

creased importance of the b₁ → b₁ configuration over the a₂ → a₂, as can be seen in Table IV. This increasing importance of the b₁ → b₁ configuration arises both from orbital energy changes, such as those discussed in connection with the PES interpretation, and from a decrease in K_{HOMO-LUMO} upon distortion, since the exchange integral, K, diminishes as the two sides of the benzene ring are brought together.

Conclusion

Photoelectron and absorption spectra reveal some evidence for the distortion of the benzene rings in fused compounds as a result of ring strain. The changes in orbital energies detected by photoelectron spectroscopy are relatively sensitive probes of distortion, while energies of transitions to the lowest singlet state are poor indicators of such effects. However, intensities, which indirectly reflect orbital energy changes, are, like ionization potentials, relatively sensitive probes of distortion as long as corrections can be made for the inductive effects of ring substituents.

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Acid-Base Properties of 1-Methyl-1,4-dihydroborabenzene, CH₃BC₅H₆

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



Abstract: Ion cyclotron resonance techniques are employed to determine the gas-phase Brønsted and Lewis acidities as well as the Brønsted basicity of 1-methyl-1,4-dihydroborabenzene, CH₃BC₅H₆. The ring proton is found to be highly acidic with PA(CH₃BC₅H₅⁻) = 337 ± 3 kcal/mol. This acidity results from the formation of a 6π electron aromatic anion CH₃BC₅H₅⁻, which is isoelectronic with toluene. Both the Lewis acidity toward F⁻ as a reference base and the proton basicity of the parent molecule suggest that there is little interaction between the diene π system and the electron-deficient boron. This is further confirmed by the similarity of both negative and positive ion chemistry of the borabenzene to that of aliphatic boranes.

Introduction

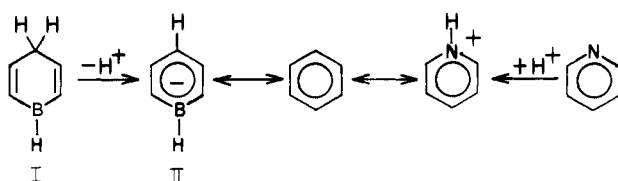
Ionic 6π electron aromatic compounds isoelectronic with benzene can be generated and studied in the gas phase where their intrinsic properties and reactivities can be probed without interference from solvent effects. For example, on protonation

of pyridine to form C₅H₅NH⁺ (Scheme I), the cation retains the aromatic properties of neutral pyridine. The low solution basicity of pyridine compared to aliphatic amines has been interpreted as the result of increased s character in the nitrogen lone pair. This hybridization change is the result of the involvement of nitrogen in the planar π system. Ion cyclotron

Table I. Gas-Phase Acidities of Selected Compounds^a

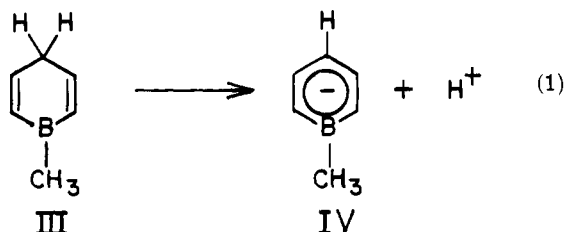
MH	PA(M ⁻)	D(M-H)	EA(M)
CH ₃ CHCH ₂	388 ^{b,c}	87 ^g	12.7 ^j
	359.7 ± 0.4 ^d	67 ^b	20.4 ± 0.3 ^j
	352.7 ± 0.2 ^d	81.2 ^h	42.4 ± 0.7 ^c
	348.5 ^d		
	335 ± 2.0 ^e	(74) ⁱ	(53) ^b
	363 ^e		
(CH ₃) ₂ B	365 ± 5 ^f		

^a All values in kcal/mol at 298 K. ^b Calculated using data in this table. ^c J. H. Richardson, L. M. Stephenson, and J. I. Brauman, *J. Chem. Phys.*, **59**, 5068 (1973). ^d Reference 6. ^e This study. ^f Reference 18. ^g S. W. Benson, "Thermochemical Kinetics", Wiley-Interscience, New York, N.Y., 1976. ^h S. Furuyama, D. M. Golden, and S. W. Benson, *Int. J. Chem. Kinet.*, **3**, 237 (1971). ⁱ Estimated as the bond strength in cyclohexadiene, ref 21. ^j J. I. Brauman, private communication.

Scheme I

resonance measurements indicate that the gas-phase basicity of pyridine is significantly greater than that of NH₃ and comparable to aliphatic amines.² Differential solvation is responsible for the discrepancy between gas-phase and solution results.

An anionic analogue of benzene can be generated by proton abstraction from dihydroborobenzene (I) (Scheme I). If boron participates effectively in π bonding, the anion II will be resonance stabilized, imposing a high acidity on the ring protons of the conjugate acid precursor. Not surprisingly, solution studies in THF indicate that the methyl-substituted 1,4-dihydroborabenzene (eq 1, III)³ is a very strong acid, consid-



erably stronger than cyclopentadiene under the same conditions.⁴

As with proton basicities, gas-phase studies indicate that molecular acidities are strongly moderated by solvation effects. For example, the lower solution acidity of fluorene ($pK = 23$) compared to cyclopentadiene ($pK = 14-15$) has been explained as the result of decreased availability of the electrons to the five-membered ring (annulation) in the fluorenyl anion.⁵ In the gas phase, fluorene is slightly more acidic than cyclopentadiene (Table I).⁶ The solution acidities are apparently strongly moderated by decreased solvation of the larger fluorenyl anion.

In addition to extensive π delocalization in the anion (IV), it is possible that the electron-rich diene system may donate

Table II. Gas-Phase Fluoride Ion Affinities^a

M	D(M-F ⁻) ^b	M	D(M-F ⁻) ^b
BF ₃	71 ^c	CH ₃ BC ₅ H ₆	~59 ^e
SiF ₄	<71 ^c	(CH ₃) ₃ B	58.5
(C ₂ H ₅) ₂ FB	64.0	(CH ₃) ₂ SiF ₂	56 ^d
(C ₂ H ₅) ₃ B	62.0	SF ₄	54 ± 12 ^f
(CH ₃) ₂ FB	61.8	SF ₅	11 ± 8 ^f
CH ₃ SiF ₃	60.2 ^d		

^a All values in kcal/mol at 298 K, listed in order of decreasing fluoride affinities. ^b Fluoride affinities of boron species from M. K. Murphy and J. L. Beauchamp, *Inorg. Chem.*, in press, and ref 18. ^c J. C. Haartz and D. M. McDaniel, *J. Am. Chem. Soc.*, **95**, 8562 (1973). ^d Estimates based on order of strengths in ref 10. ^e This study. ^f M. S. Foster and J. L. Beauchamp, unpublished results.

electron density into the deficient boron in the neutral borane. The question of π delocalization in vinyl boranes has been examined by several spectroscopic techniques including UV,⁷ NMR,⁸ and photoelectron spectroscopy (PES).⁹ It has been reported that the photoelectron spectra of vinylborane indicate little or no delocalization into the boron orbital.⁹ On the other hand, both ultraviolet spectra⁷ and NMR studies⁸ have been interpreted in terms of this delocalization. For example, a recent ¹³C NMR study relates the large deshielding of the terminal carbons in vinyl boranes to π interactions with boron.⁸ This deshielding was considerably decreased in the Lewis acid-base complexes of the vinyl boranes, in which the boron orbital is bonded to a substituent base. By similar reasoning it is expected that the availability of the boron orbital for bonding to a base would be directly affected by π delocalization in the neutral.

Gas-phase Lewis acidities of neutrals are determined by measuring the affinities of neutrals for reference anionic bases such as F⁻.¹⁰ Ion cyclotron resonance studies have provided Lewis acidities of a variety of S, Si, and B compounds toward F⁻ as a reference base (Table II).

In this study we have investigated the gas-phase acid-base properties of CH₃BC₅H₆. The proton acidity as well as the Lewis acidity and proton basicity have been determined. By comparisons with appropriate model compounds the present results provide information relating to the degree of resonance stabilization in the anion and π delocalization in the neutral.

Experimental Section

ICR instrumentation and techniques have been detailed previously.^{11,12} All experiments were performed on a spectrometer built in this laboratory, incorporating a 15-in. magnet capable of observing up to m/e 800. Pressure was measured using a Schulz-Phelps ion gauge, calibrated at higher pressures against an MKS Model 90-H1 baratron capacitance manometer. Pressure measurements are the major source of error ($\pm 20\%$) in reported reaction rate constants.

Double resonance techniques were employed to determine the preferred direction of proton transfer reactions in mixtures. Relative proton basicities and acidities result from these data. In acidity studies, the anionic conjugate bases of the neutrals to be compared were generated in proton abstraction reactions of the strong gas-phase base CD₃O⁻. In a similar manner, relative Lewis acidities toward the reference base F⁻ were determined in mixtures with SF₆, in which fluoride donors are produced by electron attachment.

Near thermal electron attachment produces CD₃O⁻ (75%) and DNO⁻ (25%) in CD₃ONO.¹³ The deuterated nitrite is used to distinguish between CH₃O⁻ and HNO⁻, which both appear at m/e 31. At moderate pressures (5×10^{-5} Torr), NO₂⁻ is formed on reaction of CD₃O⁻ with the nitrite. By variation of the partial pressures of the components of mixtures, NO₂⁻ can be generated in amounts adequate for studies of its reactions. Electron attachment processes in SF₆ result in formation of SF₆⁻ (95%) and SF₅⁻ (5%).¹⁴ F⁻ is similarly generated from NF₃.¹⁵

The methods of synthesis of the boron compounds used in this study

Table III. Summary of Measured Reaction Rates

Reaction		<i>k</i> ^a
CD ₃ O ⁻ + CH ₃ BC ₅ H ₆	→ CH ₃ BC ₅ H ₅ ⁻ + CD ₃ OH	6.3
DNO ⁻ + CH ₃ BC ₅ H ₆	→ CH ₃ BC ₅ H ₅ ⁻ + DH + NO	4.5
SF ₆ ⁻ + CH ₃ BC ₅ H ₆	→ SF ₅ ⁻ + HF + CH ₃ BC ₅ H ₅	2.1
	→ F ₂ BC ₅ H ₆ ⁻ + CH ₃ + SF ₄	0.70
SF ₅ ⁻ + CH ₃ BC ₅ H ₆	→ F(CH ₃)BC ₅ H ₆ ⁻ + SF ₄	1.1
SF ₆ ⁻ + (CH ₃) ₃ B	→ SF ₅ ⁻ + HF + (CH ₃) ₂ BCH ₂	3.7
	→ F ₂ B(CH ₃) ₂ ⁻ + SF ₄ + CH ₃	1.4
SF ₅ ⁻ + (CH ₃) ₃ B	→ FB(CH ₃) ₂ ⁻ + SF ₄	2.8

^a Thermal rate constants in units of 10⁻¹⁰ cm³ molecule⁻¹ s⁻¹.

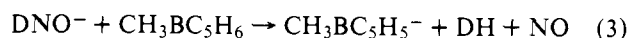
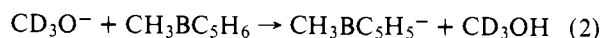
have been described previously.³ The purity and identities of CH₃BC₅H₆ and the dimethyl analogue CH₃BC₅H₄ (CH₃)₂ were checked by ¹H NMR and mass spectral analysis. The latter sample contained ~5% of an unidentified boron species at *m/e* 124–126. Since relative proton acidity studies were not affected by the impurity, no attempt was made to purify the sample. No trace of isotopic impurity (≥1%) was detected in the ¹H NMR or mass spectrum of the deuterated borabenzene CD₃BC₅H₆.

Preparation and use of alkyl nitrates have been described previously.¹⁶ All other compounds used in these experiments were from commercial sources and used without further purification except for repeated freeze-pump-thaw cycles to remove noncondensable impurities.

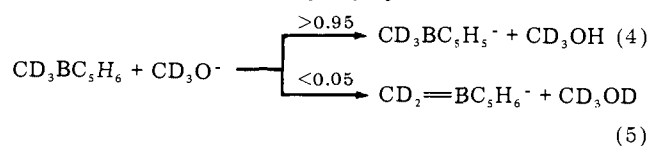
Normalized intensities of boron ions reported in tables and figures are the sum of ¹⁰B and ¹¹B isotope intensities. In all cases, the naturally occurring isotope ratios were observed (¹⁰B, 19.9% and ¹¹B, 80.1%). For simplicity, only the masses of the more abundant ¹¹B isotopes are included in the text and figures.

Results

Proton Acidity of CH₃BC₅H₆. Figure 1 presents the temporal variation of normalized ion intensity in a (1.3:1) mixture of CH₃BC₅H₆ and CD₃ONO at a total pressure of 8.0 × 10⁻⁷ Torr. Double resonance experiments confirm that both CD₃O⁻ (*m/e* 34) and DNO⁻ (*m/e* 32) react with CH₃BC₅H₆ by proton transfer to form CH₃BC₅H₅⁻ (*m/e* 91)



where neutrals are assumed. The ring proton is more acidic, as shown by the predominance of CD₃BC₅H₅⁻ (*m/e* 94) in the reaction of CD₃O⁻ with CD₃BC₅H₆:



Rates of reactions 2 and 3 are listed in Table III.

Proton transfer processes were further examined in mixtures of CD₃ONO, (CH₃)₃B, HCO₂H, HCN, HCl, C₆H₅OH, and C₆H₅CO₂H with CH₃BC₅H₆ to determine the acidity of the

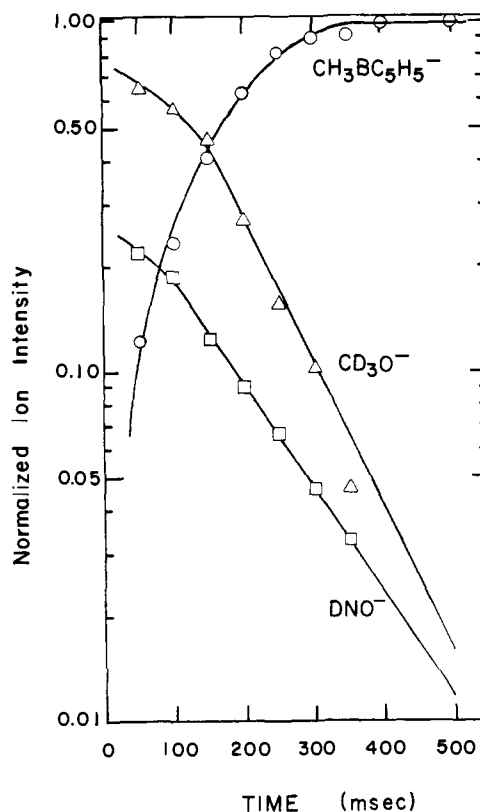
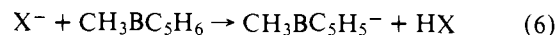
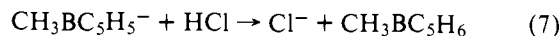


Figure 1. Temporal variation of normalized negative ion intensity in a 1.3:1 mixture of CH₃BC₅H₆ and CD₃ONO at total pressure 8.0 × 10⁻⁷ Torr. Reactants are generated by attachment of thermalized electrons scattered and trapped during a 70-eV 10-ms electron beam pulse.

latter species. In each case, CD₃ONO was added to ensure the formation of both anionic species, by reaction of the strong base CD₃O⁻. The preferred direction of proton transfer in these mixtures was determined using double resonance techniques. Proton transfer reaction 6 is observed only in the direction noted with X⁻ = CN⁻, (CH₃)₂B=CH₂⁻, HCO₂⁻ and NO₂⁻.



In contrast, CH₃BC₅H₅⁻ reacts with HCl to form Cl⁻.



Double resonance irradiation of Cl⁻ results in a slight decrease in CH₃BC₅H₅⁻ ion intensity, suggesting that reaction 7 may also occur in the reverse direction. However, equilibrium could not be achieved in this mixture by variation of the relative pressures of the neutrals. In mixtures of C₆H₅OH and C₆H₅CO₂H with CH₃BC₅H₆, the conjugate bases were formed in abundance by proton transfer to CD₃O⁻. In each case, no reactive coupling of the anions was detected by double resonance. This is not very surprising considering that reactions of conjugated anions are generally very slow.¹⁷ These experiments combined with literature data suggest that acidity increases in the order (CH₃)₃B < HCO₂H < HCN < HNO₂ < CH₃BC₅H₆ < HCl. The acidities of the reference compounds have been determined previously as listed in Table IV. Using these data, PA(CH₃BC₅H₅⁻) is estimated as 335 ± 2 kcal/mol.

Lewis Acidity of CH₃BC₅H₆. The bond strength *D*(M–F⁻) is a measure of the Lewis acidity of the species M. Relative fluoride bond strengths to a variety of neutrals have been measured previously and are listed in Table II. The acidity of a compound toward fluoride ion as a reference base can be measured by determining the preferred direction of F⁻ transfer

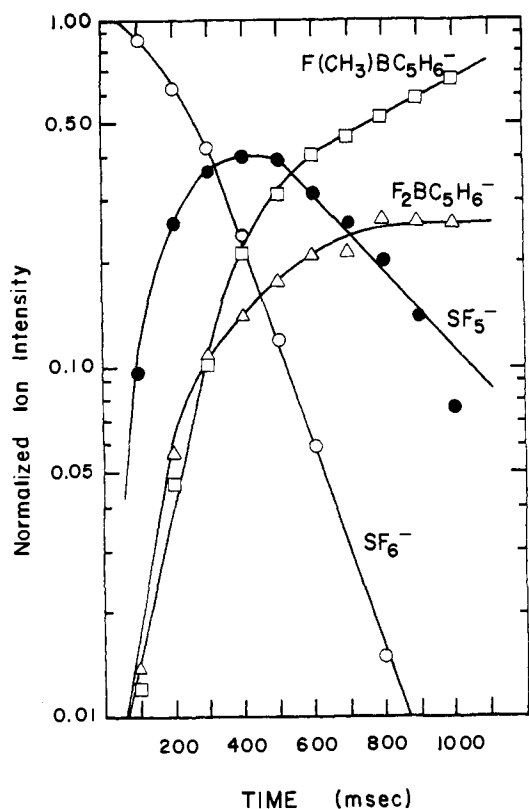
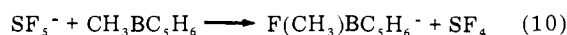
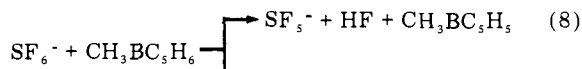


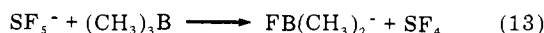
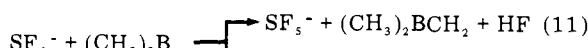
Figure 2. Temporal variation of normalized negative ion intensity in a mixture of 7.16×10^{-7} Torr $\text{CH}_3\text{BC}_5\text{H}_6$ with a trace amount of SF_6 .

in mixtures with neutrals of known acidity.¹⁰ Anionic F^- adducts are formed in these experiments by reactions of SF_6^- and/or SF_5^- .

Temporal variation of normalized ion intensity in a mixture of $\text{CH}_3\text{BC}_5\text{H}_6$ (7.16×10^{-7} Torr) with a trace amount ($<10^{-7}$ Torr) of SF_6 is presented in Figure 2. Ionic products SF_5^- (m/e 127), $\text{F}(\text{CH}_3)\text{BC}_5\text{H}_6^-$ (m/e 111), and $\text{F}_2\text{BC}_5\text{H}_6^-$ (m/e 115) increase as SF_6^- (m/e 146) decays with time. Double resonance confirms that SF_6^- reacts to form SF_5^- (eq 8) and $\text{F}_2\text{BC}_5\text{H}_6^-$ (eq 9). The F^- adduct $\text{F}(\text{CH}_3)\text{BC}_5\text{H}_6^-$ is formed only by reaction of SF_5^- (eq 10). Rates for these reactions (eq 7-10) are summarized in Table III.



Fluoride transfers were examined in mixtures of $(\text{CH}_3)_3\text{B}$ and $(\text{CH}_3)_2\text{SiF}_2$ with $\text{CH}_3\text{BC}_5\text{H}_6$ and a trace amount of SF_6 . When $(\text{CH}_3)_3\text{B}$ is added to SF_6 ,¹⁸ product ions $(\text{CH}_3)_3\text{BF}^-$ (m/e 75), $(\text{CH}_3)_2\text{BF}_2^-$ (m/e 79), and SF_5^- (m/e 127) result in the reactions



analogous to processes 8-10. These reactions are summarized in Table III with rates included for comparison to reactions of $\text{CH}_3\text{BC}_5\text{H}_6$. With addition of $\text{CH}_3\text{BC}_5\text{H}_6$, double resonance indicates that $(\text{CH}_3)_3\text{BF}^-$ reacts to form $\text{F}(\text{CH}_3)\text{BC}_5\text{H}_6^-$:

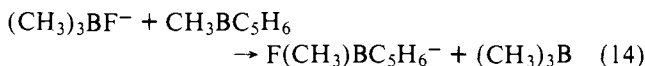
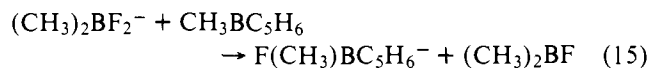


Table IV. Gas-Phase Acidities of Selected Reference Acids^a

MH	PA(M ⁻)	MH	PA(M ⁻)
CD_3OH	378.4 ^b	$\text{C}_6\text{H}_5\text{OH}$	346.9 ^f
HF	371.3 ^c	HCO_2H	342.2 ^g
$\text{CF}_3\text{CH}_2\text{OH}$	364 ± 5 ^d	$\text{C}_6\text{H}_5\text{CO}_2\text{H}$	336.7 ^g
AsH_3	360 ± 10 ^e	HCl	333.3 ^c
HCN	348.9 ^c		

^a All values in kcal/mol at 298 K. Unless otherwise noted, error limits are ± 0.5 or less. ^b R. T. McIver, Jr., and J. S. Miller, *J. Am. Chem. Soc.*, **96**, 4323 (1974); J. E. Bartmess and R. T. McIver, Jr., *ibid.*, **99**, 4163 (1977). ^c Calculated using thermochemical data from D. R. Stull and H. Prophet, "JANAF Thermochemical Tables", 2nd ed. U.S. Government Printing Office, Washington, D.C., 1971. ^d B. S. Freiser and J. L. Beauchamp, unpublished results. ^e R. H. Wyatt, D. Holtz, T. B. McMahon, and J. L. Beauchamp, *Inorg. Chem.*, **13**, 1511 (1974). ^f R. T. McIver, Jr., and J. H. Silvers, *J. Am. Chem. Soc.*, **95**, 8462 (1973). ^g T. B. McMahon and P. Kebarle, *ibid.*, **99**, 2222 (1977), and references cited therein.

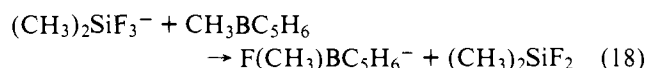
Although there is some indication that the reverse reaction occurs, the slow rate of formation of $\text{F}(\text{CH}_3)\text{BC}_5\text{H}_6^-$ from SF_5^- hinders quantitative measurement of the equilibrium constant for F^- transfer in this reaction. The difluoride ion $(\text{CH}_3)_2\text{BF}_2^-$ does not contribute to the formation of $\text{F}(\text{CH}_3)\text{BC}_5\text{H}_6^-$ suggesting that reaction 15 is endothermic.



Both SF_6^- (eq 16) and SF_5^- (eq 17) react to form $(\text{CH}_3)_2\text{SiF}_3^-$ (m/e 115) on electron impact of a mixture of $(\text{CH}_3)_2\text{SiF}_2$ and SF_6 .¹⁰

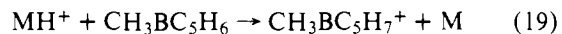


On addition of $\text{CH}_3\text{BC}_5\text{H}_6$, double resonance indicates that $(\text{CH}_3)_2\text{SiF}_3^-$ transfers F^- to $\text{CH}_3\text{BC}_5\text{H}_6$:



These results suggest that the Lewis acidities increase in the order $\text{SF}_5^- < (\text{CH}_3)_2\text{SiF}_2 < (\text{CH}_3)_3\text{B} \sim \text{CH}_3\text{BC}_5\text{H}_6 < (\text{CH}_3)_2\text{BF}_2^-$. A value of 59 kcal/mol for $D(\text{CH}_3\text{BC}_5\text{H}_6-\text{F}^-)$ is estimated from F^- bond strengths in Table II.







Proton Affinity of $\text{CH}_3\text{BC}_5\text{H}_6$. Proton transfer reactions were examined in mixtures of $\text{CH}_3\text{BC}_5\text{H}_6$ with CH_4 , $(\text{CH}_3)_2\text{CCH}_2$, CH_3CHCH_2 , $c\text{-C}_6\text{H}_{10}$, and CH_3COCH_3 to determine the basicity of the borabenzene. Protonation of $\text{CH}_3\text{BC}_5\text{H}_6$ to form $\text{CH}_3\text{BC}_5\text{H}_7^+$ (m/e 93) occurs with proton donors ($\text{MH}^+ = \text{CH}_5^+$, C_2H_5^+ , and $(\text{CH}_3)_3\text{C}^+$) as in the reaction



Double resonance indicates that reaction occurs in both directions with $\text{M} = \text{isobutene}$. Failure to observe equilibrium in this case suggests that deprotonation of $\text{CH}_3\text{BC}_5\text{H}_7^+$ is slow.

Conclusive results were not obtained in other mixtures. In mixtures of $\text{CH}_3\text{BC}_5\text{H}_6$ with $c\text{-C}_6\text{H}_{10}$ and CH_3CHCH_2 , the boron compound is preferentially protonated by the parent and fragment ions of the alkenes. In both cases, little or no protonated alkene is observed. The reverse situation obtains in mixtures of $\text{CH}_3\text{BC}_5\text{H}_6$ with CH_3COCH_3 , in which protonation of acetone predominates and proton transfer from this species to the neutral borane is not observed. These results suggest that proton affinities increase in the order $\text{CH}_4 < \text{C}_2\text{H}_4 < \text{CH}_3\text{CHCH}_2 < (\text{CH}_3)_2\text{CCH}_2 \sim \text{CH}_3\text{BC}_5\text{H}_6 <$

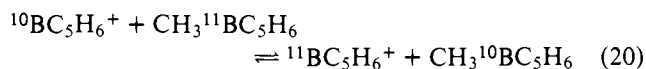
Table V. Gas-Phase Proton Affinities, Hydrogen Affinities, and Ionization Potentials of Selected Alkenes^a

M	PA-(M) ^b	HA-(M ⁺) ^b	IP(M)	ΔH _f ^c (MH ⁺)
CH ₂ CH ₂	161	89	242.4	219
CH ₃ CHCH ₂	181	92	224.6	191
	181	78	210.5	183
	182	79	210.5	183
	196	95	212.8	167
	200	84	197.6	199 ^c
	178	72	207.7	197 ^c
	195	88	207 ± 2 ^d	

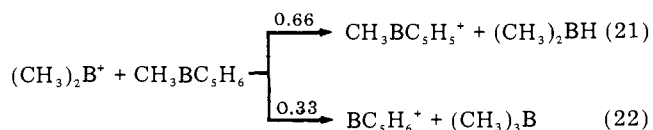
^a All values in kcal/mol at 298 K. Unless otherwise noted, IP(M) and ΔH_f(MH⁺) are taken from H. M. Rosenstock, K. Draxl, B. W. Steiner, and J. T. Herron, *J. Phys. Chem. Ref. Data*, **6**, Supplement 1 (1977). ^b Calculated from thermochemical data listed in this table. ^c Calculated using data in F. P. Lossing and J. C. Traeger, *J. Am. Chem. Soc.*, **97**, 1579 (1975). ^d Reference 20.

CH₃COCH₃, with PA(CH₃BC₅H₆) estimated as 195 kcal/mol (Table V). From the adiabatic ionization potential IP(CH₃BC₅H₆) = 9.0 ± 0.1 eV obtained from photoelectron spectroscopy,²⁰ a hydrogen affinity¹¹ HA(CH₃BC₅H₆⁺) = 89 ± 2 kcal/mol is calculated. This value is somewhat higher than expected by analogy to *trans*-2-butene (Table V).

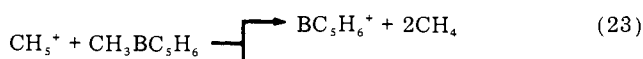
Positive Ion Chemistry of CH₃BC₅H₆. Three major ions represent ~95% of total ionization in the 70.0-eV electron-impact mass spectrum of CH₃BC₅H₆, the parent ion CH₃BC₅H₆⁺ (*m/e* 92, 12%), loss of methyl to give BC₅H₆⁺ (*m/e* 77, 22%), and loss of hydrogen to yield CH₃BC₅H₅⁺ (*m/e* 91, 61%). The latter ion, first detected at electron energies ~0.50 eV higher than the IP(CH₃BC₅H₆),²⁰ becomes the most abundant fragment above 10.0 eV. These three ions are unreactive with CH₃BC₅H₆. In particular, double resonance of the boron isotopes of BC₅H₆⁺ indicates that the thermoneutral CH₃⁻ transfer (eq 20) does not occur in contrast to reactions in (CH₃)₃B.¹⁸



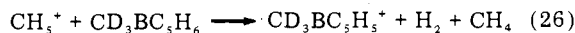
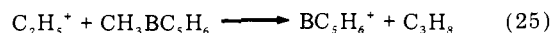
Positive Ion Chemistry in Mixtures of (CH₃)₃B and CH₄ with CH₃BC₅H₆. In trapped ion studies of mixtures of CH₃BC₅H₆ and (CH₃)₃B, double resonance confirms that the major fragment ion of (CH₃)₃B, (CH₃)₂B⁺, reacts with CH₃BC₅H₆ to form CH₃BC₅H₅⁺ (eq 21) and BC₅H₆⁺ (eq 22).



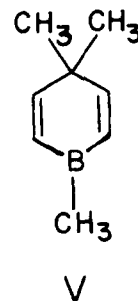
As described above, proton transfer reactions in mixtures of CH₃BC₅H₆ with a variety of proton donors were examined. With CH₄, the reactivity of CH₅⁺ and C₂H₅⁺ was studied in more detail. In addition to proton transfer reactions (eq 5), both CH₅⁺ (eq 23) and C₂H₅⁺ (eq 24) react with CH₃BC₅H₆



to form BC₅H₆⁺. CH₅⁺ also contributes to the formation of CH₃BC₅H₅⁺ (eq 25). This reaction involves cleavage of the ring hydrogen, as determined by reaction with CD₃BC₅H₆ (eq 26).

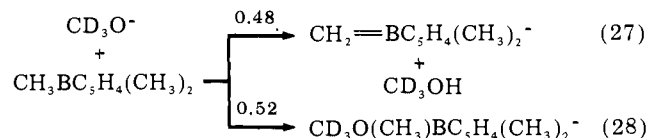


Negative Ion Chemistry. Proton transfer processes dominate the negative ion chemistry of CH₃BC₅H₆. To probe the interaction of negative ions with the vinylborane moiety, chemistry in mixtures with CH₃BC₅H₄(CH₃)₂ (V) was ex-

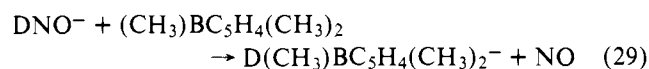


amined. These studies also provide a qualitative measure of the proton acidity of the boron methyl.

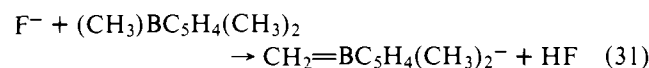
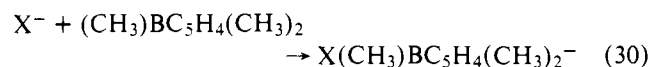
In a mixture of V with CD₃ONO, anionic products CH₂=BC₅H₄(CH₃)₂⁻ (*m/e* 119), CD₃O(CH₃)BC₅H₄(CH₃)₂⁻ (*m/e* 154), and D(CH₃)BC₅H₄(CH₃)₂⁻ (*m/e* 122) appear. Double resonance indicates that CD₃O⁻ reacts with V by proton transfer (eq 27) and direct anion addition (eq 28).



Product distributions in eq 27 and 28 are determined from drift mode single resonance ion intensities at 1 × 10⁻⁵ Torr of the borane. The anion addition product (eq 28) increases markedly relative to proton transfer as the borane pressure is increased. This is consistent with increased collisional stabilization of the adduct ion at higher pressures. In contrast to reactivity in CH₃BC₅H₆, DNO⁻ reacts with V to form only D(CH₃)BC₅H₄(CH₃)₂⁻ by deuteride transfer (eq 29).



Direct formation of anionic adducts (eq 30) is observed with anions X⁻ = CD₃O⁻, NO₂⁻, and Cl⁻. In contrast, F⁻ reacts with V only by proton transfer (eq 31).



Attempts were made to determine the preferred direction of proton transfer in mixtures of V with AsH₃ and CF₃CH₂OH. Although the anionic conjugate bases were formed by proton transfer to CD₃O⁻ in both bases, no reactive coupling of AsH₂⁻ and CF₃CH₂O⁻ with CH₂=BC₅H₄(CH₃)₂⁻ was observed. Only rough limits ~365 kcal/mol < PA(CH₂BC₅H₄(CH₃)₂⁻) < 370 kcal/mol are suggested by reaction 31 and the failure to observe proton transfer to DNO⁻ (Table IV).¹⁹ The proton affinity PA[(CH₃)₂B=CH₂⁻] was determined previously in a similar manner to be 365 ± 5 kcal/mol.¹⁸

Discussion

The acid-base properties of $\text{CH}_3\text{BC}_5\text{H}_6$ reflect the degree of interaction of the diene π system with the empty $p\pi$ orbital on boron in both the neutral and conjugate base. The unusually high acidity of $\text{CH}_3\text{BC}_5\text{H}_6$, comparable to HCl, indicates that the anion is resonance stabilized with participation of the boron orbital to form a 6π aromatic anion. In contrast, no evidence is found for π delocalization in $\text{CH}_3\text{BC}_5\text{H}_6$.

Delocalization of π electron density into the $p\pi$ orbital on boron in the neutral would be expected to decrease its availability for bonding, i.e., result in a low Lewis acidity or electron acceptor ability. There is no significant decrease in Lewis acidity of $\text{CH}_3\text{BC}_5\text{H}_6$ compared to $(\text{CH}_3)_3\text{B}$ or $(\text{C}_2\text{H}_5)_3\text{B}$ (Table II). Similarly, the basicity of the ring in $\text{CH}_3\text{BC}_5\text{H}_6$ is expected to be decreased if a favorable π interaction is disrupted by protonation. Although proton affinities vary significantly with substitution for homologous series, hydrogen affinities of the cations (homolytic bond dissociation energies) appear to be representative of the site of protonation (Table V).¹¹ As noted above, the thermochemical properties derived for $\text{CH}_3\text{BC}_5\text{H}_6$ and the protonated species $\text{CH}_3\text{BC}_5\text{H}_7^+$ are consistent with protonation of an unperturbed alkene (Table V). Finally, both positive and negative ion reactions involving the boron moiety in $\text{CH}_3\text{BC}_5\text{H}_6$ are similar to those observed with alkylboranes. The Lewis acidity, proton affinity, and ion chemistry of $\text{CH}_3\text{BC}_5\text{H}_6$ are all consistent with PES results,⁹ indicating that there is little interaction of the diene π system with boron.

Delocalization in Aromatic Anions. The proton affinity of an anion B^- , $\text{PA}(\text{B}^-)$, is related to the homolytic bond energy $D(\text{BH})$ and the electron affinity $\text{EA}(\text{B})$ by

$$\text{PA}(\text{B}^-) = D(\text{B-H}) - \text{EA}(\text{B}) + \text{IP}(\text{H}) \quad (32)$$

in which the ionization potential of H, $\text{IP}(\text{H})$, is 313.6 kcal/mol. Relative proton affinities or acidities are the result of differences in bond strengths and electron affinities, which reflect the stability of the radical B and the anion B^- , respectively. If two of the quantities in eq 32 are known, it is possible to assess how differences in radical and anion stabilities affect the acidity of a species. By comparison to appropriate model compounds with known acidities, it is possible to quantify the resonance energy of aromatic anions. For example, in the gas phase $c\text{-C}_5\text{H}_6$ is only 7 kcal/mol more acidic than the open-chain 1,4-pentadiene, C_5H_8 (Table I). Cyclopentadienyl radical has an electron affinity 22 kcal/mol higher than the open-chain diene. The 15 kcal/mol higher bond strength in $c\text{-C}_5\text{H}_6$ compared to 1,4-pentadiene is responsible for the small acidity difference in the two dienes. This change in bond strength can be attributed for the most part to ring strain in the radical $c\text{-C}_5\text{H}_5$. The difference in electron affinities $\text{EA}(c\text{-C}_5\text{H}_5) - \text{EA}(\text{C}_5\text{H}_7)$ does not directly measure the delocalization energy in $c\text{-C}_5\text{H}_6$, since it ignores structural changes required to form the strained planar anion. If it is assumed that the strain in the anion is equal to that in the radical, 15 kcal/mol, a delocalization energy of 37 kcal/mol is calculated for $c\text{-C}_5\text{H}_5^-$.

Neither the electron affinity of the borabenzene radical $\text{EA}(\text{CH}_3\text{BC}_5\text{H}_5)$ nor the strength of the ring C-H bond in the neutral has been measured. An $\text{EA}(\text{CH}_3\text{BC}_5\text{H}_5) = 58$ kcal/mol is estimated, however, by assuming that the C-H bond

strength is equal to that in 1,4-cyclohexadiene (74 kcal/mol).²¹ The delocalization energy is the quantity needed for comparison to other aromatic systems. By the same analysis used for cyclopentadienyl anion, comparisons of relative bond strengths and electron affinities of $\text{CH}_3\text{BC}_5\text{H}_6$ and 1,4-pentadiene yield a delocalization or resonance energy of 40 kcal/mol for $\text{CH}_3\text{BC}_5\text{H}_5^-$. Although admittedly dependent on the assumptions made, this indicates little difference in delocalization energies of the five-center 6π -electron cyclopentadienyl anion and the six-center 6π -electron dihydroborabenzene anion. Interestingly, the delocalization energies in both anions are approximately equivalent to that generally accepted for benzene which is determined (36 kcal/mol) from heats of hydrogenation. Simple Hückel molecular orbital theory²² predicts similar resonance energies for benzene and cyclopentadienyl anion. While the extension of these principles to borabenzene anion is not straightforward, the present results suggest that the boron has little effect on π delocalization in the six-member ring.

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- (19) Proton transfer reactions observed in mixtures of moderate acids with CD_3ONO suggest that $\text{PA}(\text{DNO}^-) \approx 365 \pm 5$ kcal/mol when the neutral products (assumed) are HD and NO (S. A. Sullivan and J. L. Beauchamp, unpublished results).
- (20) The photoelectron spectrum of 1-methyl-1,4-dihydroborabenzene has been recently recorded by H. Bock (private communication). The first band indicates adiabatic and vertical ionization potentials of 9.0 ± 0.1 and 9.75 ± 0.05 eV, respectively. This agrees with electron impact data recorded in our laboratory which give $\text{IP}(\text{CH}_3\text{BC}_5\text{H}_6) \approx 9.0 \pm 0.5$ eV, determined from $\text{CH}_3\text{BC}_5\text{H}_6^+$ intensity as a function of electron energy. In a similar way the appearance potential of the loss of hydrogen fragment $\text{AP}(\text{CH}_3\text{BC}_5\text{H}_5^+)$ was determined as $\sim 9.5 \pm 0.5$ eV.
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