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Acid-Base Properties and Gas-Phase Ion Chemistry of $(CH_3)_3B$

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Abstract: The ion-molecule reactions of trimethylborane, $(CH_3)_3B$, both alone and in mixtures with other molecules, have been investigated by ion cyclotron resonance spectroscopy. Reaction pathways, product distributions, and reaction rate constants have been determined for a variety of reactions involving both positive and negative ions. Where possible thermochemical data have been obtained, including the gas-phase Brönsted acidity, $PA[(CH_3)_2B{=}CH_2^-] = 365 \pm 5$ kcal/mol. Attempts to determine the Brönsted base strength were frustrated by failure to observe protonated $(CH_3)_3B$. Exothermic proton transfer reactions lead exclusively to the formation of $(CH_3)_2B^+$ and CH_4. The thermoneutral CH_3^- transfer reaction $(CH_3)_2{}^{10}B^+ + (CH_3)_3{}^{11}B \rightleftharpoons (CH_3)_3{}^{10}B + (CH_3)_2{}^{11}B^+$ is observed to be rapid with $k_f = k_r = 2.6 \times 10^{-10}$ cm^3 molecule^{-1} sec^{-1}. Transfer of D^- and F^- from appropriate reagent anions to $(CH_3)_3B$ produces the four-coordinate anions $(CH_3)_3BD^-$ and $(CH_3)_3BF^-$, which are discussed in light of the electron pair acceptor capabilities of the vacant B 2p valence orbital in the neutral. Photoionization efficiency curves for ions generated in $(CH_3)_3B$ between 9.7 and 10.8 eV photon energies have been obtained, yielding the adiabatic $IP[(CH_3)_3B] = 10.01 \pm 0.02$ eV, the fragmentation threshold, $AP[(CH_3)_2B^+] = 10.35 \pm 0.05$ eV, and the B-CH$_3$ bond dissociation energy in the parent radical ion, $D[(CH_3)_2B^+{-}CH_3] = 7.8 \pm 1$ kcal/mol.

Ion cyclotron resonance (ICR) mass spectrometry provides a tool uniquely suited to the detailed study of ion-molecule chemistry in the gas phase, in the absence of complicating solvation phenomena. Recently reported from this laboratory have been the reactions of Li^+, NO^+, and carbonium ions exemplary of their behavior as Lewis acids.[2-7] Studies of relative Lewis acidities of carbonium ions toward the reference bases H^-, F^-, and Br^- have been used to measure relative carbonium ion stabilities in the gas phase.[4-7] A natural extension of this work is the determination of the relative Lewis acidities of various neutral acceptors toward these same Lewis bases. Recently reported gas phase studies along these lines have discussed the relative binding energies of F^- and Cl^- to hydrogen halides (HX where X = F, Cl, Br),[8] compounds possessing the hydroxyl functional group (including water, several alcohols, and carboxylic acids)[9] and a variety of inorganic Lewis acids.[10]

As part of an extensive investigation of the group 3 Lewis acids MX_3 (where M = B, Al, ···; X = H, alkyl, halogen) in this laboratory, this report describes ICR and photoionization mass spectrometry (PIMS) studies of the thermochemical properties and reactions of positive and negative ions derived from trimethylborane, $(CH_3)_3B$. This molecule, unlike many group 3 Lewis acids, exists as a trigonal planar monomer in the gas phase at room temperature.[11] As such, an investigation of its ion chemistry may provide insights into the effects of valence shell electron deficiency, resulting from the presence of a vacant B 2p orbital in the neutral, on ionic reactivity and stability.

Investigation of Lewis acidity of boron compounds has been extensive, but has dealt largely with neutral adducts formed between acids BX_3 and various *n*-donor bases (e.g., amines, phosphines).[12,13] Previous gas phase studies of the ion chemistry of boron containing compounds have considered boron hydrides,[14] tri-*n*-butylborane,[15] boron halides,[10] and borazine.[16] Unlike $(CH_3)_3B$, interaction of boron atoms via multicenter bonding present in even the simplest boron hydrides complicates efforts to elucidate the effects of a single vacant B 2p orbital.[17] Such is also the case in the monomeric boron trihalides, where the B 2p orbital is extensively involved in dative π bonding to the halide substituents.[18]

Previous investigations of ions derived from $(CH_3)_3B$ utilizing conventional electron impact mass spectrometry deal only with positive ions.[19-22] These studies of $(CH_3)_3B$ entail ionization (IP) and appearance potential (AP) measurements, correlation of fragmentation patterns for structural determination, and the effects of isotopic substitution (^{1,2}H, ^{10,11}B, ^{12,13}C) on fragmentation patterns.[20-22] Thermochemical data on ions containing boron are limited, with considerable disagreement among reported values (Table I).

Experimental Section

The instrumentation and techniques associated with ICR spectrometry are described in detail elsewhere.[23,24] In studies reported here, both a modified Varian V-5900 spectrometer and a larger, high field instrument, constructed in the laboratory are employed.[24] Gas mixtures utilized 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 searately for each component against an MKS Baratron Model 90H1-E capacitance manometer.[5] A linear calibration of Baratron pressure vs. ionization gauge current affords pressure determinations over a range of 10^{-7} to 10^{-4} Torr. The 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.

Photoionization measurements of $(CH_3)_3B$ utilize the Caltech-JPL facility, which has been previously described.[25] Pertinent operating conditions include: source temperature, ambient (22°C); ion source sample pressure, 1.6×10^{-4} Torr; resolution, 1 Å; repeller field, 0.1 V/cm; ion energy for mass analysis, 20 eV. The hydrogen many-line spectrum is utilized as the photon source for the wavelength range studied (1290-1140 Å). Photon intensities are

Table I. Thermochemical Data for Positive Ions Derived from $(CH_3)_3B$

Species	IP or AP[a]	ΔH_f[b]	Ref
$(CH_3)_3B^+$	10.01 ± 0.02[c]	201.4[d]	This work
	8.8 ± 0.2	176	19a
	~10[e]	—	29a
	10.4[f]	—	29b
$(CH_3)_2B^+$	10.35 ± 0.05	175.3[d,g]	This work
	10.3 ± 0.2	175	19a

[a] Ionization and appearance potentials are in eV. [b] Heats of formation are in kcal/mol at 298 K. [c] Estimated to be the adiabatic IP[$(CH_3)_3B$]. [d] Calculated, based on ΔH_f data from Table IV. [e] This value is estimated from the published photoelectron spectrum of $(CH_3)_3B$, as the threshold or adiabatic IP, although no value was specifically quoted by the original authors, ref 30a. [f] This value is quoted from photoelectron spectroscopy studies of $(CH_3)_3B$, as the adiabatic IP, although the spectrum was not shown, ref 30b. [g] Calculated, based on $\Delta H_f[CH_3] = 34.8 \pm 0.2$ kcal/mol from D. R. Stull and H. Prophet, "JANAF Thermochemical Tables", 2nd ed, NSRDS-NBS 37, U.S. Government Printing Office, Washington, D.C., 1971.

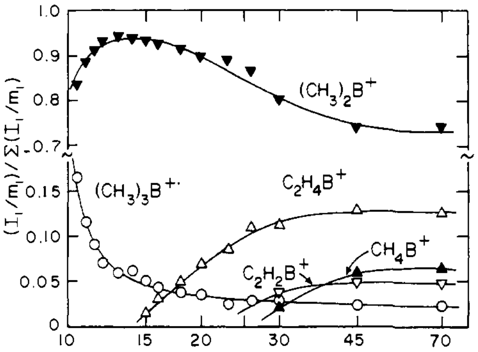


Figure 1. Breakdown diagram of $(CH_3)_3B$ at 1×10^{-6} Torr; the variation of ion abundances as a function of electron energy.

measured using a sodium salicylate scintillator and photomultiplier.

$(CH_3)_3B$ was obtained from Alfa Inorganics. CD_3ONO, C_2H_5ONO, PH_3, and AsH_3 were available from previous studies.[26] All other chemicals utilized are reagent grade and commercially available. Noncondensable impurities are removed from all samples by multiple freeze-pump-thaw cycles. Mass spectral analysis of all samples utilized show no detectable impurities.

In order to minimize pyrolytic decomposition of the alkyl nitrites on the hot filament of the Schulz-Phelps ionization gauge, sample pressures were measured before and after each experiment, but the gauge filament was turned off and allowed to cool before any data were recorded.[27]

In experiments utilizing SF_6 and alkyl nitrites, anion formation occurs via attachment of near thermal electrons produced in the ICR trapping well by inelastic collisions during the electron beam pulse.[8,26,28,29] The nominal electron beam energy utilized in these experiments is 70 eV.

Data reported in tables and figures represent total boron content, with ^{10}B and ^{11}B abundances summed. Throughout this work, isotopic boron containing species were observed in their natural abundance ratios (^{10}B, 19.8%; ^{11}B, 80.2%). Typically, ion concentrations comprising less than 1% of the total are not included in figures.

Results

Mass Spectrometry of $(CH_3)_3B$. Positive ion single resonance ICR mass spectra taken at 70 eV and low $(CH_3)_3B$ pressure ($\leq 10^{-6}$ Torr) agree well with published mass spectrometry results.[19,21] The variation of relative ion abundances with electron energy from 10 to 70 eV at low pressure is shown in Figure 1. The parent radical-ion, $(CH_3)_3B^+$, is not observed in excess of 17% of total ionization, even at the lowest electron energy for which ionization is detectable (~10 eV). By far the most abundant ion under these conditions is $(CH_3)_2B^+$, comprising >70% of ionization at all electron energies examined. Previous electron impact studies indicated the fragmentation threshold for CH_3 loss, AP[$(CH_3)_2B^+$], to occur 1.5 eV above IP[$(CH_3)_3B$] = 8.8 eV, in conflict with photoelectron spectral data indicating IP[$(CH_3)_3B$] to be approximately 10 eV.[20a,30] In order to clarify these discrepancies, the ionization threshold region near 10 eV was examined by PIMS. Photoionization efficiency curves for $(CH_3)_3B^+$ and $(CH_3)_2B^+$ ions for photon energies between 9.7 and 10.8 eV are shown in Figure 2. These are the only ions observed in this energy range.

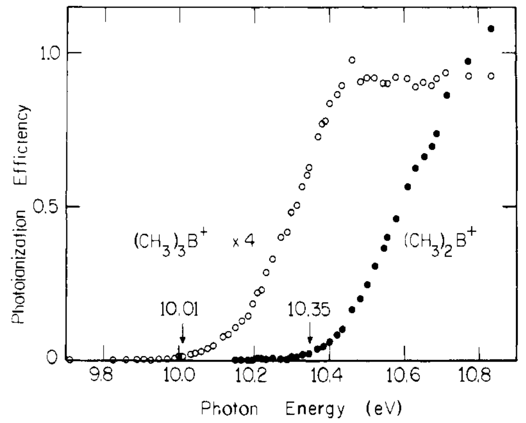


Figure 2. Photoionization efficiency curves for $(CH_3)_3B^+$ and $(CH_3)_2B^+$ ions generated from $(CH_3)_3B$ between 9.7 and 10.8 eV photon energies.

The parent ion efficiency curve exhibits a very gradual onset, characteristic of a substantial change in geometry from that of the neutral. This would be expected for ionization occurring from a strongly bonding σ_{B-C} orbital in the neutral and subsequent weakening of the B-C bond in the ion.[30a] As a result, the low energy tailing observed in the parent ion curve is due to small Franck-Condon factors for the adiabatic transition. This is supported by the observed shape of the first ionization band in the photoelectron spectrum of $(CH_3)_3B$.[30a] From Figure 2, the adiabatic ionization potential of $(CH_3)_3B$ is estimated to be 10.01 ± 0.02 eV.

The photoionization efficiency curve for $(CH_3)_2B^+$ shows a sharp onset, occurring at photon energies slightly below the abrupt leveling off of the parent ion curve, indicating dissociation of excited $(CH_3)_3B^+$. From Figure 2, AP[$(CH_3)_2B^+$] is estimated to be 10.35 ± 0.05 eV. The published photoelectron spectrum of $(CH_3)_3B$ shows a broad first ionization band of width ≥1 eV (FWHM), exhibiting a 0.6-eV Jahn-Teller splitting of the $3e'\sigma_{B-C}$ levels in the ground state of the parent ion.[30a] In the range 10.0-11.0 eV, the parent ion can thus be formed with a continuous range of internal energies. The sharp plateau observed in the photoionization efficiency curve for $(CH_3)_3B^+$ is thus evidence that the measured AP[$(CH_3)_2B^+$] is a true thermochemical fragmentation threshold.

The photoionization measurements yield directly the one-electron boron-methyl bond dissociation energy in the parent ion, $D[(CH_3)_2B^+\text{-}CH_3] = AP[(CH_3)_2B^+] - IP[(CH_3)_3B] = 0.34 \pm 0.07$ eV (7.8 ± 1.6 kcal/mol), drastically reduced from the reported 89 kcal/mol for the average $B\text{-}CH_3$ bond energy in neutral $(CH_3)_3B$.[31] In addition, the thermochemical relationship $IP[(CH_3)_2B] = AP[(CH_3)_2B^+] - D[(CH_3)_2B\text{-}CH_3]$ yields 6.5 ± 0.1 eV for the IP of $(CH_3)_2B$ radical, considerably below IP(CH_3)

Table II. Positive Ion–Molecule Reactions in Mixtures with $(CH_3)_3B^a$

	Rate constant[b]	ΔH_{rxn}[c]
$(CH_3)_2{}^{10}B^+ + (CH_3)_3{}^{11}B \longrightarrow (CH_3)_3{}^{10}B + (CH_3)_2{}^{11}B^+$	2.6 ± 0.4^d	0^e
$CH_5^+ + (CH_3)_3B \longrightarrow (CH_3)_2B^+ + 2CH_4$	14.5	-54.5
$C_2H_5^+ + (CH_3)_3B \longrightarrow (CH_3)_2B^+ + CH_4 + C_2H_4$	9.6^f	-22.5
$\longrightarrow (CH_3)_2B^+ + C_3H_8$		-41.9^h
$H_3S^+ + (CH_3)_3B \longrightarrow (CH_3)_2B^+ + CH_4 + H_2S$	4.4^g	-11.5
$\longrightarrow H_2SB(CH_3)_2^+ + CH_4$		<0
$\longrightarrow H_2SCH_3^+ + HB(CH_3)_2$		<0
$CH_2OH^+ + (CH_3)_3B \longrightarrow (CH_3)_2B^+ + CH_4 + CH_2O$	2.2	-9.5
$AsH_4^+ + (CH_3)_3B \not\longrightarrow (CH_3)_2B^+ + CH_4 + AsH_3$	<0.01	-3.5
$NH_4^+ + (CH_3)_3B \not\longrightarrow (CH_3)_2B^+ + CH_4 + NH_3$	<0.01	+26.5

[a] Neutral products are assumed. [b] Rate constants, in units of 10^{-10} cm^3 molecule^{-1} sec^{-1}, extracted from trapped-ion ICR experiments; ±20% uncertainty in the neutral gas pressures is the major source of error. [c] Heats of reaction, except as noted, are calculated based on the thermochemical data in Table IV. [d] Forward and reverse rate constants for the thermoneutral CH_3^- transfer are measured to be equal within the experimental uncertainty. [e] Neglects any boron isotope effect. [f] Total rate constant for reaction of $C_2H_5^+$ with $(CH_3)_3B$. [g] Total rate constant for reaction of H_3S^+ with $(CH_3)_3B$. [h] Calculated, based on $\Delta H_f(C_3H_8) = -24.8 \pm 0.14$ taken from J. D. Cox and G. Pilcher, "Thermochemistry of Organic and Organometallic Compounds", Academic Press, New York, N.Y., 1970.

= 9.8 eV.[32] Thus, $(CH_3)_2B^+$ by far dominates parent ion fragmentation; CH_3^+ is formed above 15 eV in $(CH_3)_3B$ but at <1% of the total ionization.

The present experimental results and derived heats of formation of boron containing ions are compared with literature values in Table I.

The only negative ion formed in significant abundance by electron impact in pure $(CH_3)_3B$ is $(CH_3)_2B{=}CH_2^-$. The cross section for its formation appears as a single, gaussian-shaped peak between 6 and 14 eV, with a broad maximum near 10 ± 0.5 eV.

Positive Ion Chemistry. Reactions in $(CH_3)_3B$ alone were first investigated. Then reactions occurring in mixtures of $(CH_3)_3B$ with several molecules which span a range of gas phase base strengths were examined in an attempt to protonate $(CH_3)_3B$ and determine its Brönsted basicity. Reaction rate constants are summarized in Table II.

$(CH_3)_3B$. The abundant primary ions in $(CH_3)_3B$, $(CH_3)_3B^+$, and $(CH_3)_2B^+$ are unreactive ($k \lesssim 10^{-12}$ cm^3 molecule^{-1} sec^{-1}) toward the parent neutral, as shown by studies of the relative ionic abundances of these species as a function of both pressure and trapping time. In trapped-ion experiments, a small fraction of $(CH_3)_3B^+$, probably containing excess internal energy, is observed to dissociate to give $(CH_3)_2B^+$.

Double resonance experiments indicate that the two isotopes of $(CH_3)_2B^+$, *m/e* 40 and 41, are reactively coupled, consistent with the CH_3^- transfer reaction (eq 1). Selective ion ejection techniques[4,5] afford determinations of both forward and reverse rate constants in reaction 1, giving $k_f = k_r = 2.6 \pm 0.4 \times 10^{-10}$ cm^3 molecule^{-1} sec^{-1}.

$$(CH_3)_2{}^{10}B^+ + (CH_3)_3{}^{11}B \rightleftharpoons (CH_3)_3{}^{10}B + (CH_3)_2{}^{11}B^+ \quad (1)$$

$(CH_3)_3B$–CH_4. The temporal variation of ion abundances in a 1.3:1 mixture of CH_4 and $(CH_3)_3B$ at 20 eV electron energy and 1.1×10^{-6} Torr is shown in Figure 3. The ions CH_3^+ and CH_4^+ react with CH_4, producing $C_2H_5^+$ and CH_5^+, respectively.[33] Reactions 2–4 of these ions with $(CH_3)_3B$ lead to formation of $(CH_3)_2B^+$ as the only boron containing product ion, as shown by double resonance. The identity of the neutral products in reaction 4 is uncertain, C_3H_8 being another energetically feasible possibility. Protonated trimethylborane was not observed under any conditions, even at pressures as high as 5×10^{-3} Torr. Limiting slopes for the decay of CH_5^+ and $C_2H_5^+$ shown in Figure 3 yield rate constants for reactions 3 and 4 of 1.45×10^{-9} and 9.6×10^{-10} cm^3 molecule^{-1} sec^{-1}, respectively.

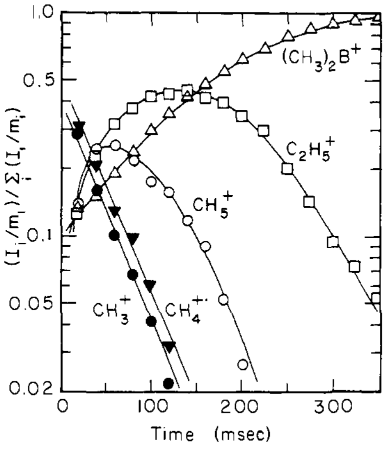


Figure 3. Temporal variation of trapped-cation abundances following a 20-msec electron beam pulse at 20 eV in a 1.3:1 mixture of CH_4 and $(CH_3)_3B$ at 1.1×10^{-6} Torr.

$$CH_4^+ + (CH_3)_3B \rightarrow (CH_3)_2B^+ + CH_4 + CH_3 \quad (2)$$

$$CH_5^+ + (CH_3)_3B \rightarrow (CH_3)_2B^+ + 2CH_4 \quad (3)$$

$$C_2H_5^+ + (CH_3)_3B \rightarrow (CH_3)_2B^+ + CH_4 + C_2H_4 \quad (4)$$

Analogous reactions were observed in mixtures of CD_4 and $(CH_3)_3B$ under similar conditions. Significantly, incorporation of deuterium in the product ion $(CH_3)_2B^+$ was not observed.

$(CH_3)_3B$–H_2S. The temporal variation of ion concentrations in a 10:1 mixture of H_2S and $(CH_3)_3B$ at 2.2×10^{-6} Torr following a 20 msec electron beam pulse at 20 eV is shown in Figure 4. Reactions of primary ions from H_2S lead to protonation of the neutral,[33] producing H_3S^+, which in turn reacts with $(CH_3)_3B$ in accordance with processes 5–7, as shown by double resonance. The limiting slope for the disappearance of H_3S^+ from Figure 4 yields the total rate constant for reaction with $(CH_3)_3B$ of 4.4×10^{-10} cm^3 molecule^{-1} sec^{-1}. Again, no protonated trimethylborane is observed.

$$H_3S^+ + (CH_3)_3B \begin{cases} \rightarrow (CH_3)_2B^+ + CH_4 + H_2S & (5) \\ \rightarrow H_2SB(CH_3)_2^+ + CH_4 & (6) \\ \rightarrow H_2SCH_3^+ + (CH_3)_2BH & (7) \end{cases}$$

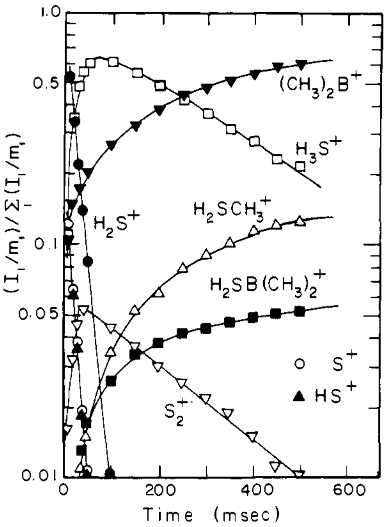


Figure 4. Temporal variation of trapped-cation abundances following a 20-msec electron beam pulse at 20 eV in a 10:1 mixture of H_2S and $(CH_3)_3B$ at 2.2 × 10^{-6} Torr. The species S_2^+ is formed by reaction of S^+ with H_2S (ref 33). This species is unreactive with H_2S, and appears to react slowly with $(CH_3)_3B$. The reaction pathway for this species was not investigated.

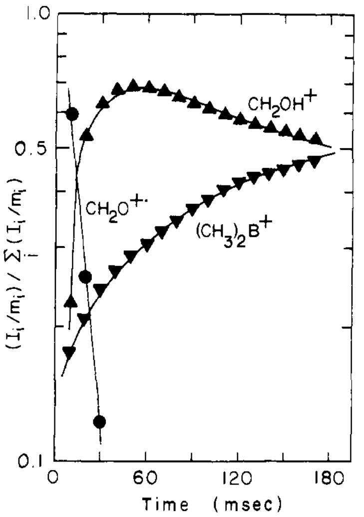


Figure 5. Temporal variation of trapped-cation abundances following a 10-msec electron beam pulse at 12 eV in a 4:1 mixture of CH_2O and $(CH_3)_3B$ at 2.0 × 10^{-6} Torr.

$(CH_3)_3B$-CH_2O. The temporal variation of ion abundances in a 4:1 mixture of CH_2O and $(CH_3)_3B$ is shown in Figure 5, at 2 × 10^{-6} Torr and 12 eV electron energy, where primry ionization produces mainly CH_2O^+ and $(CH_3)_2B^+$. Protonated formaldehyde is generated by reaction of CH_2O^+ with CH_2O[34] and possibly $(CH_3)_3B$. Double resonance indicates $(CH_3)_2B^+$ is produced by reactions 8 and 9 of CH_2O^+ and CH_2OH^+ with $(CH_3)_3B$.

$$CH_2O^+ + (CH_3)_3B \rightarrow (CH_3)_2B^+ + CH_4 + CHO \quad (8)$$

$$CH_2OH^+ + (CH_3)_3B \rightarrow (CH_3)_2B^+ + CH_4 + CH_2O \quad (9)$$

The limiting slope for the decay of CH_2OH^+ at long times in Figure 5 yields a total rate constant, $k = 2.2 \times 10^{-10}$ cm^3 $molecule^{-1}$ sec^{-1}, for reaction of CH_2OH^+ with $(CH_3)_3B$.

In a 1:1 mixture of CH_2O and $(CH_3)_3B$ at 12 eV, increasing total pressure results in a variation of ion abundances qualitatively similar to that observed in the trapped-ion experiment, with the eventual predominance of $(CH_3)_2B^+$ at the expense of both CH_2O^+ and CH_2OH^+. Protonated trimethylborane was not observed in either experiment.

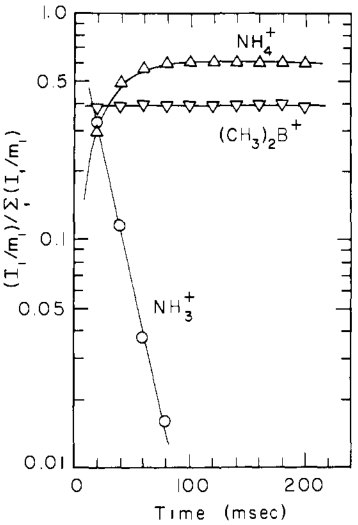


Figure 6. Temporal variation of trapped-cation abundances following a 20-msec electron beam pulse at 20 eV in a 5:1 mixture of NH_3 and $(CH_3)_3B$ at 2.6 × 10^{-6} Torr.

$(CH_3)_3B$-AsH_3, NH_3. Trapped-ion ICR studies in a 2:3 mixture of AsH_3 and $(CH_3)_3B$ at 11 eV and in a 5:1 mixture of NH_3 and $(CH_3)_3B$ at 20 eV, each at 3 × 10^{-6} Torr, indicate that parent and protonated parent ion from both arsine and ammonia are unreactive ($k \lesssim 10^{-12}$ cm^3 $molecule^{-1}$ sec^{-1}) toward neutral $(CH_3)_3B$. $(CH_3)_2B^+$ produced by primary ionization of $(CH_3)_3B$ under these conditions remains a constant fraction of total ionization as a function of time. Data for the mixture of NH_3 with $(CH_3)_3B$ are shown in Figure 6.

Negative Ion Chemistry. Initially the anion chemistry in pure $(CH_3)_3B$ was investigated. Then in order to determine the Brönsted acidity of $(CH_3)_3B$, reactions with a series of molecules spanning a known range of acid strengths were examined. In addition, reactions of $(CH_3)_3B$ with anions generated from SF_6 were investigated, in hopes of observing fluoride ion transfer, as a probe of the pair acceptor properties of the vacant B 2p orbital in the neutral $(CH_3)_3B$. Reaction rate constants for processes involving negative ions are summarized in Table III.

$(CH_3)_3B$. As noted above, $(CH_3)_2B{=}CH_2^-$ is the only anion produced in pure $(CH_3)_3B$ by electron impact. Variation of $(CH_3)_3B$ pressure between 10^{-5} and 10^{-4} Torr indicates $(CH_3)_2B{=}CH_2^-$ to be unreactive ($k \lesssim 10^{-12}$ cm^3 $molecule^{-1}$ sec^{-1}) toward the parent neutral. At higher sample pressures ($\gtrsim 3 \times 10^{-4}$ Torr), the cluster of $(CH_3)_2B{=}CH_2^-$ with $(CH_3)_3B$ is observed.

$(CH_3)_3B$-CD_3ONO. Methyl nitrite-d_3, CD_3ONO, serves as a source of methoxide anion, CD_3O^-, produced as the major product from dissociative attachment of low energy electrons.[28] At 1 × 10^{-6} Torr CD_3ONO, observed negative ions include CD_3O^- (68%), DNO^- (26%), and NO_2^- (6%). The latter species is formed in the nucleophilic displacement reaction (eq 10).

$$CD_3O^- + CD_3ONO \rightarrow NO_2^- + (CD_3)_2O \quad (10)$$

The temporal variation of ion concentrations in a 1.4:1 mixture of CD_3ONO and $(CH_3)_3B$ at 1.9 × 10^{-6} Torr, following a 10-msec 70-eV electron beam pulse, is shown in Figure 7. Under these conditions, formation of boron con-

Table III. Negative Ion–Molecule Reactions in Mixtures with $(CH_3)_3B^a$

	Rate constant^b	$\Delta H_{rxn}{}^c$
$CD_3O^- + (CH_3)_3B \longrightarrow (CH_3)_2B{=}CH_2^- + CD_3OH$	3.85	−11.8
$C_2H_5O^- + (CH_3)_3B \longrightarrow (CH_3)_2B{=}CH_2^- + C_2H_5OH$	4.6	−9.9
$PH_2^- + (CH_3)_3B \longrightarrow (CH_3)_2B{=}CH_2^- + PH_3$	—^{d}	−5
$(CH_3)_2B{=}CH_2^- + AsH_3 \longrightarrow AsH_2^- + (CH_3)_3B$	—^{d}	−4
$DNO^- + (CH_3)_3B \longrightarrow (CH_3)_3BD^- + NO$	7.0	$<0^f$
$SF_6^- + (CH_3)_3B \xrightarrow{90\%} SF_5^- + HF + (CH_3)_2BCH_2$	1.98^e	$<0^g$
$ \xrightarrow{10\%} (CH_3)_2BF_2^- + SF_4 + CH_3$	0.22^e	$<0^h$
$SF_5^- + (CH_3)_3B \longrightarrow (CH_3)_3BF^- + SF_4$	1.5	$<0^i$
$(CH_3)_2BF_2^- + (CH_3)_3B \not\longrightarrow (CH_3)_3BF^- + (CH_3)_2BF$	<0.01	>0

[a] Neutral products are assumed. [b] Rate constants, in units of 10^{-10} cm^3 molecule^{-1} sec^{-1}, extracted from trapped–ion ICR experiments; ±20% uncertainty in neutral gas pressures are the major source of error. [c] Heats of reaction, except as noted, are calculated based on the thermochemical data in Table IV. [d] Not determined. [e] Estimated from the total rate of disappearance of SF_6^- with time of 2.2×10^{-10} cm^3 molecule^{-1} sec^{-1} and the observed product distribution at long times in Figure 8, where $[(CH_3)_2BF_2^-] \cong 10\%$ and $[(CH_3)_3BF^-] \cong 90\%$. [f] $\Delta H_f[(CH_3)_3BD^-] \leqslant -30.1 \pm 5$ kcal/mol, calculated using $\Delta H_f[NO] = 21.58 \pm 0.04$ and $\Delta H_f[HNO] = 23.8$ kcal/mol, from D. R. Stull and H. Prophet, "JANAF Thermochemical Tables", 2nd ed, NSRDS-NBS 37, U.S. Government Printing Office, Washington, D.C., 1971, and $\Delta H_f[HNO^-] = 20.8$ kcal/mol derived from the author's estimate of EA[HNO] ≅ 3 kcal/mol. [g] $\Delta H_f[(CH_3)_2BCH_2] \leqslant 29.4 \pm 12$ kcal/mol, calculated using $\Delta H_f[HF] = -65.14 \pm 0.2$ kcal/mol from the reference quoted in *f* and $\Delta H_f[SF_6^-] = -304.4 \pm 3.5$ and $\Delta H_f[SF_5^-] = -298 \pm 6$ kcal/mol from ref 8. [h] $\Delta H_f[(CH_3)_2BF_2^-] \leqslant -185.5 \pm 12$ kcal/mol, calculated using $\Delta H_f[SF_4] = -183 \pm 6$ kcal/mol from ref 8, and $\Delta H_f[CH_3] = 34.8 \pm 0.2$ from the reference quoted in *f*. [i] $\Delta H_f[(CH_3)_3BF^-] \leqslant -144.3 \pm 12$ kcal/mol, calculated using thermochemical data quoted in *g* and *h*.

taining anions is observed only in the presence of alkyl nitrite. Double resonance experiments indicate the occurrence of reactions 11 and 12,

$$CD_3O^- + (CH_3)_3B \rightarrow (CH_3)_2B{=}CH_2^- + CD_3OH \quad (11)$$

$$DNO^- + (CH_3)_3B \rightarrow (CH_3)_3BD^- + NO \quad (12)$$

in addition to reaction 10, accounting for the product ions observed in Figure 7 at long times. The products of reactions 10–12 are unreactive toward CD_3ONO and $(CH_3)_3B$. Bimolecular rate constants, extracted from the limiting slopes for disappearance of reactant ions, for reaction 10 in pure CD_3ONO and for reactions 11 and 12 in a CD_3ONO-$(CH_3)_3B$ mixture (Figure 7) are determined to be 0.75, 3.85, and 7.0×10^{-10} cm^3 molecule^{-1} sec^{-1}, respectively.

$(CH_3)_3B$-C_2H_5ONO. Trapped-ion ICR experiments analogous to those described above for CD_3ONO-$(CH_3)_3B$ mixtures were performed with a 1.4:1 mixture of C_2H_5ONO and $(CH_3)_3B$ at 1.6×10^{-6} Torr. Dissociative electron capture by C_2H_5ONO produces predominantly $C_2H_5O^-$ and HNO^-, with lesser amounts of NO_2^- and $C_2H_3O^-$. Formation of NO_2^- occurs via a displacement analogous to reaction 10. $C_2H_3O^-$ concentration is found to be a function of sample exposure to hot filaments in the ICR cell. $C_2H_3O^-$ probably results from the pyrolysis of ethyl nitrite to acetaldehyde followed by its deprotonation by ethoxide ion.[27] Double resonance indicates $C_2H_5O^-$ to be the precursor to $C_2H_3O^-$, supporting this argument. Double resonance experiments indicate the occurrence of reaction 13 as well as a hydride analogue to the deuteride transfer reaction (eq 12) above. NO_2^-, $C_2H_3O^-$, $(CH_3)_2B{=}CH_2^-$, and $(CH_3)_3BH^-$ product ions are all found to be unreactive toward C_2H_5ONO and $(CH_3)_3B$.

$$C_2H_5O^- + (CH_3)_3B \rightarrow (CH_3)_2B{=}CH_2^- + C_2H_5OH \quad (13)$$

$(CH_3)_3B$-AsH_3, PH_3. Negative ions, observed in the single resonance ICR spectrum of a 1:1 mixture of AsH_3 and $(CH_3)_3B$, at 5×10^{-5} Torr and 6.3 eV electron energy, include AsH_2^-, $(CH_3)_2B{=}CH_2^-$, and minor amounts of ions formed in arsine alone.[25c] With increasing total pressure of this mixture, AsH_2^- increases at the expense of $(CH_3)_2B{=}CH_2^-$. Double resonance confirms that reaction 14 occurs only in the direction indicated.

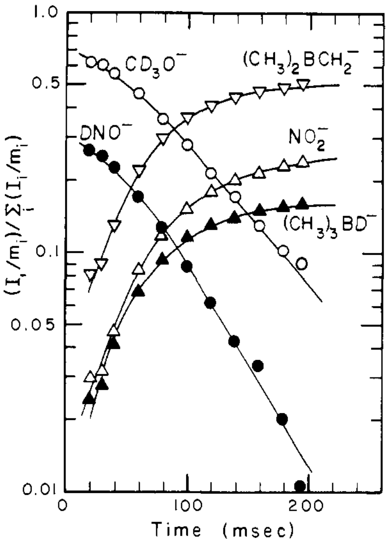


Figure 7. Temporal variation of trapped-anion abundances following a 10-msec electron beam pulse at 70 eV in a 1.4:1 mixture of CD_3ONO and $(CH_3)_3B$ at 1.9×10^{-6} Torr.

$$(CH_3)_2B{=}CH_2^- + AsH_3 \rightarrow AsH_2^- + (CH_3)_3B \quad (14)$$

Analogous studies in a 3:2 mixture of PH_3 and $(CH_3)_3B$, at 5×10^{-5} Torr and 6.2 eV electron energy, reveal the presence of PH_2^- and $(CH_3)_2B{=}CH_2^-$. With increasing pressure of the mixture, $(CH_3)_2B{=}CH_2^-$ increases at the expense of PH_2^-. Double resonance shows that reaction 15 proceeds only in the direction indicated.

$$PH_2^- + (CH_3)_3B \rightarrow (CH_3)_2B{=}CH_2^- + PH_3 \quad (15)$$

$(CH_3)_3B$-SF_6. Electron capture processes in Sf_6 lead to the observation of SF_6^- (95%) and SF_5^- (5%) at 70 eV and relatively low pressure ($<10^{-6}$ Torr).[29] Figure 8 illustrates the temporal variation of ion abundances observed fol-

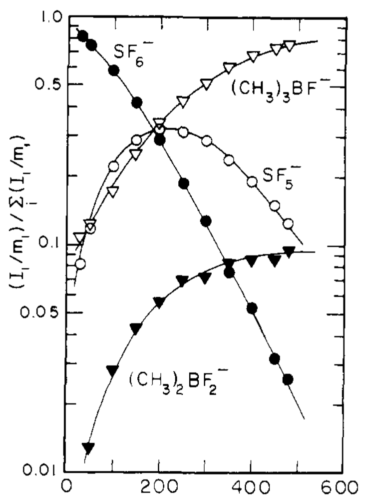


Figure 8. Temporal variation of trapped-anion abundances following a 10-msec electron beam pulse at 70 eV in a 1:2.3 mixture of SF_6 and $(CH_3)_3B$ at 1.8×10^{-6} Torr.

lowing a 10-msec 70-eV electron beam pulse in a 1:2.3 mixture of SF_6 and $(CH_3)_3B$ at 1.8×10^{-6} Torr. Boron containing anions $(CH_3)_3BF^-$ and $(CH_3)_2BF_2^-$ are observed only in the presence of SF_6. Double resonance experiments identify reactions 16–18 as accounting for the observed changes in ion abundance with time. In particular, cyclotron ejection of SF_5^- results in complete disappearance of $(CH_3)_3BF^-$. This indicates that $(CH_3)_3BF^-$ results entirely from reaction of SF_5^- and is not formed in a bimolecular process involving SF_6^-. The limiting slope for the decay of SF_6^- in Figure 8 yields the total rate constant $k = 2.2 \times 10^{-10}$ cm^3 molecule^{-1} sec^{-1} for reaction of SF_6^- with $(CH_3)_3B$. The relative intensities of product ions, $(CH_3)_3BF^-$ and $(CH_3)_2BF_2^-$, at long times indicate that reaction 16 occurs about nine times faster than reaction 17, with rate constants 1.98 and 0.22×10^{-10} cm^3 molecule^{-1} sec^{-1}, respectively. The limiting slope for the disappearance of SF_5^- at long times yields the rate constant $k = 1.5 \times 10^{-10}$ cm^3 molecule$^-$ sec^{-1} for reaction 18. Product ions of reactions 17 and 18 do not react further with SF_6 or $(CH_3)_3B$. In particular, no evidence was obtained for the occurrence of reaction 19, which was investigated by double resonance techniques.

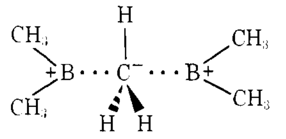
$$SF_6^- + (CH_3)_3B \begin{cases} \xrightarrow{90\%} SF_5^- + HF + (CH_3)_2BCH_2 & (16) \\ \xrightarrow{10\%} (CH_3)_2BF_2^- + CH_3 + SF_4 & (17) \end{cases}$$

$$SF_5^- + (CH_3)_3B \longrightarrow (CH_3)_3BF^- + SF_4 \qquad (18)$$

$$(CH_3)_2BF_2^- + (CH_3)_3B \not\longrightarrow (CH_3)_3BF^- + (CH_3)_2BF \qquad (19)$$

Discussion

$(CH_3)_3B$. The positive ion chemistry of $(CH_3)_3B$ is strongly influenced by the valence shell electron deficiency of boron. In all studies reported here, in pure $(CH_3)_3B$ and in mixtures with a variety of molecules, $(CH_3)_2B^+$ is invariably the most abundant cation observed, whether it be produced reactively or by primary ionization of neutral $(CH_3)_3B$. The only reaction of $(CH_3)_2B^+$ observed in $(CH_3)_3B$ alone is the thermoneutral CH_3^- transfer equilibrium reaction (eq 1) between $(CH_3)_2B^+$ and neutral $(CH_3)_3B$. The mechanism for CH_3^- transfer likely involves the symmetrical intermediate I, involving electrophilic attack at carbon, where one $(CH_3)_2B^+$ cation displaces another. Recent molecular orbital calculations, by Kato et al. and by Cowley et al., indicate significant B^+–C^- polarity across the boron-methyl bond in $(CH_3)_3$, making carbon susceptible to electrophilic attack.[35,36]



I

Reactants and products of reaction 1 differ only in isotopic boron content. Neglecting isotope effects, forward and reverse rate constants, k_f and k_r, for reaction 1 should be equal. Experimentally determined rate constants, $k_f = k_r = 2.6 \pm 0.4 \times 10^{-10}$ cm^3 molecule^{-1} sec^{-1}, equal within experimental error, can be compared with theoretical predictions of the ion-induced dipole model for nonpolar neutrals, given by $k = 2\pi e(\alpha/\mu)^{1/2} = 1.37$ and 1.36×10^{-9} cm^3 molecule^{-1} sec^{-1}, for k_f and k_r, respectively, where e = the electronic charge, α = the polarizability of $(CH_3)_3B$ (estimated to be 8.0×10^{-24} cm^3), and μ = the reduced mass of the collision pair.[37] In accordance with the postulated intermediate I, CH_3^- has 50% probability of remaining on the boron atom from which it originated, so the experimental rate constant must be doubled to give 5.2×10^{-10} cm^3 molecule^{-1} sec^{-1} as the actual reactive encounter rate. Thus only about half of the $CH_3)_2B^+$–$(CH_3)_3B$ collisions result in reaction.

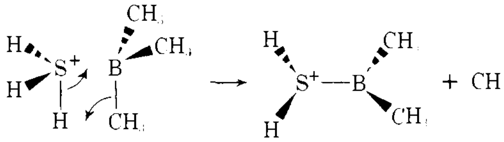
Reactions of $(CH_3)_3B$ with Proton Donors. Ion-molecule reactions in mixtures of $(CH_3)_3B$ with self-protonating gases CH_4, H_2S, CH_2O, AsH_3, and NH_3 were examined in an effort to determine the proton affinity of $(CH_3)_3B$. Such efforts were frustrated by failure to observe the species $C_3H_{10}B^+$, corresponding to protonated $(CH_3)_3B$. Rather, $(CH_3)_2B^+$ is invariably the predominant product as indicated in reaction 20, where M = CH_4, C_2H_4, H_2S, and CH_2O.

$$MH^+ + (CH_3)_3B \rightarrow (CH_3)_2B^+ + M + CH_4 \qquad (20)$$

AsH_4^+ and NH_4^+ do not react with $(CH_3)_3B$. The overall reaction (eq 20) is exothermic only for a species M with PA(M) < 179 kcal/mol. Reported proton affinities of CH_4, C_2H_4, H_2S, CH_2O, AsH_3, and NH_3 are 126, 159, 169, 171, 177, and 207 kcal/mol, respectively.[38,39] Based on the thermochemistry, it appears that reactions generating $(CH_3)_2B^+$ may be rationalized by a mechanism involving the decomposition of the reaction intermediate $[MH^+\cdots(CH_3)_3B]^*$ to M, CH_4, and $(CH_3)_2B^+$. There is no evidence that proton transfer to $(CH_3)_3B$ ever occurs. Thermochemical data are summarized in Table IV.

Protonated hydrogen sulfide undergoes reaction 6 with $(CH_3)_3B$ to yield $H_2SB(CH_3)_2^+$ in addition to the major product $(CH_3)_2B^+$. Generation of $H_2SB(CH_3)_2^+$ and neutral CH_4 may result from the four-center reaction depicted in Scheme I. Dative bond formation between the remaining lone pair on sulfur and the empty B 2p orbital would lend to the stability of the proposed product ion in Scheme I.

Scheme I



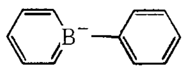
Negative Ion Chemistry. $(CH_3)_3B$. The negative ion $C_3H_8B^-$ observed in $(CH_3)_3B$ alone very likely has the structure $(CH_3)_2B{=}CH_2^-$. Significant stabilization would result from π-bond formation yielding a species isoelectronic with and structurally similar to $(CH_3)_2C{=}CH_2$ and $(CH_3)_2N{=}CH_2^+$.

Table IV. Thermochemical Properties Used in Calculations[a]

MH	ΔH_f(MH)[b]	PA-(MH)[d]	ΔH_f-(MH_2^+)[f]	PA(M^-)	ΔH_f-(M^-)[f]
$(CH_3)_3B$	−29.3 ± 5	—	—	365	−31.5
CH_4	−17.9 ± 0.1	126	223.3	—	—
C_2H_4	12.5 ± 0.1	158	221.7	—	—
H_2S	−4.9 ± 0.14	169	193.3	—	—
CH_2O	−26.0 ± 0.12	171	170.2	—	—
AsH_3	14.6[c]	177[e]	204.8	360[g]	7.4
NH_3	−11.0 ± 0.1	207	149.2	—	—
PH_3	5.5 ± 0.4	—	—	369[g]	7.3
C_2H_5OH	−56.2 ± 0.1	—	—	374.9[h]	−48.5
CH_3OH	−48.1 ± 0.05	—	—	376.8[h]	−38.5

[a] All values are in kcal/mol at 298 K. [b] Neutral heats of formation, except as noted, are from J. D. Cox and G. Pilcher, "Thermochemistry of Organic and Organometallic Compounds", Academic Press, New York, N.Y., 1970, and D. R. Stull and H. Prophet, "JANAF Thermochemical Tables", 2nd ed, NSRDS-NBS 37, U.S. Government Printing Office, Washington, D.C., 1971. [c] S. R. Gunn, *Inorg. Chem.*, 11, 796 (1972). [d] Proton affinities of neutrals, except as noted, are taken from ref 38. [e] Reference 39. [f] Calculated using thermochemical data from this table and $\Delta H_f(H^+)$ = 367.2 kcal/mol. [g] Reference 26b. [h] R. T. McIver, Jr. and J. S. Miller, *J. Am. Chem. Soc.*, 96, 4323 (1974).

Several solution phase studies support the proposed $C_3H_8B^-$ structure, including species $R_2B{=}CR'_2{}^-$ (R = H, cyclohexyl, ethyl, 9-borabicyclononyl; R′ = H, methyl, *n*-butyl) and the *B*-phenylborabenzenide anion II observed in



II

hydroboration and in deprotonation reactions in hydrocarbon-THF solutions and benzene suspensions.[40-43] The present ICR observations of $(CH_3)_2B{=}CH_2^-$ anion, produced by dissociative electron capture in the neutral and by proton transfer from $(CH_3)_3B$ to strong anionic bases, constitute the first report of a boron-stabilized carbanion as an isolated, stable species in the gas phase.

Proton Affinity of $(CH_3)_2B{=}CH_2^-$: Brönsted Acidity of $(CH_3)_3B$. The proton affinity (PA) of an anion M^- is defined as the enthalpy change accompanying reaction 21 and is a quantitative measure of the gas phase Brönsted acidity of MH.

$$MH \rightarrow M^- + H^+ \qquad \Delta H \equiv PA(M^-) \tag{21}$$

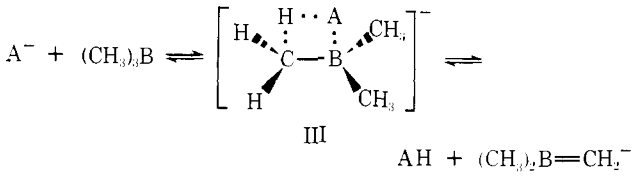
Under the assumption that gas phase proton transfer proceeds without activation, the relative acidities of anions M_1^- and M_2^- may be inferred from the observed preferred direction of reaction 22.[7]

$$M_1^- + M_2H \rightleftharpoons M_1H + M_2^- \tag{22}$$

The observed deprotonation of $(CH_3)_3B$ effected by CD_3O^- (reaction 11), $C_2H_5O^-$ (reaction 13), and PH_2^- (reaction 15) and the protonation of $(CH_3)_2B{=}CH_2^-$ by neutral AsH_3 (reaction 14) serve, in conjunction with previous experiments, to establish the relative gas phase acidity order: $CD_3OH < C_2H_5OH < PH_3 < (CH_3)_3B < AsH_3$. PA[$AsH_2^-$] and PA[$PH_2^-$] are reported to be 360 and 369 kcal/mol,[26b] respectively, and serve to bracket PA[$(CH_3)_2B{=}CH_2^-$] = 365 ± 5 kcal/mol. Thus, $(CH_3)_3B$ is moderately acidic, in a range comparable to CF_3CH_2OH and HF.[44,45]

Reactions leading to formation of the conjugate base of $(CH_3)_3B$ are envisioned to involve an intermediate as depicted in Scheme II, where anion A^- possesses an electron lone pair available for coordination to boron. Subsequent decomposition of intermediate III to products occurs to yield the anion of lower PA and the less acidic neutral.

Scheme II



From the proton affinity of $(CH_3)_2B{=}CH_2^-$ determined above, $\Delta H_f[(CH_3)_2B{=}CH_2^-]$ = −31.5 ± 5 kcal/mol is calculated. Assuming D[$(CH_3]_2BCH_2$–H] = 90 kcal/mol (probably an upper limit), the electron affinity of $(CH_3)_2BCH_2$ radical is estimated to be 39 ± 10 kcal/mol (1.7 ± 0.4 eV). Pertinent thermochemical data utilized in the calculations are collected in Table IV.

Adducts of Strong Bases with $(CH_3)_3B$: Formation of $(CH_3)_3BD^-$, $(CH_3)_3BF^-$, and $(CH_3)_2BF_2^-$. In 1923, Lewis first proposed a theory of acids and bases, which states that an acid is a species which can accept an electron pair from a base to form a covalent bond. This generalization requires only that the acid possess an empty valence orbital and the base an accessible electron pair. The Lewis acid properties of boron compounds, specifically the formation of neutral adducts between trisubstituted boranes (mainly BX_3 with X = H, alkyl, or halogen) and various *n*-donor bases, have been extensively investigated.[12] Adduct bond strengths, measured by enthalpies of dissociation, between $(CH_3)_3B$ and a variety of nitrogen bases span a narrow range of 14-20 kcal/mol.[46] $(CH_3)_3B$ is a weaker Lewis acid than BH_3 and BF_3 toward these same nitrogen bases, where ΔH_{diss} is typically between 35 and 45 kcal/mol.[46]

McDaniel has recently demonstrated the utility of ICR techniques for determining relative fluoride affinities of a variety of Lewis acids including BF_3 and BCl_3, but boron trialkyls were not considered.[10a] It was pointed out that use of a monatomic reference base for determination of relative Lewis acidities would provide a better measure of intrinsic acceptor strengths, eliminating steric influences of substituents and orbital rehybridization energies inherent in polyatomic reference bases.[12a]

Studies reported here describe the formation of anionic Lewis adducts of $(CH_3)_3B$ with hydride and fluoride via bimolecular processes under conditions such that they do not react further with neutral species present. HNO^-, generated by dissociative electron capture processes in alkyl nitrites (CD_3ONO and C_2H_5ONO), undergoes the hydride transfer reaction (eq 12) with $(CH_3)_3B$ to generate $(CH_3)_3BH^-$. In mixtures of SF_6 and $(CH_3)_3B$, reaction 16 generates SF_5^- which subsequently reacts with $(CH_3)_3B$ in accordance with the fluoride transfer reaction (eq 18). In addition, SF_6^- undergoes reaction (eq 17) with $(CH_3)_3B$ to generate $(CH_3)_2BF_2^-$. $(CH_3)_2BF_2^-$ is not observed to react further with $(CH_3)_3B$, indicating fluoride transfer to $(CH_3)_3B$ to be endothermic, i.e., D[$(CH_3)_3B$–F^-] < D[$(CH_3)_2FB$–F^-].

These adducts are direct analogues to BH_4^- and BF_4^- which are known to be tetrahedral ions, involving simple electron pair donation from H^- and F^- to the empty B 2p orbital in the neutral borane. The observed results serve to establish the Lewis acidity order toward H^- ion as $(CH_3)_3B$ > NO and toward F^- ion as $(CH_3)_2FB > (CH_3)_3B > SF_4$. Further quantification of the acidity order relative to hydride is hampered by lack of thermochemical data describing HNO^-. The reported D[SF_4–F^-] = 54 ± 12 kcal/mol places a lower limit on the fluoride affinity of $(CH_3)_3B$ of this value.[8] The observation that fluoride transfer from $(CH_3)_2BF_2^-$ to $(CH_3)_3B$ (reaction 19) does not occur serves to place the Lewis acidity of $(CH_3)_2BF$ above that of $(CH_3)_3B$, toward fluoride as reference base. Utilizing the thermochemical data in Table IV, heats of formation for the ionic products of reactions 17 and 18 are calculated to be $\Delta H_f[(CH_3)_2BF_2^-] \leqslant -185.5 \pm 12$ and $\Delta H_f[(CH_3)_3BF^-] \leqslant -144.3 \pm 12$ kcal/mol, respectively. These estimated upper limits are consistent with reported values of $\Delta H_f[BF_4^-] = -413$ and $D[F_3B\text{-}F^-] = 71$ kcal/mol and expected trends of decreasing ΔH_f and increasing fluoride affinity with increasing fluorine substitution on boron.[10a]

Conclusions and Implications for Further Study. In the ion chemistry of $(CH_3)_3B$, the dominant role of the electron deficiency of boron is manifest in: (a) rapid fragmentation of and low one-electron B-CH_3 bond dissociation energy in the parent radical ion $(CH_3)_3B^+$, resulting in dominance of $(CH_3)_2B^+$ in positive ion chemistry of the neutral; (b) formation of the boron-stabilized carbanion $(CH_3)_2B{=}CH_2^-$ where π delocalization into the vacant B 2p orbital leads to enhanced stability and decrease of the carbanion PA much below that observed in hydrocarbons; and (c) formation of anionic Lewis adducts, including $(CH_3)_3BH^-$ and $(CH_3)_3BF^-$, where dative σ-bonding between pair donors and the vacant B 2p orbital results in closed shell anions isoelectronic with saturated carbon neutrals.

The ability to generate $(CH_3)_2B{=}CH_2^-$, $(CH_3)_3BH^-$, $(CH_3)_3BF^-$, and $(CH_3)_2BF_2^-$ species in bimolecular processes under conditions such that they do not react with neutrals present affords the opportunity for further investigation of their properties and reactions. The presence of a charge in the B-C π system in $(CH_3)_2B{=}CH_2^-$ makes its study by ICR techniques of interest in light of the isoelectronic analogy to neutral carbon-carbon π systems. Further investigation of anionic Lewis adducts, by examination H^- and F^- transfer reactions, will yield quantitative Lewis acid strengths of a variety of trisubstituted boranes and provide insight into the effects of substitution on acceptor strength of boron. Such information would be valuable to understanding the selectivity of reductions of functional groups in organic synthesis effected by boron reagents.[47]

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