inherent in the data but also because the results are somewhat sensitive to the ratio of hydroxo to aquo proton coupling constants, a^B/a^C. If we assume a coupling of 1.1 G for the aquo protons (the value found for $VO(H_2O)_5^{2+}$)[21] then the hydroxo proton coupling which best fits the line width data is about 4.4 G, corresponding to an average coupling of 3.1 G.

The ^2H NMR line widths provide an independent check on the conclusions drawn from the ^1H NMR and ESR experiments. Equation 9a can be used to calculate the ^2H normalized line widths, $PT_{2p}{}^D$, from τ_m and $T_{2C}{}^D$, data entirely independent of the ^2H NMR results. Values of τ_m were obtained from the ^1H NMR data as described above; values of $T_{2C}{}^D$ were computed from the ESR data and the assumption that $A_C{}^D = 4.9 \times 10^5$ Hz and are given in Table II. $PT_{2p}{}^D$ was computed for various assumed values of R ranging from 1 to 20. The best overall fit was for $R = 16$, corresponding to $A^B/A^C = 4.0$, in remarkable agreement with the virtually identical conclusion reached from the ESR line width analysis. Furthermore, the normalized widths obtained for $R = 16$ are plotted as the dashed curve of Figure 3 and are seen to be in excellent agreement with the experimental values. The success in predicting the ^2H normalized widths, while probably not absolutely conclusive, does give us considerably greater confidence in the procedures used to obtain the rate constants and in the conclusions reached regarding the ligand proton hyperfine coupling.

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Registry No. $VO(OH)_3(H_2O)_2^-$, 56586-21-1.

Supplementary Material Available: A derivation of eq 7 and the procedure for corrections of inhomogeneously broadened lines (5 pages). Ordering information is given on any current masthead page.

References and Notes

(1) M. M. Iannuzzi and P. H. Rieger, *Inorg. Chem.*, **14**, 2895 (1975).
(2) M. M. Iannuzzi, C. P. Kubiak, and P. H. Rieger, *J. Phys. Chem.*, **80**, 541 (1976).
(3) J. Reuben and D. Fiat, *Inorg. Chem.*, **6**, 579 (1967); K. Wüthrich and R. E. Connick, *ibid.*, **6**, 583 (1967).
(4) E. Grunwald and D.-W. Fong, *J. Am. Chem. Soc.*, **94**, 7371 (1972).
(5) B. F. Melton and V. L. Pollack, *J. Phys. Chem.*, **73**, 3669 (1969).
(6) J. Reuben and D. Fiat, *J. Am. Chem. Soc.*, **91**, 4652 (1969).
(7) R. R. Reeder and P. H. Rieger, *Inorg. Chem.*, **10**, 1258 (1971).
(8) A. L. Van Geet, *Anal. Chem.*, **42**, 679 (1970).
(9) The results of the ESR intensity vs. [V(IV)] experiment reported in ref 1 are in error by a factor of 10; ESR intensity was linear in [V(IV)] up to about 1.5 mM.
(10) C. Weiske, Dissertation, Technischen Universität Berlin, 1960.
(11) Supplementary material.
(12) R. Wilson and D. Kivelson, *J. Chem. Phys.*, **44**, 154 (1966).
(13) D. Kivelson, *J. Chem. Phys.*, **33**, 1094 (1960).
(14) P. W. Atkins and D. Kivelson, *J. Chem. Phys.*, **44**, 169 (1966).
(15) M. Eigen, W. Kruse, G. Maas, and L. De Maeyer, *Prog. React. Kinet.*, **2**, 285 (1964).
(16) T. J. Swift and R. E. Connick, *J. Chem. Phys.*, **37**, 307 (1962).
(17) J. Reuben and D. Fiat, *J. Am. Chem. Soc.*, **91**, 1242 (1969).
(18) B. M. Fung, *J. Chem. Phys.*, **58**, 192 (1972).
(19) A. Johnson and G. W. Everett, Jr., *J. Am. Chem. Soc.*, **94**, 1419 (1972).
(20) G. W. Everett, Jr., and A. Johnson, *J. Am. Chem. Soc.*, **94**, 6398 (1972).
(21) J. Reuben and D. Fiat, *Inorg. Chem.*, **8**, 1821 (1969).
(22) P. S. Hubbard, *Phys. Rev.*, **131**, 1155 (1963).
(23) T. A. Stephenson, T. J. Swift, and J. B. Spencer, *J. Am. Chem. Soc.*, **90**, 4291 (1968).
(24) T. J. Swift, T. A. Stephenson, and G. R. Stein, *J. Am. Chem. Soc.*, **89**, 1611 (1967).
(25) R. P. Bell, "The Proton in Chemistry", Cornell University Press, Ithaca, N.Y., 1973, p 194.
(26) D.-W. Fong and E. Grunwald, *J. Am. Chem. Soc.*, **91**, 2413 (1969).
(27) K. Wüthrich and R. E. Connick, *Inorg. Chem.*, **7**, 1377 (1968).
(28) A. H. Zeltmann and L. O. Morgan, *Inorg. Chem.*, **10**, 2739 (1971).
(29) M. W. Kendig and P. H. Rieger, *Inorg. Chim. Acta*, **17**, 175 (1976).

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Fluorine and Alkyl Substituent Effects on the Gas-Phase Lewis Acidities of Boranes by Ion Cyclotron Resonance Spectroscopy

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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-C_3H_7, and F) is 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

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

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

bond energies $D[A\text{–}B]$ and provide a methodology suitable 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] c-$C_5H_5Ni^+$[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 eq 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 (reaction 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 eq 2, thus providing a suitable methodology for the investigation of substituent effects on the Lewis acidity of neutral alkylboranes. 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 of formation of the various boron-containing anions and neutrals are derived.

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

Experimental Section

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 in. 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 vs. 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 semilog plots of trapped-ion abundance vs. 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} to 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 were 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-ms electron beam pulse.[12,16-18] SF_6 is present only in trace concentration (~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.

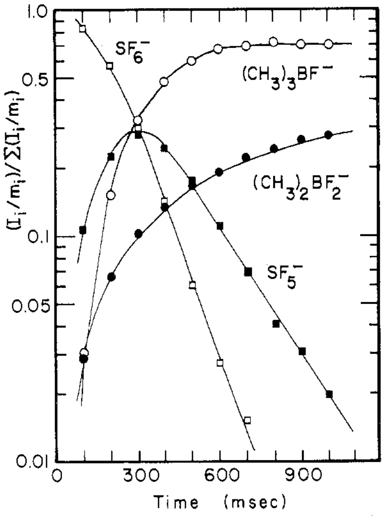

Figure 1. Temporal variation of trapped-anion abundances initiated by a 10-ms 70-eV electron beam pulse in 4.8 × 10^{-7} Torr $(CH_3)_3B$ in the presence of traces of SF_6.

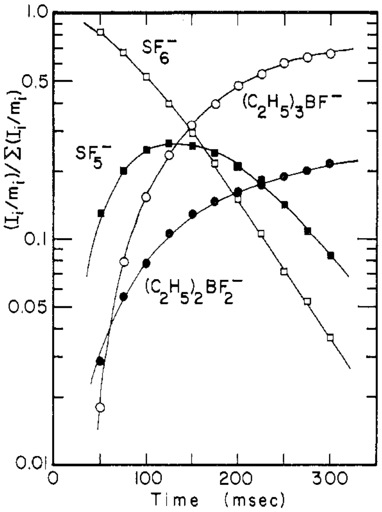

Figure 2. Temporal variation of trapped-anion abundances initiated by a 10-ms 70-eV electron beam pulse in 1.0 × 10^{-6} Torr $(C_2H_5)_3B$ in the presence of traces of SF_6.

Reactions of anions derived from SF_6 with each of the trialkylboranes R_3B (R = CH_3, C_2H_5, i-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 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 $(CH_3)_3B$.

$$SF_6^- + (CH_3)_3B \xrightarrow{72\%} SF_5^- + HF + (CH_3)_2BCH_2 \tag{4}$$

$$SF_6^- + (CH_3)_3B \xrightarrow{28\%} (CH_3)_2BF_2^- + SF_4 + CH_3 \tag{5}$$

$$SF_5^- + (CH_3)_3B \rightarrow (CH_3)_3BF^- + SF_4 \tag{6}$$

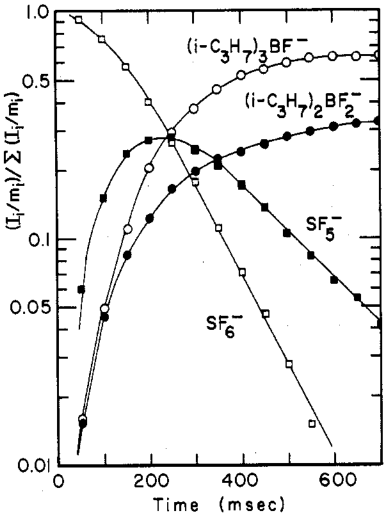

Figure 3. Temporal variation of trapped-anion abundances initiated by a 10-ms 70-eV electron beam pulse in 7.1 × 10^{-7} Torr $(i\text{-}C_3H_7)_3B$ in the presence of traces of SF_6.

$SF_6/(C_2H_5)_3B$. 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 processes observed in trimethylborane,

$$SF_6^- + (C_2H_5)_3B \begin{cases} \xrightarrow{76\%} SF_5^- + HF + (C_2H_5)_2BC_2H_4 & (7) \\ \xrightarrow{24\%} (C_2H_5)_2BF_2^- + SF_4 + C_2H_5 & (8) \end{cases}$$

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

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

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

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

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/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 observed formation of SF_5^- in

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

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

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.

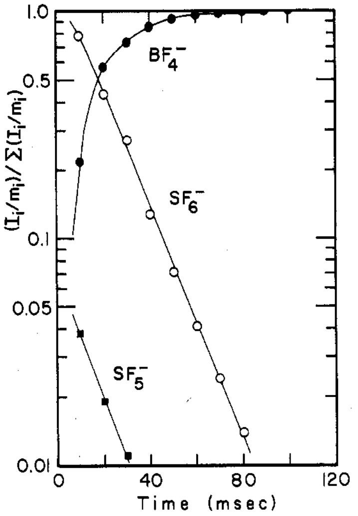

Figure 4. Temporal variation of trapped-anion abundances initiated by a 10-ms 70-eV electron beam pulse in 1.5 × 10^{-6} Torr BF_3 in the presence of traces of SF_6.

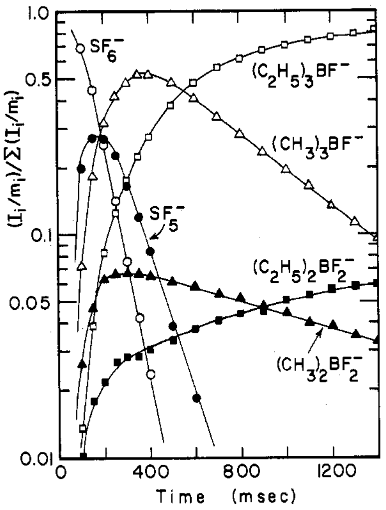

Figure 5. Temporal variation of trapped-anion abundances initiated by a 10-ms 70-eV electron beam pulse in a 3:1 mixture of $(CH_3)_3B$ and $(C_2H_5)_3B$ at 9.6 × 10^{-7} Torr in the presence of traces of SF_6.

$SF_6/(CH_3)_3B/(C_2H_5)_3B$. 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 $(CH_3)_3BF^-$ 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.

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

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

$SF_6/(C_2H_5)_3B/(i\text{-}C_3H_7)_3B$. 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, $(C_2H_5)_3BF^-$, $(C_2H_5)_2BF_2^-$, $(i\text{-}C_3H_7)_3BF^-$,

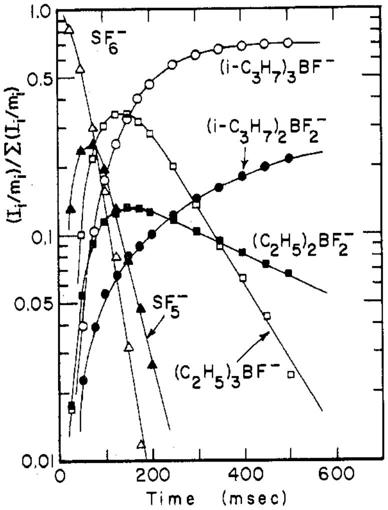

Figure 6. Temporal variation of trapped-anion abundances initiated by a 10-ms 70-eV electron beam pulse in a 2.2:1 mixture of $(C_2H_5)_3B$ and $(i\text{-}C_3H_7)_3B$ at 2.0 × 10^{-6} Torr in the presence of traces of SF_6.

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.

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

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

$(i\text{-}C_3H_7)_3BF^-$ and $(i\text{-}C_3H_7)_2BF_2^-$ do not react further under these conditions.

$SF_6/BF_3/(i\text{-}C_3H_7)_3B$. In an ~1:1 mixture of BF_3 and $(i\text{-}C_3H_7)_3B$ at ~1 × 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.

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

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

Discussion

SF_6/R_3B 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 eq 21–23 and terminates in formation of stable borane–fluoride Lewis adducts (where R = CH_3, C_2H_5, and $i\text{-}C_3H_7$; R′ = R − H).

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

$$SF_5^- + R_3B \rightarrow R_3BF^- + SF_4 \tag{23}$$

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 eq 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_2H, H_2S, and $(CH_3)_2SiF_2$).[14c,19] Interestingly, reactions analogous to eq 21 do not occur with H_2O, CH_3OH, C_2H_5OH, or with simple alkanes.[19]

Processes 22 yield the dialkylfluoroborane–fluoride adducts R_2FBF^- 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., $D[R_2FB\text{–}F^-] > D[R_3B\text{–}F^-]$).

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 eq 22 (where R = F).

SF_6/R_3B, R'_3B 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 eq 24 and 25, are observed in binary mixtures of the boranes (reactions 15–20).

$$R_3BF^- + R'_3B \rightarrow R'_3BF^- + R_3B \tag{24}$$

$$R_2FBF^- + R'_3B \rightarrow R'_3BF^- + R_2FB \tag{25}$$

These 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. Consideration of the energetics of observed exothermic reactions generalized in eq 21–23 yields 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.

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/mol,[20] respectively. Using the group additivity method of Benson,[21] $\Delta H_f°$ values of −29.3, −36.0, and −56.3 kcal/mol, respectively, are calculated (with uncertainty estimates of ±3 kcal/mol). 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 $\Delta H_f°$ values are within the quoted uncertainties. In the absence of more precise experimental determinations,

Table I. Ion–Molecule Processes Observed

Reaction	No.[a]	Rate const,[b] *k*	Thermochemical implications
	$SF_6/(CH_3)_3B$ System		
$SF_6^- + (CH_3)_3B \xrightarrow{72\%} SF_5^- + HF + (CH_3)_2BCH_2$	4	3.7	
$\xrightarrow{28\%} (CH_3)_2BF_2^- + SF_4 + CH_3$	5	1.4	
$SF_5^- + (CH_3)_3B \rightarrow (CH_3)_3BF^- + SF_4$	6	2.8	$D[(CH_3)_3B\text{–}F^-] > D[SF_4\text{–}F^-]$
$(CH_3)_2BF_2^- + (CH_3)_3B \not\rightarrow (CH_3)_3BF^- + (CH_3)_2BF$	*c*	<0.01	$D[(CH_3)_2FB\text{–}F^-] > D[(CH_3)_3B\text{–}F^-]$
	$SF_6/(C_2H_5)_3B$ System		
$SF_6^- + (C_2H_5)_3B \xrightarrow{76\%} SF_5^- + HF + (C_2H_5)_2BCHCH_3$	7	3.2	
$\xrightarrow{24\%} (C_2H_5)_2BF_2^- + SF_4 + C_2H_5$	8	1.1	
$SF_5^- + (C_2H_5)_3B \rightarrow (C_2H_5)_3BF^- + SF_4$	9	2.7	$D[(C_2H_5)_3B\text{–}F^-] > D[SF_4\text{–}F^-]$
$(C_2H_5)_2BF_2^- + (C_2H_5)_3B \rightarrow (C_2H_5)_3BF^- + (C_2H_5)_2BF$	*c*	<0.01	$D[(C_2H_5)_2FB\text{–}F^-] > D[(C_2H_5)_3B\text{–}F^-]$
	$SF_6/(i\text{-}C_3H_7)_3B$ System		
$SF_6^- + (i\text{-}C_3H_7)_3B \xrightarrow{70\%} SF_5^- + HF + (i\text{-}C_3H_7)_2BC(CH_3)_2$	10	2.5	
$\xrightarrow{30\%} (i\text{-}C_3H_7)_2BF_2^- + SF_4 + i\text{-}C_3H_7$	11	1.2	
$SF_5^- + (i\text{-}C_3H_7)_3B \rightarrow (i\text{-}C_3H_7)_3BF^- + SF_4$	12	3.8	$D[(i\text{-}C_3H_7)_3B\text{–}F^-] > D[SF_4\text{–}F^-]$
$(i\text{-}C_3H_7)_2BF_2^- + (i\text{-}C_3H_7)_3B \not\rightarrow (i\text{-}C_3H_7)_3BF^- + (i\text{-}C_3H_7)_2BF$	*c*	<0.01	$D[(i\text{-}C_3H_7)_2FB\text{–}F^-] > D[(i\text{-}C_3H_7)_3B\text{–}F^-]$
	SF_6/BF_3 System		
$SF_6^- + BF_3 \rightarrow BF_4^- + SF_5$	13	11.8	$D[BF_3\text{–}F^-] > D[SF_5\text{–}F^-]$
$SF_5^- + BF_3 \rightarrow BF_4^- + SF_4$	14	12.9	$D[BF_3\text{–}F^-] > D[SF_4\text{–}F^-]$
	$SF_6/(CH_3)_3B/(C_2H_5)_3B$ System		
$(CH_3)_3BF^- + (C_2H_5)_3B \rightarrow (C_2H_5)_3BF^- + (CH_3)_3B$	15	2.4	$D[(C_2H_5)_3B\text{–}F^-] > D[(CH_3)_3B\text{–}F^-]$
$(CH_3)_2BF_2^- + (C_2H_5)_3B \rightarrow (C_2H_5)_3BF^- + (CH_3)_2BF$	16	0.9	$D[(C_2H_5)_3B\text{–}F^-] > D[(CH_3)_2BF\text{–}F^-]$
	$SF_6/(C_2H_5)_3B/(i\text{-}C_3H_7)_3B$ System		
$(C_2H_5)_3BF^- + (i\text{-}C_3H_7)_3B \rightarrow (i\text{-}C_3H_7)_3BF^- + (C_2H_5)_3B$	17	3.7	$D[(i\text{-}C_3H_7)_3B\text{–}F^-] > D[(C_2H_5)_3B\text{–}F^-]$
$(C_2H_5)_2BF_2^- + (i\text{-}C_3H_7)_3B \rightarrow (i\text{-}C_3H_7)_3BF^- + (C_2H_5)_2BF$	18	1.1	$D[(i\text{-}C_3H_7)_3B\text{–}F^-] > D[(C_2H_5)_2FB\text{–}F^-]$
	$SF_6/(i\text{-}C_3H_7)_3B/BF_3$ System		
$(i\text{-}C_3H_7)_3BF^- + BF_3 \rightarrow BF_4^- + (i\text{-}C_3H_7)_3B$	19	*d*	$D[BF_3\text{–}F^-] > D[(i\text{-}C_3H_7)_3B\text{–}F^-]$
$(i\text{-}C_3H_7)_2BF_2^- + BF_3 \rightarrow BF_4^- + (i\text{-}C_3H_7)_2BF$	20	*d*	$D[BF_3\text{–}F^-] > D[(i\text{-}C_3H_7)_2FB\text{–}F^-]$

[a] Reaction numbers refer to reactions specified in the text. [b] Rate constants in units of 10^{-10} cm^3 molecule^{-1} s^{-1}, determined from limiting slopes of trapped-ion disappearance vs. time data for the respective systems, taking into account product distributions where applicable. [c] Reaction not observed. [d] Rate constants not determined.

Table II. Thermochemical Inferences from Observed Reactions[a]

R	$\Delta H_f°$ (R_3B)[b]	$\Delta H_f°$ $(R_2BF_2^-)$[c]	$\Delta H_f°$ (R_3BF^-)[d]
CH_3	−29.3	⩽−184.7	⩽−144.3
C_2H_5	−36.0	⩽−183.1	⩽−151.0
$i\text{-}C_3H_7$	−56.3	⩽−195.3	⩽−171.3

[a] All $\Delta H_f°$ values in units of kcal/mol 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 eq 22 to be exothermic. [d] Calculated by considering reactions 6, 9, and 12 as generated in eq 23 to be exothermic.

Table III. Thermochemical Quantities Used in Calculations[a]

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

[a] All $\Delta H_f°$ values in units of kcal/mol at 298 K. [b] $\Delta H_f°$ values for the trialkylboranes calculated using Benson's group additivity method 21 (see text for discussion). [c] Reference 12. [d] Reference 29. [e] References 20 and 21. [f] Calculated using data quoted in this table and $D[BF_3\text{–}F^-]$ = 71 kcal/mol, taken from ref 14a.

$\Delta H_f°$ values of the boranes (Table II) obtained from the group methods are preferred and utilized in all calculations herein.

Previously reported values of $D[BF_3\text{–}F^-]$ = 71[14a] and $D[SF_4\text{–}F^-]$ = 54 ± 12 kcal/mol[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 eq 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 eq 26, is related to the free energy change for fluoride

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

transfer, $\Delta G° = -RT \ln K_{eq}$. The data in 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/mol, 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/mol. 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 further quantification of the Lewis acidities of the boranes examined in the present study. Using the same methodology, the fluoride transfer equilibrium (eq 27) is observed involving

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

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

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

[a] All data in units of kcal/mol at 298 K. [b] Fluoride affinities estimated as discussed in the text; see also ref 22. [c] Calculated using limits given in Table II.

$(C_2H_5)_3B$ and CH_3SiF_3. The measured equilibrium constant $K_{eq} = 2.3$ corresponds to a $\Delta G°$ of -0.5 ± 0.1 kcal/mol favoring F^- transfer to the right as written.

A quantity more relevant to discussion of adduct bond energies is the enthalpy, which is related to free energy by eq 28. The entropy change accompanying reaction 27 is esti-

$$\Delta G° = \Delta H° - T\Delta S° = -RT \ln K_{eq} \qquad (28)$$

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

In the same study,[22] reaction 29 is observed only in the

$$(CH_3)_3BF^- + CH_3SiF_3 \rightarrow CH_3SiF_4^- + (CH_3)_3B \qquad (29)$$

$$(CH_3)_2FBF^- + CH_3SiF_3 \nrightarrow CH_3SiF_4^- + (CH_3)_2FB \qquad (30)$$

forward direction, while reaction 30 does not occur. Limits obtained for reaction 29 are $K_{eq} \geq 50.8$ and $\Delta G° \leq -2.3$ kcal/mol. 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/mol. In addition, F^- transfer reactions 31–34 proceed

$$(CH_3)_2SiF_3^- + (CH_3)_3B \rightarrow (CH_3)_3BF^- + (CH_3)_2SiF_2 \qquad (31)$$

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

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

$$SiF_5^- + BF_3 \rightarrow BF_4^- + SiF_4 \qquad (34)$$

rapidly (with rate constants in the range of 10^{-10} to 10^{-9} cm^3 mol^{-1} s^{-1}) toward completion.[22] With the exception of reaction 33, it should have been possible to detect the reverse reaction; none was observed. Limiting values of equilibrium constants obtained are $K_{eq} \geq 34.9$, 18.9, and 49.0 with corresponding free energy changes of $\Delta G° \leq -2.1$, −1.7, and −2.3 kcal/mol 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/mol 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 $D[\text{A-F}^-]$. Values of $D[R_2FB\text{-}F^-]$ are simply chosen intermediate between bracketing species,[22] since the neutrals R_2FB were not present. 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_2FBF^- 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.

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 14–20 kcal/mol 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/mol.[25]

Inasmuch 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 $(CH_3)_3N\cdot BR_3 \rightleftarrows (CH_3)_3N + BR_3$ comprise the only extended comparison available. ΔH_{diss} values (in kcal/mol) 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 were 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/mol.

Apparent from a comparison of adduct dissociation energies with both reference bases, replacement of alkyl substituents by fluorine on boron results in increased Lewis acidity of the neutral borane. This mainly reflects the higher electronegativity of fluorine. The overall increases in acidity in going from $(CH_3)_3B$ to BF_3 are approximately the same (~16 kcal/mol) for both reference bases, even though bond strengths toward F^- are 30–40 kcal/mol 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 the two reference bases considered: 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 involving alkyl substituents. 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^- as the reference base, with the possible exception of repulsions among the bulky alkyl groups on the acid moiety (analogous to B strain for the base) which 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 studies demonstrate, for example, 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 understand the highly selective reductions of functional groups effected by organoborane–hydride reagents in organic synthesis.[32]

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Registry No. $(CH_3)_2BF_2^-$, 59244-66-5; $(C_2H_5)_2BF_2^-$, 63599-28-0; $(i\text{-}C_3H_7)_2BF_2^-$, 63599-29-1; $(CH_3)_3BF^-$, 63599-30-4; $(C_2H_5)_3BF^-$, 63599-31-5; $(i\text{-}C_3H_7)_3BF^-$, 63599-32-6; $(CH_3)_2FB$, 353-46-8; $(C_2H_5)_2FB$, 367-45-3; $(i\text{-}C_3H_7)_2FB$, 22086-63-1; $(CH_3)_3B$, 593-90-8; $(C_2H_5)_3B$, 97-94-9; $(i\text{-}C_3H_7)_3B$, 1776-66-5; SF_6^-, 25031-39-4; SF_5^-, 31140-82-6; BF_3, 7637-07-2; BF_4^-, 14874-70-5.

References and Notes

(1) Camille and Henry Dreyfus Teacher–Scholar (1971–1976).

(2) (a) G. N. Lewis, "Valence and the Structure of Molecules", The Chemical Catalogue Co., New York, N.Y., 1923; (b) G. N. Lewis, *J. Franklin Inst.*, **226**, 293 (1938).

(3) J. L. Beauchamp, *Annu. Rev. Phys. Chem.*, **22**, 527 (1971).

(4) J. L. Beauchamp, *Adv. Mass Spectrom.*, **8**, 717 (1974).

(5) (a) W. G. Henderson, D. Holtz, J. L. Beauchamp, and R. W. Taft, *J. Am. Chem. Soc.*, **94**, 4728 (1972); (b) M. Taagepera, W. G. Henderson, R. T. C. Brownlee, D. Holtz, J. L. Beauchamp, and R. W. Taft, *ibid.*, **94**, 1369 (1972); (c) E. M. Arnett, F. M. Jones III, M. Taagepera, W. G. Henderson, J. L. Beauchamp, D. Holtz, and R. W. Taft, *ibid.*, **94**, 4727 (1972).

(6) (a) R. D. Wieting, R. H. Staley, and J. L. Beauchamp, *J. Am. Chem. Soc.*, **97**, 924 (1975); (b) R. H. Staley and J. L. Beauchamp, *ibid.*, **97**, 5920 (1975); (c) R. L. Woodin and J. L. Beauchamp, submitted for publication in *J. Am. Chem. Soc.*

(7) A. D. Williamson and J. L. Beauchamp, *J. Am. Chem. Soc.*, **97**, 5714 (1975).

(8) R. R. Corderman and J. L. Beauchamp, *J. Am. Chem. Soc.*, **98**, 3998 (1976).

(9) (a) R. J. Blint, T. B. McMahon, and J. L. Beauchamp, *J. Am. Chem. Soc.*, **96**, 1269 (1974); (b) R. D. Wieting, R. H. Staley, and J. L. Beauchamp, *ibid.*, **96**, 7552 (1974); (c) J. L. Beauchamp and J. Y. Park, *J. Phys. Chem.*, **80**, 575 (1976); (d) M. K. Murphy and J. L. Beauchamp, *J. Am. Chem. Soc.*, **98**, 5781 (1976); (e) M. K. Murphy and J. L. Beauchamp, to be submitted for publication in *J. Am. Chem. Soc.*

(10) J. H. J. Dawson, W. G. Henderson, R. M. O'Malley, and K. R. Jennings, *Int. J. Mass Spectrom. Ion Phys.*, **11**, 61 (1973).

(11) Related studies of appearance potentials of carbonium and siliconium ions using high-resolution electron and photon impact include: (a) A. D. Willianson, P. R. LeBreton, and J. L. Beauchamp, *J. Am. Chem. Soc.*, **98**, 2705 (1976); (b) F. P. Lossing, *Bull. Soc. Chim. Belg.*, **81**, 125 (1972); (c) F. P. Lossing and G. P. Semeluk, *Can. J. Chem.*, **48**, 955 (1970); (d) B. Steiner, G. F. Giese, and M. A. Inghram, *J. Chem. Phys.*, **34**, 189 (1961); (e) W. A. Chupka and J. Berkowitz, *ibid.*, **47**, 2921 (1967); (f) M. Krause, J. A. Walker, and V. H. Diebler, *J. Res. Natl. Bur. Stand., Sect. A*, **72**, 281 (1968); (g) M. K. Murphy and J. L. Beauchamp, *J. Am. Chem. Soc.*, **99**, 2085 (1977).

(12) M. S. Foster, S. A. Sullivan, and J. L. Beauchamp, unpublished results.

(13) R. Yamdagni and P. Kebarle, *J. Am. Chem. Soc.*, **93**, 7139 (1971), and references contained therein.

(14) (a) J. C. Haartz and D. H. McDaniel, *J. Am. Chem. Soc.*, **95**, 8562 (1973); (b) T. C. Rhyne and J. G. Dillard, *Inorg. Chem.*, **10**, 730 (1971); (c) M. K. Murphy and J. L. Beauchamp, *J. Am. Chem. Soc.*, **98**, 1433 (1976); (d) J. A. Stockdale, D. F. Nelson, F. J. Davis, and R. N. Compton, *J. Chem. Phys.*, **56**, 3336 (1972).

(15) (a) T. B. McMahon and J. L. Beauchamp, *Rev. Sci. Instrum.*, **43**, 509 (1972); (b) M. S. Foster and J. L. Beauchamp, *J. Am. Chem. Soc.*, **97**, 4808 (1975).

(16) K. Jaeger and A. Henglein, *Z. Naturforsch. A.*, **22**, 700 (1967).

(17) (a) D. Holtz, J. L. Beauchamp, and J. R. Eyler, *J. Am. Chem. Soc.*, **92**, 7045 (1970); (b) R. H. Wyatt, D. Holtz, T. B. McMahon, and J. L. Beauchamp, *Inorg. Chem.*, **13**, 1511 (1974); (c) D. P. Ridge and J. L. Beauchamp, *J. Am. Chem. Soc.*, **96**, 637 (1974).

(18) (a) J. G. Dillard and T. C. Rhyne, *J. Am. Chem. Soc.*, **91**, 6521 (1969); (b) M. S. Foster and J. L. Beauchamp, *Chem. Phys. Lett.*, **31**, 482 (1975).

(19) M. S. Foster and J. L. Beauchamp, *Chem. Phys.* Lett., **31**, 479 (1975).

(20) From a critical compilation, J. D. Cox and G. Pilcher, "Thermochemistry of Organic and Organometallic Compounds", Academic Press, New York, N.Y., 1970.

(21) S. W. Benson "Thermochemical Kinetics", Wiley, New York, N.Y., 1968.

(22) M. K. Murphy and J. L. Beauchamp, *J. Am. Chem. Soc.*, **99**, 4992 (1977).

(23) (a) S. K. Searles and P. Kebarle, *Can. J. Chem.*, **47**, 2619 (1969); (b) for reaction 27, $\Delta S = \Delta S_{\text{transl}} + \Delta S_{\text{vibr}} + \Delta S_{\text{rot}} + \Delta S_{\text{electr}}$ where $\Delta S_{\text{transl}} = +0.01$ eu, $\Delta S_{\text{electr}} = 0$, $\Delta S_{\text{vibr}} \sim 0$ (assumed), and $\Delta S_{\text{rot}} \sim 0$ (no change in symmetry numbers, and changes in moments of inertia assumed to approximately cancel).

(24) For reviews of Lewis acidity studies of various group 3 compounds see (a) D. P. N. Satchell and R. S. Satchell, *Chem. Rev.*, **69**, 251 (1969); (b) F. G. A. Stone, *ibid.*, **58**, 101 (1958), and references contained therein.

(25) P. Love, R. B. Cohen, and R. W. Taft, *J. Am. Chem. Soc.*, **90**, 2455 (1968).

(26) H. I. Schlesinger, N. W. Flodin, and A. G. Burg, *J. Am. Chem. Soc.*, **61**, 1078 (1939).

(27) (a) E. M. Arnett, E. J. Mitchell, and T. S. S. R. Murty, *J. Am. Chem. Soc.*, **96**, 3875 (1974); (b) R. L. Woodin, F. A. Houle, and W. A. Goddard III, *Chem. Phys.*, **14**, 461 (1976).

(28) H. C. Brown, H. Bartholomay, Jr., and M. D. Taylor, *J. Am. Chem. Soc.*, **66**, 435 (1944).

(29) J. A. Kerr, *Chem. Rev.*, **66**, 465 (1966), and references contained therein.

(30) J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, K. Draxl, and F. H. Field, *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand.*, **No. 26** (1969).

(31) M. K. Murphy and J. L. Beauchamp, unpublished results. $(CH_3)_3BD^-$ and $(C_2H_5)_3BD^-$ are produced by D^- transfer from DNO^- (generated by dissociative e^- capture processes in CD_3ONO; see ref 14c). While the complexity of anion–molecule reactions in $CD_3ONO/(CH_3)_3B/(C_2H_5)_3B$ mixtures renders a complete analysis difficult, double resonance experiments unambiguously indicate the rapid transfer of D^- from $(CH_3)_3BD^-$ to $(C_2H_5)_3B$. No evidence was obtained for the occurrence of the reverse reaction.

(32) (a) R. M. Schubert, Ph.D. Thesis, Purdue University, West Lafayette, Ind., 1972; (b) H. C. Brown and W. C. Dickason, *J. Am. Chem. Soc.*, **92**, 709 (1970); (c) R. E. Ireland, D. R. Marshall, and J. W. Tiley, *ibid.*, **92**, 4754 (1970).