-$
SF_6^-
SF_5^-

$$SF_6^- + (CH_3)_2SiF_2 \xrightarrow{90\%} (CH_3)_2SiF_3^- + SF_5 \tag{8}$$

$$SF_6^- + (CH_3)_2SiF_2 \xrightarrow{10\%} SF_5^- + \left\{\begin{array}{c} HF + (CH_3)F_2SiCH_2 \\ \text{or} \\ CH_3F + CH_3SiF_2 \end{array}\right. \tag{9}$$

$$SF_5^- + (CH_3)_2SiF_2 \longrightarrow (CH_3)_2SiF_3^- + SF_4 \tag{10}$$

previously been reported in reactions of SF_6^- with a variety of molecules (e.g., HX, where X = Cl, Br, I;[28a] R_3B, where R = CH_3, C_2H_5, i-C_3H_7;[29, 35] HCO_2H, CH_3CO_2H, H_2S[33b]). The neutral products in reaction 9 remain uncertain. Formation of CH_3F and CH_3SiF_2 radical is calculated to be ~3.5 kcal/mole exothermic.[36] $(CH_3)_2SiF_3^-$ appears stable to further reaction under these conditions.

$SF_6/(CH_3)_3SiF$ and $SF_6/SO_2/(CH_3)_3SiF$. Under a variety of experimental conditions, no silicon-containing anions are produced in either SF_6 - $(CH_3)_3SiF$ or SF_6 - SO_2 - $(CH_3)_3SiF$ mixtures. Specifically, no pentacoordinate $(CH_3)_3SiF_2^-$ is observed. These gas mixtures were examined by variation of pressure (up to $\sim 10^{-4}$ torr) and of ion trapping time at constant pressure ($\sim 10^{-6}$ torr $(CH_3)_3SiF$). In the $SF_6/(CH_3)_3SiF$ mixture, SF_6^- (~95%) and SF_5^- (~5%), generated by electron capture processes in SF_6, remain completely unreactive as a function of pressure and trapping time. Generation of SF_5^- by processes analogous to (9) are not observed. In the presence of SO_2, SF_6^- and SF_5^- react to generate SO_2F^- and $SO_2F_2^-$.[28a] The latter anion reacts further with SO_2 by fluoride transfer to yield SO_2F^- as the final stable product ion. SO_2F^- and $SO_2F_2^-$ do not react with $(CH_3)_3SiF$. In particular, fluoride transfer reactions 11 and 12 are not observed.

$$SO_2F^- + (CH_3)_3SiF \not\rightarrow (CH_3)_3SiF_2^- + SO_2 \qquad (11)$$

$$SO_2F_2^- + (CH_3)_3SiF \not\rightarrow (CH_3)_3SiF_2^- + SO_2F \qquad (12)$$

$SF_6/(CH_3)_3SiF/(CH_3)_2SiF_2$. In further attempts to generate $(CH_3)_3SiF_2^-$ from $(CH_3)_3SiF$, anion reactions in mixtures of SF_6, $(CH_3)_3SiF$ and $(CH_3)_2SiF_2$ are examined as a function of pressure and trapping time. The only silicon-containing anion detected is $(CH_3)_2SiF_3^-$ produced by reactions 8-10 as described above. Notably, fluoride transfer from $(CH_3)_2SiF_3^-$ to $(CH_3)_3SiF$ (reaction 13) is not observed.

$$(CH_3)_2SiF_3^- + (CH_3)_3SiF \not\rightarrow (CH_3)_3SiF_2^- + (CH_3)_2SiF_2 \qquad (13)$$

$SF_6/(CH_3)_2SiF_2/CH_3SiF_3$. The variations in trapped-anion abundances initiated by the electron beam pulse in a 4.7:1 mixture of $CH_3)_2SiF_2$ and CH_3SiF_3 (in the presence of traces of SF_6) at 3.4×10^{-6} torr pressure total pressure are displayed in Figure 3. In addition to reactions 6-10 described above, fluoride transfer reaction 14 accounts

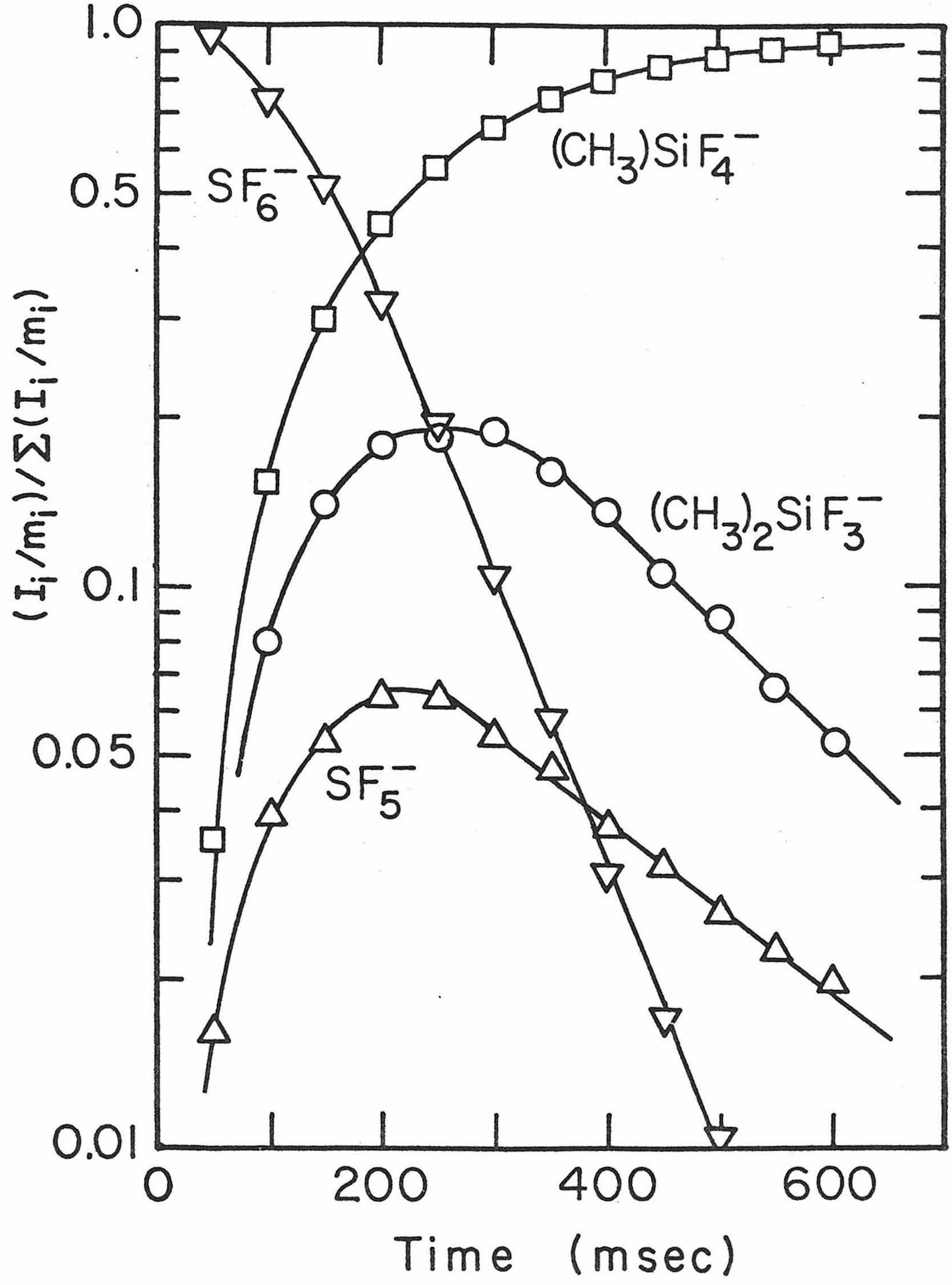
$$(CH_3)_2SiF_3^- + CH_3SiF_3 \rightarrow CH_3SiF_4^- + (CH_3)_2SiF_2 \qquad (14)$$

for the disappearance of $(CH_3)_2SiF_3^-$ at long times in Figure 3. $CH_3SiF_4^-$ in unreactive in this mixture.

$SF_6/CH_3SiF_3/SiF_4$. In an ~1:1 mixture of CH_3SiF_4 and SiF_4 at $\sim 2 \times 10^{-6}$ torr, $CH_3SiF_3^-$ and SiF_5^- are produced initially by reactions 4-7 described above. Difficulties in maintaining constant pressure in the mixture[37] precluded detailed examination of the kinetics, but is

Figure 3

The temporal variation of trapped-anion abundances following a 10 msec 70 eV electron beam pulse in a 4.7:1 mixture of $(CH_3)_2SiF_2$ and CH_3SiF_3 at 3.4×10^{-6} torr in the presence of trace amounts of SF_6.


1.0
0.5
0.1
0.05
0.01
0
200
400
600
Time (msec)
$(I_i/m_i)/\Sigma(I_i/m_i)$
SF_6^-
$(CH_3)SiF_4^-$
$(CH_3)_2SiF_3^-$
SF_5^-

apparent that fluoride transfer reaction 15 (confirmed by double

$$\mathrm{CH_3SiF_4^- + SiF_4 \rightarrow SiF_5^- + CH_3SiF_3} \tag{15}$$

resonance) proceeds rapidly to completion.

$SF_6/(CH_3)_3B/(CH_3)_2SiF_2$. The temporal variation in anion abundances initiated by the electron beam pulse in a 7.5:1 mixture of $(CH_3)_2SiF_2$ and $(CH_3)_3B$ at a constant pressure of 2.2×10^{-6} torr in the presence of traces of SF_6 is shown in Figure 4. Reactions 16-18 have

$$\mathrm{SF_6^- + (CH_3)_3B} \begin{cases} \longrightarrow \mathrm{SF_5^- + HF + (CH_3)_2BCH_2} & (16) \\ \longrightarrow \mathrm{(CH_3)_2BF_2^- + SF_4 + CH_3} & (17) \end{cases}$$

$$\mathrm{SF_5^- + (CH_3)_3B \longrightarrow (CH_3)_3BF^- + SF_4} \tag{18}$$

been previously reported in $SF_6/(CH_3)_3B$ mixtures.[29, 35] In addition to reactions 8-10 described above, fluoride transfer from $(CH_3)_2SiF_3^-$ to $(CH_3)_3B$ (reaction 19) is detected by double resonance, accounting for

$$\mathrm{(CH_3)_2SiF_3^- + B(CH_3)_3 \rightarrow (CH_3)_3BF^- + (CH_3)_2SiF_2} \tag{19}$$

the decay of $(CH_3)_2SiF_3^-$ at long times in Figure 4. Both $(CH_3)_3BF^-$ and $(CH_3)_2BF_2^-$ are stable to further reaction in this mixture.

$SF_6/(CH_3)_3B/CH_3SiF_3$. Figure 5 shows the time evolution of anion concentrations following the electron beam pulse in a 4.4:1 mixture of $(CH_3)_3B$ and CH_3SiF_3 at a total pressure of 5.4×10^{-7} torr in the presence of trace amounts of SF_6. In addition to reactions 6 and 7

Figure 4

The temporal variation of trapped-anion abundances following a 10 msec 70 eV electron beam pulse in a 7.5:1 mixture of $(CH_3)_2SiF_2$ and $(CH_3)_3B$ at 2.2×10^{-6} torr in the presence of trace amounts of SF_6.

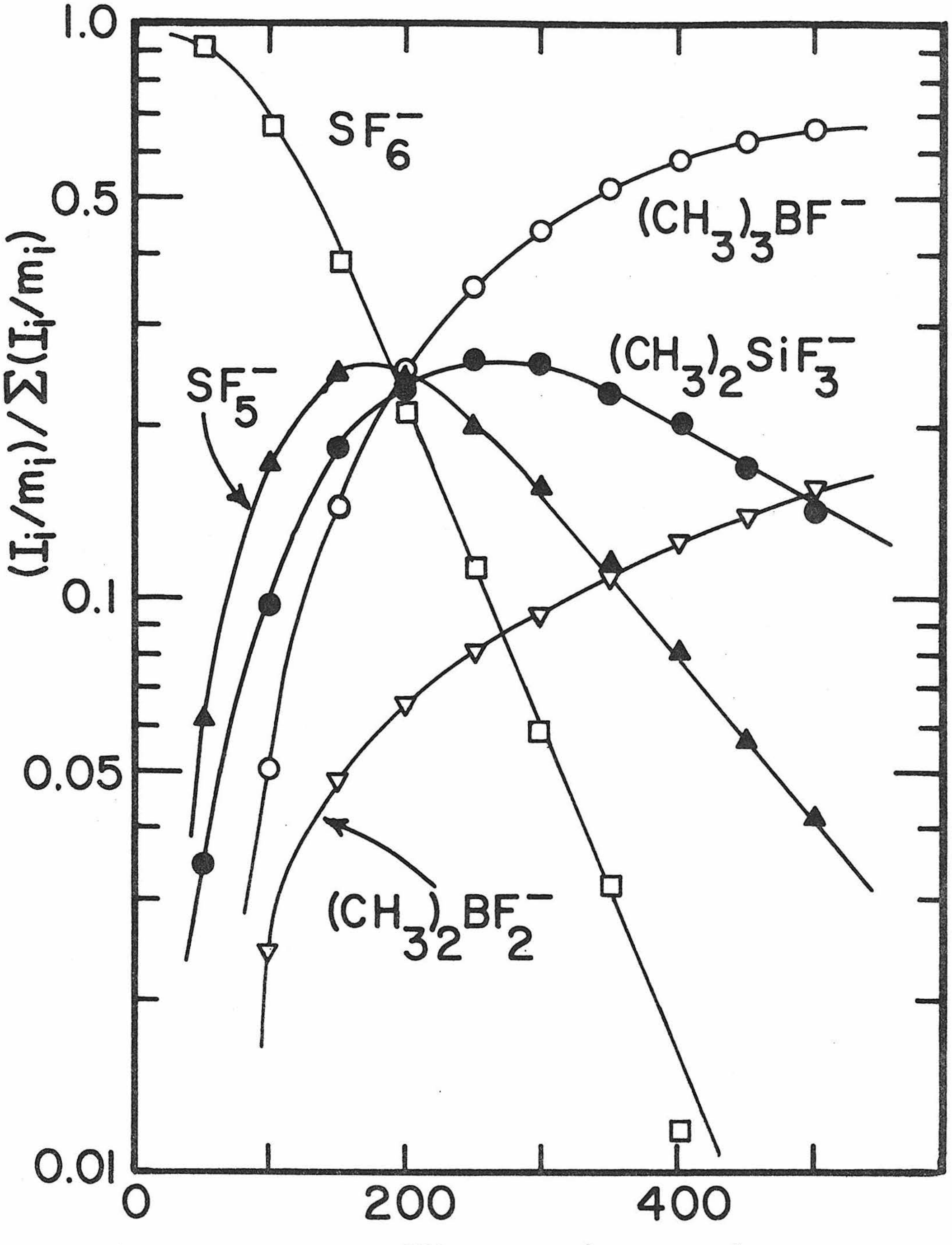
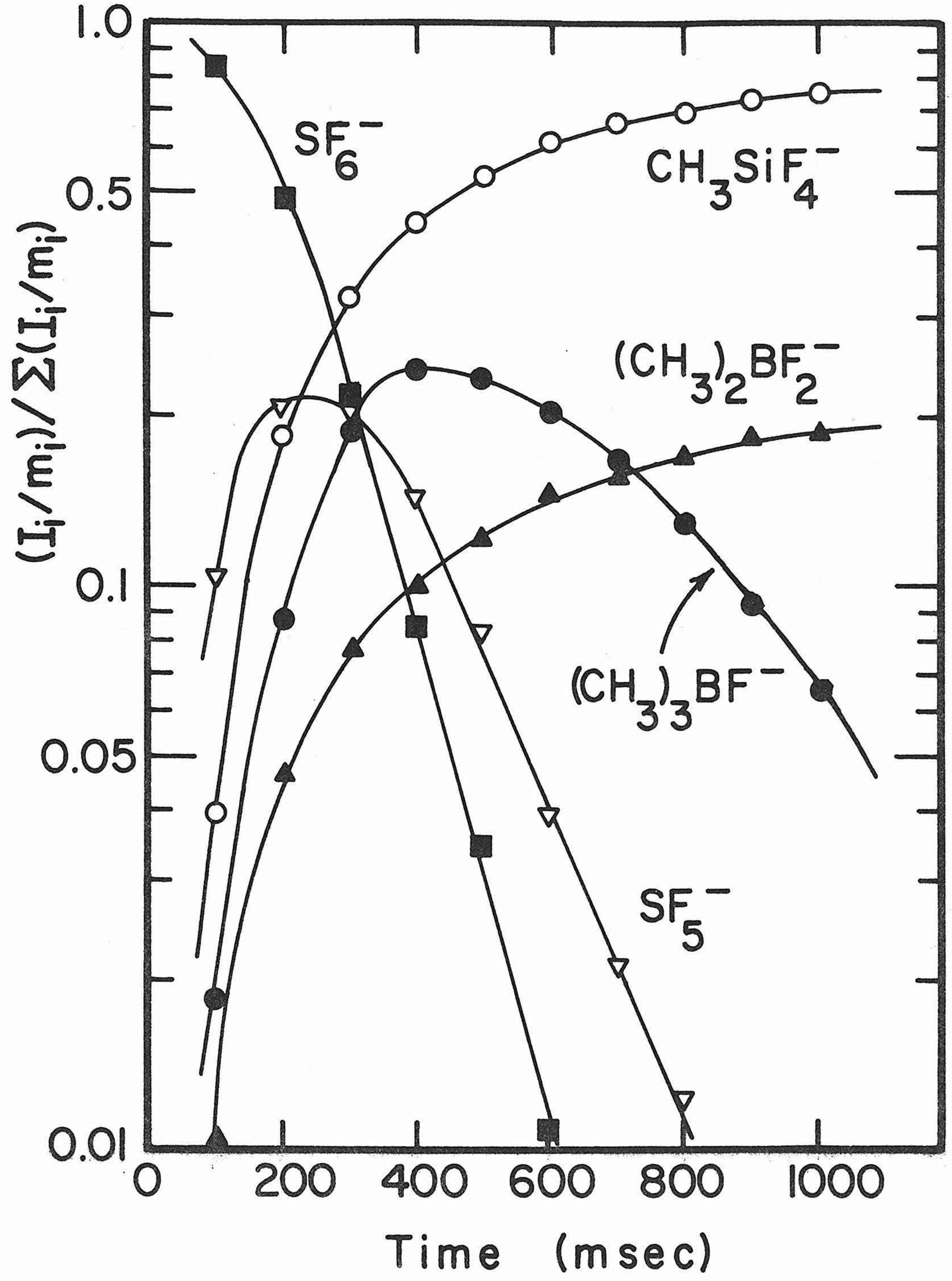

1.0
0.5
0.1
0.05
0.01
0
200
400
Time (msec)
$(I_i/m_i)/\Sigma(I_i/m_i)$
SF_6^-
$(CH_3)_3BF^-$
$(CH_3)_2SiF_3^-$
SF_5^-
$(CH_3)_2BF_2^-$

Figure 5

The temporal variation of trapped-anion abundances following a 10 msec 70 eV electron beam pulse in a 4.4:1 mixture of $(CH_3)_3B$ and CH_3SiF_3 at 5.4×10^{-7} torr in the presence of trace amounts of SF_6.


1.0
0.5
0.1
0.05
0.01
0
200
400
600
800
1000
Time (msec)
$(I_i/m_i)/\sum(I_i/m_i)$
SF_6^-
$CH_3SiF_4^-$
$(CH_3)_2BF_2^-$
$(CH_3)_3BF^-$
SF_5^-

described above and reactions 16-18 previously reported in the $SF_6/B(CH_3)_3$ system,[29, 35] fluoride transfer reaction 20 is observed

$$(CH_3)_3BF^- + CH_3SiF_3 \rightarrow CH_3SiF_4^- + B(CH_3)_3 \qquad (20)$$

in the $SF_6/(CH_3)_3B/CH_3SiF_3$ mixture. $(CH_3)_2BF_2^-$ does not react with CH_3SiF_3. $CH_3SiF_4^-$ is also stable to further reaction in the mixture.

$SF_6/B(C_2H_5)_3/CH_3SiF_3$. In a 1:1 mixture of $(C_2H_5)_3B$ and CH_3SiF_3 at a constant pressure of 7.9×10^{-7} torr containing traces of SF_6, the temporal variation of anion abundances depicted in Figure 6 is initiated by the electron beam pulse. Boron-containing anions, $(C_2H_5)_3BF^-$ and $(C_2H_5)_2BF_2^-$, are initially produced via reactions 21-23, previously

$$SF_6^- + (C_2H_5)_3B \begin{cases} \longrightarrow SF_5^- + HF + (C_2H_5)_2BC_2H_4 & (21) \\ \longrightarrow (C_2H_5)_2BF_2^- + SF_4 + C_2H_5 & (22) \end{cases}$$

$$SF_5^- + (C_2H_5)_3B \longrightarrow (C_2H_5)_3BF^- + SF_4 \qquad (23)$$

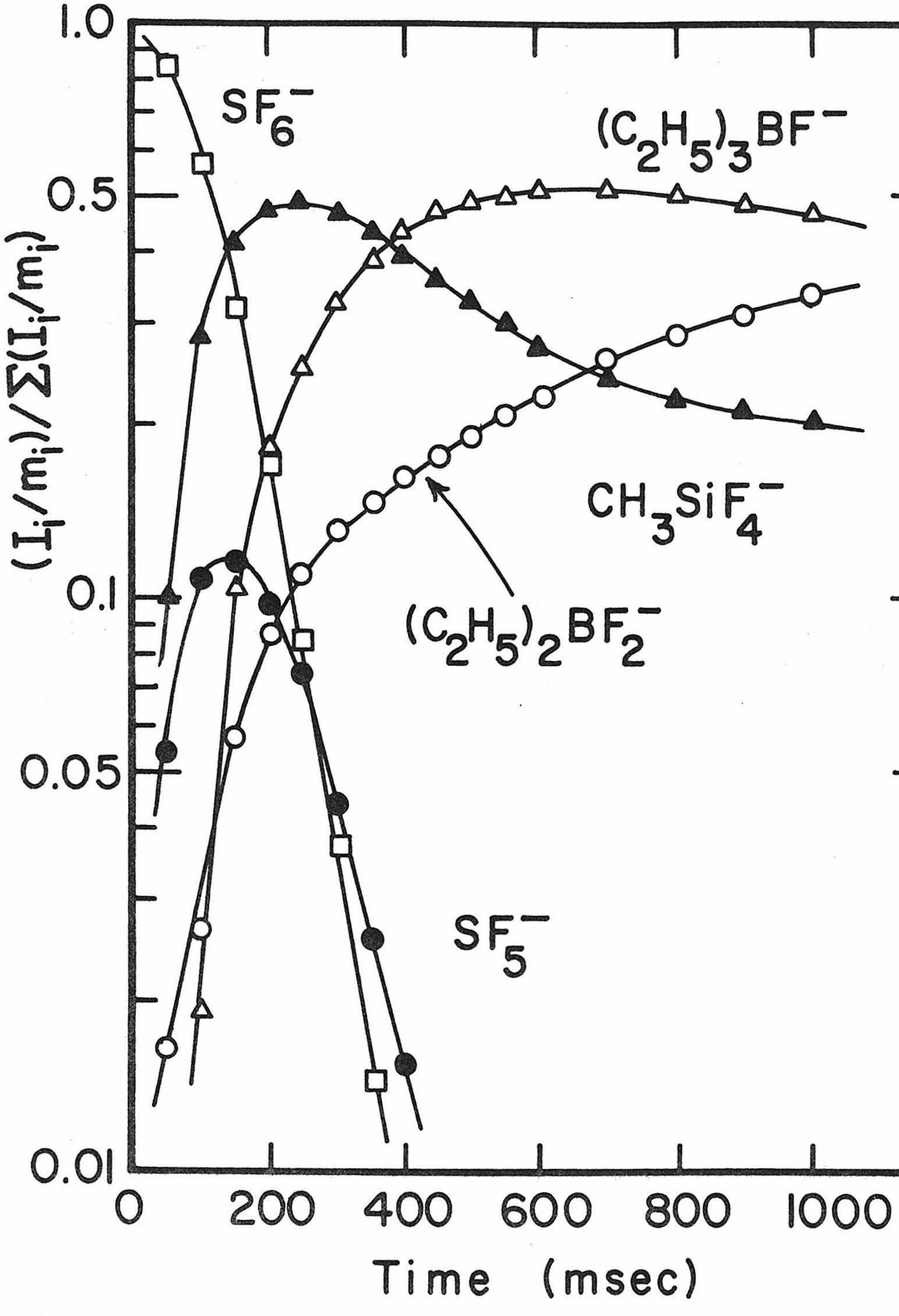
reported from studies of $SF_6/(C_2H_5)_3B$ mixtures.[29] $CH_3SiF_4^-$ is produced, at short reaction times in Figure 6, by processes 6 and 7 described above. For trapping times beyond ~500 msec in Figure 6, the relative concentrations of $(C_2H_5)_3BF^-$ and $CH_3SiF_4^-$ approach a constant ratio of 2.30 ± 0.05. Double resonance indicates that reaction 24

$$CH_3SiF_4^- + (C_2H_5)_3B \rightleftharpoons (C_2H_5)_3BF^- + CH_3SiF_3 \qquad (24)$$

proceeds in both forward and reverse directions. These results suggest that a fluoride transfer equilibrium is established between

Figure 6

The temporal variation of trapped-anion abundances following a 10 msec 70 eV electron beam pulse in a 1:1 mixture of $(C_2H_5)_3B$ and CH_3SiF_3 at 7.9×10^{-7} torr in the presence of trace amounts of SF_6.


1.0
0.5
0.1
0.05
0.01
0
200
400
600
800
1000
Time (msec)
$(I_i/m_i)/\sum(I_i/m_i)$
SF_6^-
$(C_2H_5)_3BF^-$
$CH_3SiF_4^-$
$(C_2H_5)_2BF_2^-$
SF_5^-

$(C_2H_5)_3B$ and CH_3SiF_3 with the balance lying preferentially to the right in reaction 24. The equilibrium constant $K_{eq} = 2.3$ is determined,[38] corresponding to a free energy change $\Delta G = -0.5 \pm 0.1$ kcal/mole. With the conditions used, $(C_2H_5)_2BF_2^-$ is not observed to react further with CH_3SiF_3.

$SF_6/(C_2H_5)_3B/SiF_4$. In trapped-ion experiments on a 5.4:1 mixture of $(C_2H_5)_3B$ and SiF_4 at 1.2×10^{-6} torr in the presence of trace amounts of SF_6, ions SiF_5^-, $(C_2H_5)_3BF^-$ and $(C_2H_5)_2BF_2^-$ are formed initially via processes 4, 5 and 21-23 described above for the individual components. At long reaction times SiF_5^- abundance continues to increase at the expense of $(C_2H_5)_3BF^-$ and $(C_2H_5)_2BF_2^-$. Double resonance indicates the occurrence of rapid fluoride transfer reactions 25 and 26. SiF_5^- eventually comprises ~100% of the ion abundance and is not observed to react further under the present conditions.

$$(C_2H_5)_3BF^- + SiF_4 \rightarrow SiF_5^- + (C_2H_5)_3B \tag{25}$$

$$(C_2H_5)_2BF_2^- + SiF_4 \rightarrow SiF_5^- + (C_2H_5)_2FB \tag{26}$$

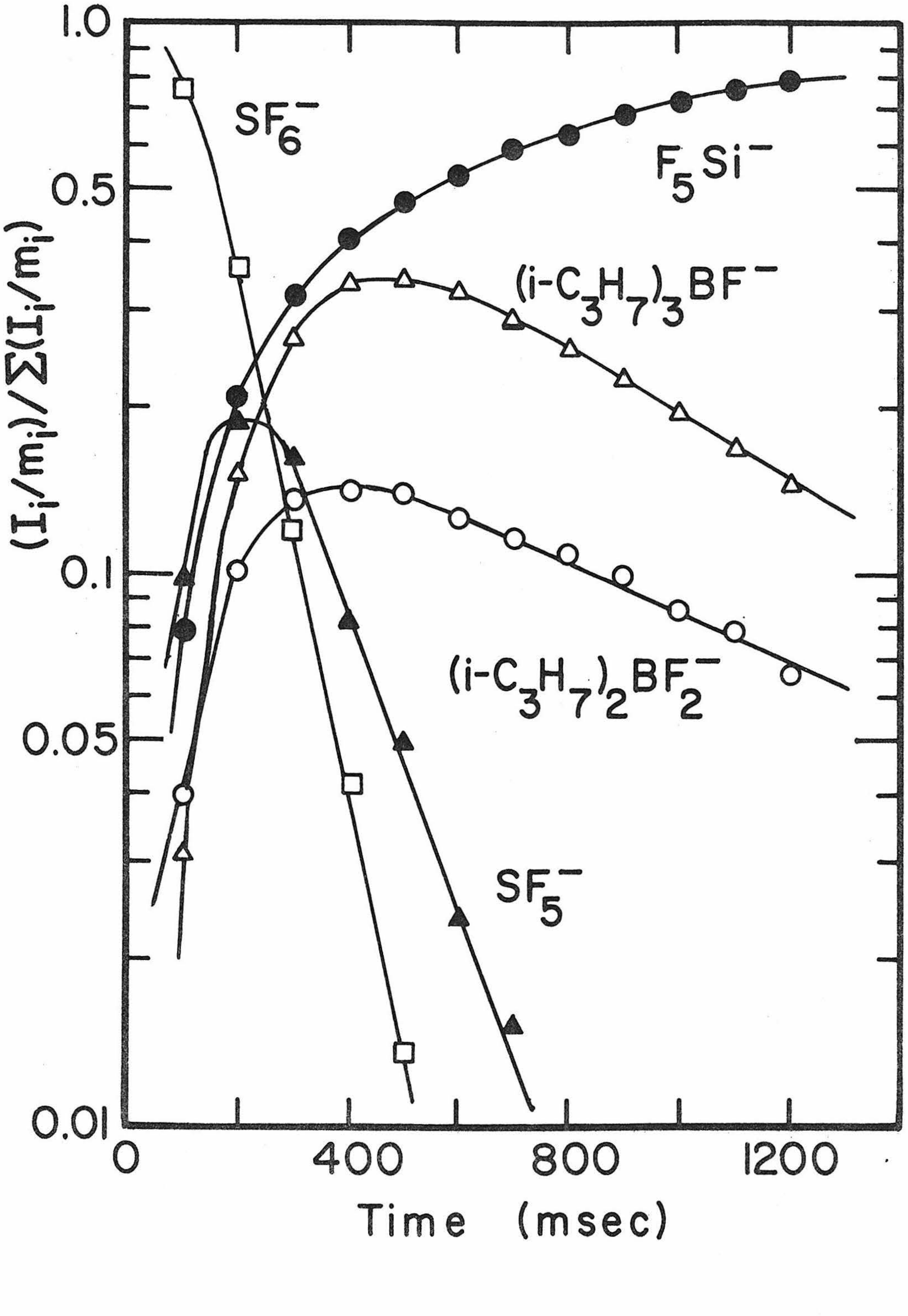
$SF_6/B(i\text{-}C_3H_7)_3/SiF_4$. The temporal variation of ion concentrations following the electron beam pulse in a 3.5:1 mixture of $B(i\text{-}C_3H_7)_3$ and SiF_4 at 9.4×10^{-7} torr total pressure (in the presence of trace SF_6) is displayed in Figure 7. Boron-containing anions are formed initially by reactions 27-29, previously observed in $SF_6/(i\text{-}C_3H_7)_3B$ mixtures.[29]

$$SF_6^- + B(i\text{-}C_3H_7)_3 \rightarrow SF_5^- + HF + (i\text{-}C_3H_7)_2BC_3H_6 \tag{27}$$

$$SF_6^- + B(i\text{-}C_3H_7)_3 \rightarrow (i\text{-}C_3H_7)_2BF_2^- + SF_4 + i\text{-}C_3H_7 \tag{28}$$

Figure 7

The temporal variation of trapped-anion abundances following a 10 msec 70 eV electron beam pulse in a 3.5:1 mixture of $(i\text{-}C_3H_7)_3B$ and SiF_4 at 9.4×10^{-7} torr in the presence of trace amounts of SF_6.


1.0
0.5
0.1
0.05
0.01
0
400
800
1200
Time (msec)
$(I_i/m_i)/\Sigma(I_i/m_i)$
SF_6^-
F_5Si^-
$(i\text{-}C_3H_7)_3BF^-$
$(i\text{-}C_3H_7)_2BF_2^-$
SF_5^-

$$SF_5^- + B(i\text{-}C_3H_7)_3 \rightarrow (i\text{-}C_3H_7)_3BF^- + SF_4 \qquad (29)$$

In addition to processes 4 and 5 described above, SiF_5^- is generated by fluoride transfer reactions 30 and 31 and is not observed to react

$$(i\text{-}C_3H_7)_3BF^- + SiF_4 \rightarrow SiF_5^- + B(i\text{-}C_3H_7)_3 \qquad (30)$$

$$(i\text{-}C_3H_7)_2BF_2^- + SiF_4 \rightarrow SiF_5^- + (i\text{-}C_3H_7)_2FB \qquad (31)$$

further under the present conditions.

$SF_6/BF_3/CH_3SiF_3$. In trapped-ion experiments on a 1.1:1 mixture of CH_3SiF_3 and BF_3 at 1.2×10^{-6} torr pressure containing trace amounts of SF_6, $CH_3SiF_4^-$ is produced initially via reactions 6 and 7 described above and BF_4^- is generated by previously reported processes 32 and 33.[27, 29, 33a] BF_4^- is produced by fluoride transfer from $CH_3SiF_4^-$ (reaction 34). No evidence is obtained for the reverse of

$$SF_6^- + BF_3 \rightarrow BF_4^- + SF_5 \qquad (32)$$

$$SF_5^- + BF_3 \rightarrow BF_4^- + SF_4 \qquad (33)$$

$$CH_3SiF_4^- + BF_3 \rightarrow BF_4^- + CH_3SiF_3 \qquad (34)$$

reaction 34, and BF_4^- appears stable to further reaction under the conditions utilized.

$SF_6/BF_3/SiF_4$. In an ~1:1 mixture of SiF_4 and BF_3 at $\sim 1 \times 10^{-6}$ torr pressure in the presence of trace amounts of SF_6, fluoride transfer reactions 4, 5, 32, and 33 described above lead to the formation of SiF_5^- and BF_4^-. Although experimental difficulties in maintaining stable gas pressures in this mixture[37] inhibit detailed examination of the reaction kinetics, it is clear that fluoride transfer from SiF_5^- to BF_3 (reaction 35) proceeds rapidly to completion. No evidence is

$$SiF_5^- + BF_3 \rightarrow BF_4^- + SiF_4 \qquad (35)$$

obtained for the back reaction and BF_4^- does not appear to react further under the present conditions.

Discussion

SF_6^-, $SF_5^-/(CH_3)_nF_{4-n}Si$, (n = 0-3). Observations of pentacoordinate anions SiF_5^-, $CH_3SiF_4^-$ and $(CH_3)_2SiF_3^-$ formed by fluoride transfer reactions, between the respective neutral silanes and SF_6^- and SF_5^- (Table I), are in agreement with previous studies.[26] However, under no conditions was fluoride transfer to $(CH_3)_3SiF$ observed in the present work. The discrepancy between this result and the observations of Dillard[26] are not fully understood, although differences in the energy of reactants SF_6^- and SF_5^- between the two studies may be responsible. In trapped-ion ICR, inelastic collisions with neutral molecules during the long trapping times effectively thermalize the ions. Thus, reactions observed are assumed to be exothermic or thermoneutral for thermal energy reactants.

Reactions 5, 7, and 10 require that the fluoride affinities of $(CH_3)_2SiF_2$, CH_3SiF_3, and SiF_4 exceed ~ 54 kcal/mole, the value previously reported[28a] for $D[SF_4{-}F^-]$. Failure to detect $(CH_3)_3SiF_2^-$ by reaction with SF_6^- implies that $D[(CH_3)_3FSi{-}F^-] < D[SF_5{-}F^-] = 11 \pm 8$ kcal/mole,[28a] a drastic decrease in Lewis acidity of $(CH_3)_3SiF$

as compared with the more highly fluorinated silanes. It is possible that fluoride transfer from SF_6^- to $(CH_3)_3SiF$ is not observed due to kinetic rather than thermodynamic effects.[28a] The fluoride affinity of SO_2, though not known precisely, is very near that of SF_4.[27, 28a] Failure to observe $(CH_3)_3SiF_2^-$ by reaction of SO_2F^- or SF_5^- requires that $D[(CH_3)_3FSi-F^-]$ be less than 54 kcal/mole.

SF$_6$/Silane Mixtures. Reactions 13, 14, and 15 imply the order of Lewis acidities $(CH_3)_3SiF < (CH_3)_2SiF_2 < CH_3SiF_3 < SiF_4$. As previously observed in studies of anion transfer processes in borane Lewis acids,[29, 35] alkyl substitution in place of fluorine α to the acceptor center results in decreased acidity.

SF$_6$/Silane-Borane Mixtures. The fluoride affinity of SiF_4 is known from previous studies to be below that of BF_3 (71 kcal/mole).[27] Quantification of the fluoride affinities of $(CH_3)_2SiF_2$, CH_3SiF_3, and SiF_4, within the 17 kcal range bracketed by SF_4 and BF_3, is obtained from the preferred directions of fluoride transfer reactions with borane Lewis acids previously shown to span this same fluoride affinity range.[29] Taken collectively with previous results,[29] these reactions (Table I) establish the fluoride affinity order $(CH_3)_3SiF < SF_4 < (CH_3)_2SiF_2 < (CH_3)_3B < CH_3SiF_3 < (CH_3)_2FB < (C_2H_5)_3B < (C_2H_5)_2FB < (i\text{-}C_3H_7)_3B < (i\text{-}C_3H_7)_2FB < SiF_4 < BF_3$ in the gas phase. Only in the case of reaction 24 in the $SF_6/(C_2H_5)_3B/CH_3SiF_3$ system is evidence of an equilibrium obtained.

Thermochemical Considerations. The observed $K_{eq} = 2.3$ favoring fluoride bound to $(C_2H_5)_3B$ requires that a free energy change of ~0.5 kcal/mole accompany reaction 24. Trapped-ion ICR techniques are generally able to provide accurate determinations of similar anion transfer equilibria and associated free energy changes up to values of ~3 kcal/mole. Larger free energy changes yield equilibrium constants (and forward and reverse rate constants) exceeding the dynamic range of the technique.

Considering the relative order of fluoride affinities stated above, it is noteworthy that reactions 14, 19, and 30 proceed only in the forward direction. This conclusion is apparent from data in Figures 3, 4, and 7 and the failure to detect the reverse reactions by double resonance. The ratios of reactant and product ions at long times and ratios of neutral acid pressures place lower limits on K_{eq} of > 83.2, > 34.9, and > 18.9 for reactions 14, 19, and 30, respectively, corresponding to free energy changes of < -2.6, < -2.1, and < -1.7 kcal/mole. Similar limits apply to reactions 15 and 30.

A quantity more relevant to discussion of adduct bond energies $D[A\text{–}F^-]$ is the enthalpy change ΔH, which is related to the free energy change $\Delta G = \Delta H - T\Delta S = -RT \ln K_{eq}$. The present ICR instrumentation is limited to measurements at ambient temperatures, precluding experimental determination of ΔH from variations of K_{eq} and thus ΔG with temperature. Within reasonable assumptions, the statistical mechanical formalism of Searles and Kebarle[39] may be used to estimate that ΔS for reaction 24 is negligible. Thus $\Delta H \cong -0.5$ kcal/mole for fluoride transfer from $CH_3SiF_4^-$ to $(C_2H_5)_3B$.

Evaluation of the present results along with the results of the previous study of the boranes,[29] assuming a minimum separation of ~ 3 kcal/mole in cases where no reverse reactions were evidenced, affords a quantitative scale of fluoride affinities, which is fully consistent with all available data, as displayed schematically in Figure 8. Using available thermochemical data (Table II) and estimates of 68, 61.5, and 55.5 kcal/mole for the fluoride affinities of SiF_4, CH_3SiF_3, and $(CH_3)_2SiF_2$, heats of formation for the silane-fluoride Lewis adduct anions can be derived (Table III). Taking -3, -0.5, and -3 kcal/mole for the enthalpy changes for reactions 19, 24, and 35, respectively, yields estimates of ΔH_f $(CH_3)_2SiF_3^-$ = -328.5, ΔH_f $CH_3SiF_4^-$ = -418.5, and ΔH_f SiF_5^- = -515.3 kcal/mole. Failure to observe $(CH_3)_3SiF_2^-$ by reaction of $(CH_3)_3SiF$ with SF_5^- or SO_2F^- requires that ΔH_f $(CH_3)_3SiF_2^-$ exceed -241.0 kcal/mole. Thermochemical data describing the neutral silane Lewis acids and fluoride adducts are summarized in Table III.

Substituent Effects on Silane Lewis Acidity. From the data in Figure 8 and Table III, which quantitatively describe the gas phase Lewis acidities of the fluoromethylsilanes with fluoride ion as the reference base, it is apparent that the intrinsic acceptor strengths (measured as fluoride affinities, $D[A-F^-]$) of borane and silane Lewis acids are quite comparable in absolute magnitude. The effects of fluorine and alkyl substituents on boron and silicon follow similar trends, namely that alkyl groups lower the acidity relative to fluorine substituents. Alkyl groups appear to more strongly destabilize the silane-fluoride relative to the borane-fluoride adducts (Figure 8). In

Figure 8

Schematic representation of Lewis acidities of neutral acceptors A using F^- ion as reference base (expressed as fluoride affinities $D[A-F^-]$).

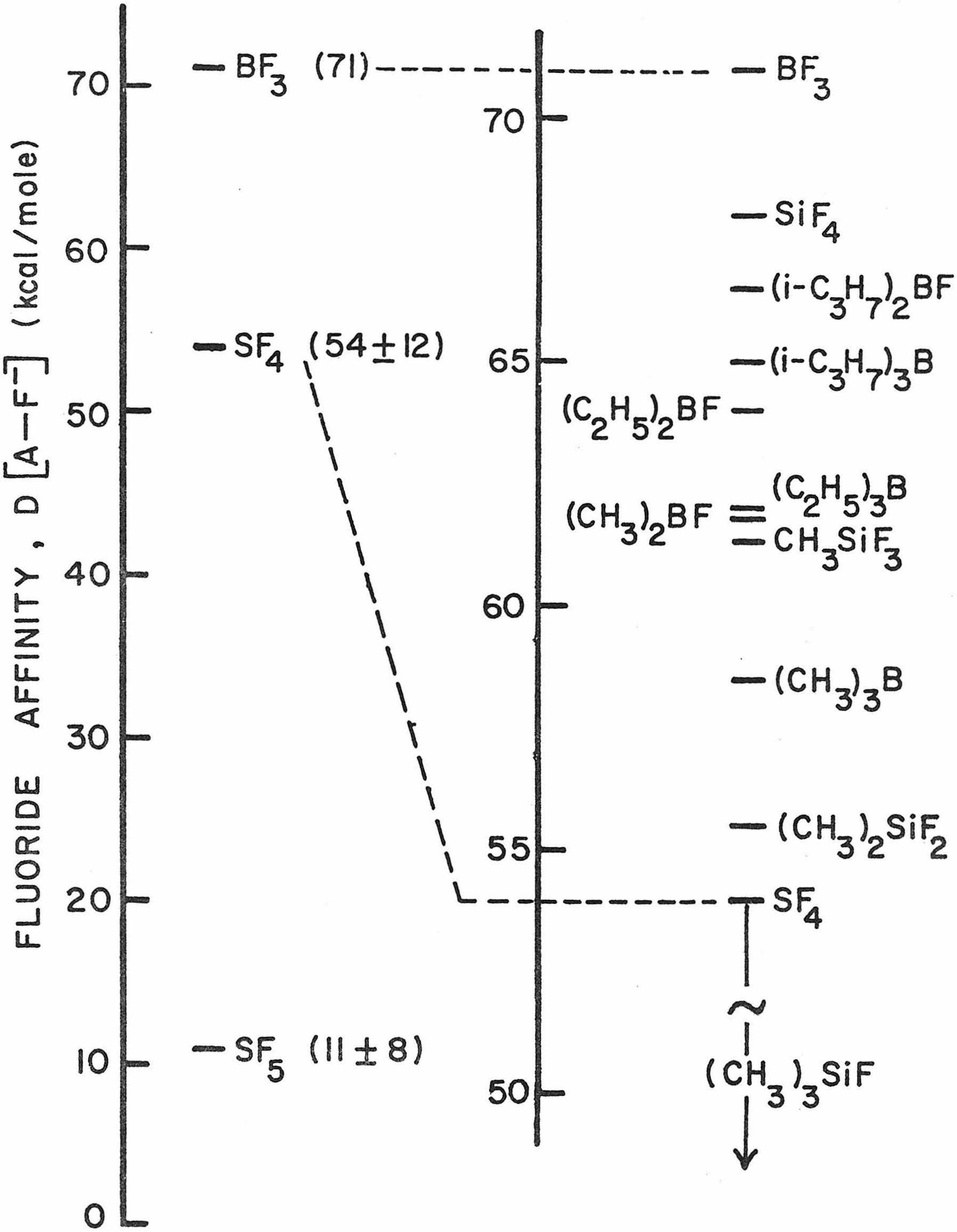

FLUORIDE AFFINITY, D [A—F⁻] (kcal/mole)
0
10
20
30
40
50
60
70
BF3 (71)
SF4 (54 ± 12)
SF5 (11 ± 8)
70
65
60
55
50
BF3
SiF4
(i-C3H7)2BF
(i-C3H7)3B
(C2H5)2BF
(C2H5)3B
(CH3)2BF
CH3SiF3
(CH3)3B
(CH3)2SiF2
SF4
(CH3)3SiF

Table II. Thermochemical Quantities[a] Utilized in the Calculations

A	ΔH_f (A)	D[A–F$^-$]
SF_4	-183 ± 6[b]	54 ± 12[b]
SF_5	-232 ± 4[b]	11 ± 8[b]
SF_5^-	-298 ± 6	---
SF_6^-	-304.4 ± 3.5[b]	---
CH_3F	- 55.9[c]	---
HF	- 64.9 ± 0.3[b]	---
CH_3SiF_2	-166.0[d]	---
$(CH_3)_3SiF$	-126.0[d]	---
$(CH_3)_2SiF_2$	-212.0[d]	---
CH_3SiF_3	-296.0[d]	---
SiF_4	-386.0[d]	< 71[f]
$(CH_3)_3B$	- 29.3[e]	58.5[e]
$(CH_3)_2FB$	⩽ - 61.9[e]	61.8[e]
$(C_2H_5)_3B$	- 36.0[e]	62.0[e]
$(C_2H_5)_2FB$	⩽ - 58.1[e]	64.0[e]
$(i\text{-}C_3H_7)_3B$	- 56.3[e]	65.0[e]
$(i\text{-}C_3H_7)_2FB$	⩽ - 67.5[e]	66.5[e]
BF_3	-271.7[e]	71[f]
BF_4^-	-404.0[e]	---
F^-	- 61.3 ± 0.3[b]	---

[a] All data are in units of kcal/mole at 298°K.

[b] Taken from Ref. 28a.

[c] Taken from Ref. 44.

[d] Taken from Ref. 45.

[e] Taken from Ref. 29.

[f] Taken from Ref. 27.

Table III. Thermochemical Quantities[a] Describing Ions and Neutrals of Silicon

Acid, A	$D[A{-}F^-]$[b]	$\Delta H_f[A]$[c]	$\Delta H_f[AF^-]$[d]
SiF_4	68.0	-386.0	-515.3[e]
CH_3SiF_3	61.5	-296.0	-418.5[f]
$(CH_3)_2SiF_2$	55.5	-212.0	-328.5[g]
$(CH_3)_3SiF$	$<$ 54	-126.0	$>$ -241.0[h]

[a] All data are in units of kcal/mole at 298 °K.

[b] Bond dissociation energies determined as specified in the text.

[c] Heats of formation of the silanes taken from Ref. 50.

[d] Calculated using data in Table II and this table.

[e] Calculated from $\Delta H_f[SiF_5^-] = \Delta H_f[SiF_4] + \Delta H_f[BF_4^-] - \Delta H_f[BF_3] - \Delta H_r$, where $\Delta H_r = -3$ kcal/mole for reaction 35.

[f] Calculated from $\Delta H_f[CH_3SiF_4^-] = \Delta H_f[CH_3SiF_3] + \Delta H_f[(C_2H_5)_3BF^-] - \Delta H_f[(C_2H_5)_3B] - \Delta H_r$, where $\Delta H_r = -0.5$ kcal/mole for reaction 24.

[g] Calculated from $\Delta H_f[(CH_3)_2SiF_3^-] = \Delta H_f[(CH_3)_3BF^-] + \Delta H_f[(CH_3)_2SiF_2] - \Delta H_f[(CH_3)_3B] - \Delta H_r$, where $\Delta H_r = -3$ kcal/mole for reaction 19.

[h] Estimated from $\Delta H_f[(CH_3)_3SiF_2^-] > \Delta H_f[SF_5^-] + \Delta H_f[(CH_3)_3SiF] - \Delta H_f[SF_4]$ from failure to observe F^- transfer from SF_5^- to $(CH_3)_3SiF$.

contrast to the present results, adduct strengths of these same silanes toward $(CH_3)_3N$ as reference base have been previously shown to be much lower than those for borane Lewis acids.[22b] Measurements of gas phase dissociation equilibria for processes such as (1) where $B = (CH_3)_3N$ indicate a Lewis acidity order $(CH_3)_3B \gg SiF_4 \gg CH_3SiF_3$.[19-21, 22b, 40] The steric requirements of the bulky amine base clearly have a marked effect on the stability of adducts with the silanes. Attenuation of steric effects are expected for adducts involving the smaller monoatomic fluoride ion as reference base.

Upon replacement of F by CH_3, the fluoride affinity of CH_3SiF_3 is decreased by ~ 6.5 kcal/mole relative to that of SiF_4. Similarly, $(CH_3)_2SiF_2$ binds F^- ~ 6 kcal/mole less strongly than does CH_3SiF_3. While the actual value of the fluoride affinity of $(CH_3)_3SiF$ is yet to be determined, the failure to observe F^- transfer from SF_6^- $\{D[SF_5{-}F^-] = 11 \pm 8$ kcal/mole[28a]$\}$ implies a dramatic decrease in acceptor strength of ~ 40 kcal/mole resulting from substitution of a third CH_3 for F on silicon.

Methyl substituent effects on the stability of pentacoordinate fluoromethylsilyl anions observed in the present work have interesting analogies in the isoelectronic neutral methylfluorophosphorane series PF_5, CH_3PF_4, $(CH_3)_2PF_3$, and $(CH_3)_3PF_2$.[41, 42] The species $(CH_3)_4PF$ is unknown and it has been proposed that this least stable member of the phosphorane series would better be described as an ionic phosphorium salt $[(CH_3)_4P]^+F^-$.[42] By a variety of spectroscopic techniques, it has been conclusively demonstrated that the phosphoranes have trigonal-bipyramidal geometry with the less electronegative organic groups preferentially occupying equatorial sights.[41] Apical metal-substituent bond lengths are substantially longer than bonds at equatorial positions. Low temperature ^{1}H and ^{19}F NMR spectra of SiF_5^-, $CH_3SiF_4^-$ and $(C_6H_5)SiF_4^-$ in low polarity solvents[24] indicate that these fluorosilicate anions also have trigonal-bipyramidal structures with the organic groups occupying equatorial sights. This positional preference, governed primarily by differences in substituent electronegativity, has previously been termed "the polarity rule" and is known to be general to a variety of trigonal-bipyramidal complexes.[5, 41]

Analogous to the present observations of decreasing silane-fluoride bond strengths accompanying successive substitution of CH_3 for F, axial P—F bonds are known to lengthen and weaken in going from PF_5 to CH_3PF_4, $(CH_3)_2PF_3$, and $(CH_3)_3PF_2$.[41, 42] Under the influence of the electrostatic field imposed by a trigonal-bipyramidal array of electronegative fluorine substituents, the $3d_{z^2}$ orbital contracts sufficiently to make its inclusion in the bonding energetically favorable.[42, 43] Successive replacement of F by the more electropositive CH_3 would result then in a concommitant decrease in the net positive character of the central atom and lead to a gradual withdrawal of the d orbitals from the bonding scheme. Ultimately the five-coordinate trigonal-bipyramidal structure would cease to be energetically attractive.[42] In the pentacoordinate silicon anions, the $3d_{z^2}$ orbital is probably much more diffuse than in the neutral phosphorus compounds. Thus, abrupt decrease in stability of the adducts occurs upon substitution of just three CH_3 groups on the central atom.

References and Notes

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(38) For an equilibrium such as reaction 2, $K_{eq} = [A_2B][A_1]/[A_1B][A_2]$; for reaction 24 $[A_1B]$ and $[A_2B]$ are the ion abundances of $CH_3SiF_4^-$ and $(C_2H_5)_3BF^-$, respectively, from data at long time in Figure 6 and A_1 and A_2 are the pressures of neutrals CH_3SiF_3 and $(C_2H_5)_3B$, respectively.

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