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Gas-Phase Reactions of Dicoordinated Boron Cations with Alcohols

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The intrinsic gas-phase reactivity of simple dicoordinated boron cations toward alcohols was studied using a dual-cell Fourier-transform ion cyclotron resonance device. Reactions of the ions $CH_3BCH_3^+$, $CH_3OBOCH_3^+$, and $CH_3(CH_2)_2OBOH^+$ occur at or near collision rate with simple alcohols and are dominated by abstraction of water or a hydroxyl group by the ion. These two reactions likely occur via the same proton-bound intermediate, analogous to the dissociation of protonated ethanol to ethylene and H_3O^+. The branching ratio depends primarily on the stability of the alkyl cation formed in the hydroxyl abstraction reaction. Hence, hydroxyl abstraction dominates for longer chain alcohols. The proton affinity of $(CH_3)_2BOH$ was determined to be 179 kcal/mol through proton affinity bracketing experiments. Using this value, the heat of formation of $(CH_3)_2BOH_2^+$ is estimated to be 86 kcal/mol. Hence, dehydration of ethanol by $CH_3BCH_3^+$ is concluded to be exothermic by 21 kcal/mol. The same reaction for $CH_3OBOCH_3^+$ to yield $(CH_3O)_2BOH_2^+$ is exothermic by about 33 kcal/mol; a reaction yielding $(CH_3O)(HO)B(HOCH_3)^+$ as the final ionic product is significantly more exothermic, by about 54 kcal/mol. Relative to water abstraction, hydroxyl abstraction is thermodynamically more favorable for the ion $CH_3BCH_3^+$ than for $CH_3OBOCH_3^+$. Analogous to these water and hydroxyl abstraction reactions of alcohols, competitive ethanol and ethoxy abstractions were observed when the boron cations were allowed to react with ethyl acetate.

Introduction

Dicoordinated boron cations have been proposed to exist as transient intermediates in condensed-phase reactions.[1,2] Over the past years, there have been several attempts to synthesize and characterize these coordinately unsaturated boron compounds in the condensed phases.[1,2] One of the difficulties faced in these studies is the strong interaction of the highly electron-deficient boron ion with counterions. Bulky substituents which are strongly π-back-bonded to boron are needed to form stable, coordinately unsaturated borocations. On the other hand, simple dicoordinated boron cations are readily generated in the gas phase upon electron ionization of boron-containing organic molecules.[3] Therefore, gas-phase studies can provide invaluable insights into the intrinsic chemical properties of these highly reactive ions.

Mass spectrometric study of dicoordinated boron cations has been of some interest in the past few years.[4−11] The reactions reported include halide abstraction from alkyl halides and thermoneutral CH_3^- abstraction from $(CH_3)_3B$ by the ion $CH_3BCH_3^+$.[7,9] Further, it was recently demonstrated that BF_2^+ induces polymerization of gaseous acetylene via C_2HBF^+ formed through elimination of HF.[10]

The reactivity of coordinately unsaturated boron cations toward oxygen-containing compounds is still largely unexplored. We recently reported the first study on the solvent-free reactions of $CH_3OBOCH_3^+$ and $CH_3BCH_3^+$ with organic ethers.[11] Interestingly, these ions were found to dehydrate ethers via stepwise elimination of two alkene molecules via proton-bound intermediates. This paper discusses the gas-phase reactivity of $CH_3OBOCH_3^+$, $CH_3BCH_3^+$, and $CH_3(CH_2)_2OBOH^+$ toward alcohols, another important group of oxygen-containing molecules.

Experimental Section

An Extrel FT/MS Model 2001 Fourier transform ion cyclotron resonance instrument equipped with a dual cell was used to carry out all the experiments. The dual cell consists of two identical 2-in. cells, and it is aligned collinearly with the magnetic field produced by a 3 T superconducting magnet operated at 2.2 T. The dual cell is differentially pumped with two Balzer turbomolecular pumps (330 L/s) which are backed by Alcatel 2012 mechanical pumps. The base pressure in each side of the dual cell is less than 1×10^{-9} Torr, as measured with an ionization gauge on each side of the dual cell. All the samples were introduced into the instrument using two Extrel FTMS heated single-batch inlet systems equipped with a variable leak valve.

Electron impact was used to ionize the neutral molecules in one side of the dual cell. The electron energy, filament current, and electron beam time were optimized for each experiment. The ions were then transferred into the other side of the dual cell that contained the desired neutral reagent. This was accomplished by grounding the middle plate (conductance limit plate) for 100–200 μs, which causes transfer of the ions from one cell into other through a 2 mm hole in the conductance limit plate. The ions were then collisionally cooled by pulsing a relatively high pressure of argon into the cell. The desired reactant ion was isolated by ejecting unwanted ions from the cell through the application of several fixed frequency pulses and radio frequency sweeps to the excitation plates of the cell or by using the stored waveform inverse Fourier transform method (using the Extrel FTMS

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Table 1. Rate Constants and Product Distributions Measured for Reactions of $CH_3O^{11}BOCH_3^+$, $CH_3O^{10}BOCH_3^+$, and $CD_3O^{11}BOCD_3^+$ with Neutral Organic Reagents

reactant ion (*m/z*)	neutral reagent	ionic products[a] (*m/z*)	branching ratio, %	k_{exp}[b]	k_{coll}[c]	k_{exp}/k_{coll}
$CH_3O^{11}BOCH_3^+$ (73)	CH_3OH	no products			1.9	
	CD_3OD	$CH_3OBOCD_3^+$ (76)[d]	100	0.4	1.9	0.2
		$CD_3OBOCD_3^+$ (79)				
	CH_3CH_2OH	$[(CH_3O)_2BOH]H^+$ (91)[d]	100	1.0	1.8	0.6
		$[(CH_3CH_2O)(CH_3O)BOH]H^+$ (105)				
		$[(CH_3CH_2O)_2BOH]H^+$ (119)				
	$CH_3CH_2CH_2OH$	$[(CH_3O)_2BOH]H^+$ (91)[d]	100	1.7	1.7	1.0
		$[(CH_3)_2CHO(CH_3O)BOH]H^+$ (119)				
		$[(CH_3)_2CHO]_2BOH]H^+$ (147)				
	$(CH_3)_2CHOH$	$[(CH_3O)_2BOH]H^+$ (91)[d]	100	1.1	1.7	0.6
		$[(CH_3CH_2CH_2O)(CH_3O)BOH]H^+$ (119)				
		$[(CH_3CH_2CH_2O)_2BOH]H^+$ (147)				
	$C_6H_{11}OH$ (cyclohexanol)	$C_6H_{11}^+$ (83)[d]	59	1.6	2.5	0.6
		$[(CH_3O)_2BOH]H^+$ (91)[d]	41			
		$[C_6H_{11}OH]H^+$ (101)				
		$[(C_6H_{11}O)(CH_3O)BOH]H^+$ (159)				
	$(CH_3)_3CCH_2OH$	$C_5H_{11}^+$ (71)[d]	80			
		$[(CH_3O)_2BOH]H^+$ (91)[d]	20			
	$CH_3COOCH_2CH_3$	CH_3CO^+ (43)[d]	30	2.0	1.9	1.1
		$[(CH_3O)_2BOCH_2CH_3]H^+$ (119)[d]	50			
		$(CH_3O)_2BOC(OH)CH_3^+$ (133)[d]	20			
		$CH_3C(OH)OCH_2CH_3^+$ (89)				
		$(CH_3O)_2B(CH_3COOCH_2CH_3)^+$ (161)				
$CH_3O^{10}BOCH_3^+$ (72)	CH_3CH_2OH	$[(CH_3O)_2{}^{10}BOH]H^+$ (90)[d]	100	0.7	1.8	0.4
		$[(CH_3CH_2O)(CH_3O)^{10}BOH]H^+$ (104)				
		$[(CH_3CH_2O)_2{}^{10}BOH]H^+$ (118)				
$CD_3O^{11}BOCD_3^+$ (79)	CH_3CH_2OH	$[(CD_3O)_2B(OH)]H^+$ (97)[d]	100	1.2	1.8	0.7
		$[(CH_3CH_2O)(CD_3O)BOH]H^+$ (108)				
		$[(CH_3CH_2O)_2BOH]H^+$ (119)				

[a] The most likely structure is shown. [b] k_{exp} is the measured reaction rate constant given in units of 10^{-9} cm^3 molecule^{-1} s^{-1}. [c] k_{coll} is the collision rate constant given in units of 10^{-9} cm^3 molecule^{-1} s^{-1}. [d] Denotes primary products.

SWIFT module).[12] All the attempts were made to avoid exciting the ions to be isolated. After isolation, the ions were allowed to react with the neutral reagent for a variable time period to examine the product distribution at different reaction times. The rate constants of the reactions were calculated from the slope of the logarithm of the relative abundance of the reactant ion as a function of time.

The nominal sample pressures were $1.0 \times 10^{-7}-1.2 \times 10^{-7}$ Torr. The pressure readings were corrected for the sensitivity of the ion gauges toward each of the neutral molecules studied.[13] The rates of several temperature-independent reactions with known rate constants were determined in order to calibrate for the pressure gradient between the cell and the ion gauges as described previously[14,15] (e.g., $CH_3OH_2^+ + CH_3OH$, $CH_3OH_2^+ + C_2H_5OH$, $CH_3OH_2^+ + (CH_3)_2CHOH$, $CH_3OH_2^+ + C_6H_{11}OH_2$, and $CH_3OH_2^+ + CH_3COOC_2H_5$). The precision of the rate measurements is better than 10%, and the accuracy is estimated to be better than 50%.

Some ions were subjected to collision-activated dissociation (CAD) with argon (nominal pressure 1×10^{-7} Torr) in a cell with only argon in it. The ions were accelerated by using an excitation pulse with a fixed amplitude (3 or 3.5 V_{p-p}) and a variable duration. This was followed by a fixed collision time of 100 ms, unless otherwise specified. The ion kinetic energies reported for the CAD experiments are laboratory kinetic energies corrected as recommended by Grosshans and Marshall,[16] i.e., by taking half the value computed according to the infinite parallel plate approximation. With variation of the duration of the excitation pulse, dissociation products for different estimated laboratory kinetic energies were measured (25–200 eV).

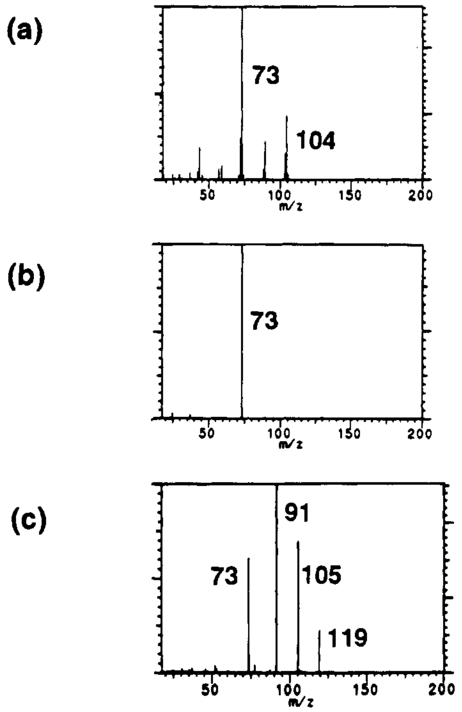

Figure 1. (a) Electron impact ionization of $(CH_3O)_3B$ (mol wt 104). (b) Transfer of ions into the other reaction chamber, followed by isolation of the fragment ion $CH_3OBOCH_3^+$ (*m/z* 73). (c) Reaction of the ion $CH_3OBOCH_3^+$ for 800 ms with ethanol (uncorrected pressure 1.2×10^{-7} Torr). The only primary product is $[(CH_3O)_2BOH]H^+$ (*m/z* 91); the secondary products are $[(CH_3CH_2O)(CH_3O)BOH]H^+$ (*m/z* 105) and $[(CH_3CH_2O)_2BOH]H^+$ (*m/z* 119).

All the spectra were acquired at a digitizer rate of 5.4 MHz and by using an excitation "chirp" sweep with an amplitude of 107 or 124 V_{p-p} 2.7 MHz bandwidth and 3.0–3.2 kHz/μs sweep rate. The spectra

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Table 2. Rate Constants and Product Distributions Measured for Reactions of $CH_3BCH_3^+$ and $CH_3(CH_2)_2OBOH^+$ with Neutral Organic Reagents

reactant ion (*m/z*)	neutral reagent	ionic products[a] (*m/z*)	branching ratio, %	k_{exp}[b]	k_{coll}[c]	k_{exp}/k_{coll}
$CH_3BCH_3^+$ (41)	CH_3CH_2OH	$(CH_3)_2BOH_2^+$ (59)[d]	100	1.8	2.1	0.9
		$[(CH_3)_2BOCH_2CH_3]H^+$ (87)				
		$CH_3CH_2OH_2^+$ (47)				
	$CH_3CH_2CH_2OH$	$C_3H_7^+$ (43)[d]	80	1.8	2.0	0.9
		$(CH_3)_2BOH_2^+$ (59)[d]	20			
		$(CH_3)_2CHOH_2^+$ (61)				
		$(CH_3)_2BO(H)CH_2CH_2CH_3^+$ (101)				
	$(CH_3)_2CHOH$	$C_3H_7^+$ (43)[d]	66	2.2	2.0	1.1
		$(CH_3)_2BOH_2^+$ (59)[d]	34			
		$(CH_3)_2CHOH_2^+$ (61)				
		$(CH_3)_2BO(H)C_3H_7^+$ (101)				
	$CH_3COOCH_2CH_3$	CH_3CO^+ (43)[d]	86	1.6	2.3	0.7
		$(CH_3)_2BO(H)CH_2CH_3^+$ (87)[d]	14			
		$CH_3C(OH)OCH_2CH_3^+$ (89)				
$CH_3(CH_2)_2OBOH^+$ (87)	$CH_3CH_2CH_2OH$	$C_3H_7^+$ (43)	66	1.0	1.7	0.6
		$[CH_3(CH_2)_2OB(OH)_2]H^+$ (105)	34			
		$CH_3CH_2CH_2OH_2^+$ (61)				
	$CH_3COOCH_2CH_3$	CH_3CO^+ (43)[d]	18	1.8	1.8	1.0
		$CH_3C(OH)OC_2H_5^+$ (89)[d]	55			
		$[(CH_3(CH_2)_2O)(CH_3CH_2O)BOH]H^+$ (133)[d]	27			

[a] The most likely structure is shown. [b] k_{exp} is the measured reaction rate constant in units of 10^{-9} cm^3 $molecule^{-1}$ s^{-1}. [c] k_{coll} is the collision rate constant given in units of 10^{-9} cm^3 $molecule^{-1}$ s^{-1}. [d] Denotes primary products.

Table 3. Rate Constants and Product Distributions Measured for Reactions of $(CH_3)_2B(OH)_2^+$ (*m/z* 59) with Neutral Reagents with Different Proton Affinities (Proton Affinity Bracketing Experiments for $(CH_3)_2BOH$)

ion (*m/z*)	neutral reagent (mol wt)	proton affinity,[a] kcal/mol	products (*m/z*)	branching ratio, %	k_{exp}[b]	k_{coll}[c]	k_{exp}/k_{coll}
$(CH_3)_2B(OH_2)^+$ (59)	C_2H_5I (100)	176.0	no reaction			1.7	
	HCOOH (46)	178.6	no reaction			2.1	
	4-chlorotoluene (126)	180.2	$[C_6H_4CH_3(Cl)]H^+$ (127, 129)[4]	100	1.1	2.2	0.5
	2-chlorotoluene (126)	184.2	$[C_6H_4CH_3(Cl)]H^+$ (127,129)[4]	100	1.0	1.8	0.6
	C_6H_5Br (156)	188.2	$(C_6H_5Br)H^+$ (157, 159)[4]	100	0.3	1.7	0.2
	CH_3CH_2OH (46)	188.3	$C_2H_5OH_2^+$ (47)[4]	40	1.4	1.9	0.7
			$[(CH_3)_2BOCH_2CH_3]H^+$ (87)[4]	60			

[a] Proton affinity values obtained from ref 15. [b] k_{exp} is the measured reaction rate constant in units of 10^{-9} cm^3 $molecule^{-1}$ s^{-1}. [c] k_{coll} is the collision rate constant in units of 10^{-9} cm^3 $molecule^{-1}$ s^{-1}. [d] Denotes primary products.

were recorded as 32 k data points and subjected to one zero fill before Fourier transformation.

The ions $CH_3OBOCH_3^+$, $CD_3OBOCD_3^+$, $CH_3BCH_3^+$, and $CH_3(CH_2)_2OBOH^+$ were generated by electron ionization of $(CH_3O)_3B$, $(CD_3O)_3B$, $(CH_3)_2BBr$, and $(CH_3(CH_2)_2O)_3B$, respectively. $(CD_3O)_3B$ was synthesized by a reaction of B_2O_3 with CD_3OD.[17] All other reagents were obtained from Aldrich and were used without further purification. The purity of the reagents was verified by mass spectrometric comparison and by gas chromatography.

Results

The reactant ions $CH_3OBOCH_3^+$, $CH_3BCH_3^+$, and $CH_3(CH_2)_2OBOH^+$ were produced by electron ionization in one side of the dual-cell reaction chamber of the FT-ICR mass spectrometer (see Figure 1a). The ions were then transferred into the other side of the cell, followed by collisional cooling and isolation of the reactant ion (Figure 1b). The isolated ions were allowed to react with a neutral reagent (Figure 1c) for a variable period of time to determine the reaction rate constants and product branching ratios (Figure 1, Tables 1 and 2).

Estimation of the heat of formation of the dehydration product $(CH_3)_2BOH_2^+$ required determination of the proton affinity of $(CH_3)_2BOH$. This was accomplished by bracketing experiments wherein the ion $(CH_3)_2BOH_2^+$ was generated by reaction of $CH_3BCH_3^+$ with ethanol, transferred into the other side of the dual cell, and collisionally cooled, isolated, and allowed to react with neutral reagents with different proton affinities (Table 3). From these experiments, the proton affinity of $(CH_3)_2BOH$ was concluded to be 179.4 kcal/mol.

Table 4. CAD Products of Selected Boron Cations

fragmenting ion (*m/z*)	kinetic energy (lab), (eV)	fragment ion *m/z* (%)
$CH_3BCH_3^+$ (41)	5, 10, 15, 25, 50, 100	no fragmentation
$CH_3OBOCH_3^+$ (73)	5, 10, 15, 25, 50, 100	no fragmentation
$CH_3CH_2CH_2OBOH^+$ (87)	5	43 (100),[a] 45 (63)[b]
	10	43 (100), 45 (75)
	15	43 (100), 45 (80)
	25	43 (70), 45 (100)
	50	43 (50), 45 (100)
$(CH_3CH_2CH_2O)_2B^+$ (129)	2.5, 5, 15, 25, 50	59 (100)[c]

[a] $C_3H_7^+$. [b] $B(OH)_2^+$. [c] CH_3OBOH^+.

Collision-activated dissociation experiments were carried out to examine the stability of the dicoordinated boron cations. The fragmentation patterns were studied at several collision energies (E_{lab} = 5−100 eV). The relative fragment ion abundances measured for each laboratory ion kinetic energy are shown in Table 4. Even at very high collision energies (100 eV), no fragmentation was observed for the ions $CH_3OBOCH_3^+$ and $CH_3BCH_3^+$. However, $CH_3(CH_2)_2OBOH^+$ dissociates even at very low collision energies (5 eV) to yield $C_3H_7^+$ (*m/z* 43; lower-energy fragment) and $B(OH)_2^+$ (*m/z* 45; dominates at high energies). Similarly, the ion $[CH_3(CH_2)_2O]_2B^+$ dissociates readily to yield a fragment ion of *m/z* 59, likely to have the structure CH_3OBOH^+.

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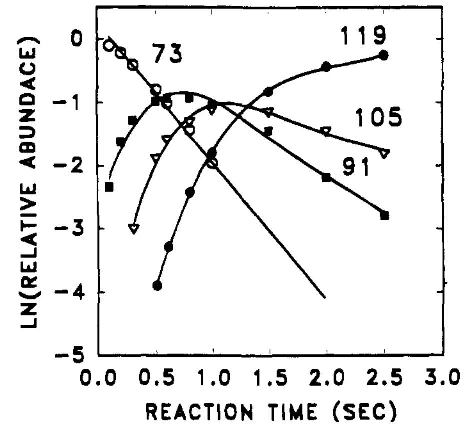

Figure 2. Temporal variation of the ion abundances for the reaction of $CH_3OBOCH_3^+$ (*m/z* 73) with ethanol (uncorrected pressure 1.2 × 10^{-7} Torr).

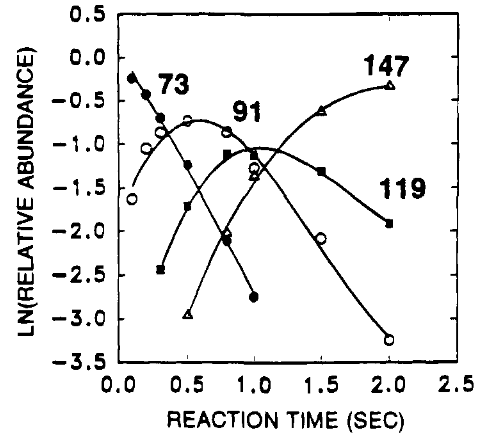

Figure 3. Temporal variation of the ion abundances for the reaction of $CH_3OBOCH_3^+$ (*m/z* 73) with 1-propanol (uncorrected pressure 1.2 × 10^{-7} Torr).

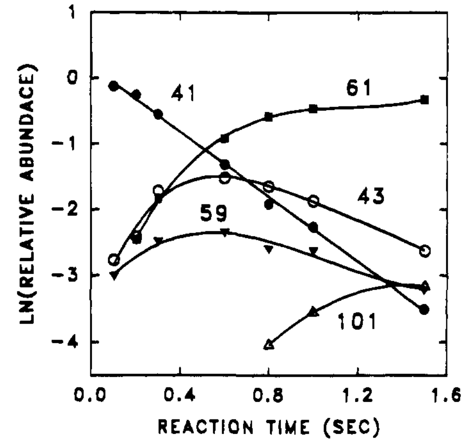

Figure 4. Temporal variation of the ion abundances for the reaction of $CH_3BCH_3^+$ (*m/z* 41) with 1-propanol (uncorrected pressure 1.2 × 10^{-7} Torr).

Discussion

Reactions with Alcohols. The ions $CH_3OBOCH_3^+$, $CH_3BCH_3^+$, and $CH_3(CH_2)_2BOH^+$ undergo facile reactions with all the alcohols studied, with the exception of methanol (Tables 1 and 2; Figures 2–4). The predominant reaction channel in most cases is abstraction of a water molecule from the alcohol by the boron cation (Scheme 1; see Scheme 2 for reaction for CD_3OD). This finding provides strong support for the mechanism proposed earlier to rationalize the facile dehydration of organic ethers by dicoordinated boron cations. For example, elimination of ethylene from an adduct of $CH_3OBOCH_3^+$ and diethyl ether was proposed[11] to yield the intermediate ion **a** shown in Scheme 1. Elimination of the second alkene from the adduct formally corresponds to dehydration of ethanol by the boron cation.[11]

The high electron deficiency of $CH_3OBOCH_3^+$ and $CH_3BCH_3^+$ makes these ions strong Lewis acids, and they rapidly attack the oxygen atom in alcohols. The following 1,2-elimination of an alkene probably occurs via a proton-bound adduct such as ion **b** shown in Scheme 1 for the reaction of $CH_3OBOCH_3^+$ with ethanol. Intermediate **b** eliminates ethylene rather than $(CH_3O)_2BOH$ since ethylene elimination is significantly more exothermic: the proton affinity (PA) of $(CH_3O)_2BOH$ is equal to or greater than 176 kcal/mol (the proton affinity[18] of $B(OH)_3$) while the proton affinity of ethylene is only 163 kcal/mol.[19] The fact that water abstraction occurs efficiently for both borocations $CH_3OBOCH_3^+$ and $CH_3BCH_3^+$ (Table 2) demonstrates that the oxygen atoms in $CH_3OBOCH_3^+$ are not a requirement for the dehydration reaction.

A mechanism involving concerted 1,2-elimination of ethylene through a four-membered transition state (Scheme 3b) is ruled out on the basis of the observation that $CH_3OBOCH_3^+$ reacts with neopentyl alcohol by abstraction of water (Scheme 3a; Table 1). In contrast to ethanol, neopentyl alcohol does not have a hydrogen atom at the β-carbon. The reaction of this alcohol probably occurs by cleavage of the C–O bond in the initially formed adduct, followed by a methyl shift to generate a proton-bound complex of 2-methyl-2-butene and $(CH_3O)_2BOH$. This complex then decomposes to yield the water abstraction product.

Interestingly, two major products, a boron-containing ion from the dehydration reaction and a hydrocarbon ion arising from hydroxyl abstraction, are formed in some of the reactions studied. For example, the reaction of $CH_3OBOCH_3^+$ with cyclohexanol yields an abundant hydrocarbon ion $C_6H_{11}^+$ (*m/z* 83) from abstraction of a hydroxyl group by the borocation, together with the water abstraction product $[(CH_3O)_2BOH]H^+$ (*m/z* 91; Table 1). The competition between these two reaction channels can be explained by considering the relative proton affinities of the neutral molecules in the proton-bound intermediates **a** and **b**, Scheme 4. In intermediate **b**, the proton is more strongly bound to cyclohexene (PA = 189 kcal/mol[19]) than to the OH group in $(CH_3O)_2BOH$ (PA at OH ≥ 176 kcal/mol[18]), resulting in $C_6H_{11}^+$ (*m/z* 83) as the major ionic product. On the other hand, if the boron molecule can rotate to produce intermediate **a**, the proton will be more strongly bound to the OCH_3 group in $(CH_3O)_2BOH$ (PA = 197 kcal/mol[20]) than to cyclohexene. Thus, the resulting product is $[(CH_3O)_2BOH]H^+$ (*m/z* 91).

The reaction of neopentyl alcohol with $CH_3OBOCH_3^+$ also yields a major hydrocarbon product ion (Table 1) that arises from hydroxyl abstraction. In this case, the competition for the proton likely occurs between 2-methyl-2-butene (PA = 197.6 kcal/mol; see above) and $(CH_3O)_2BOH$ (PA(OH) ≥ 176 kcal/mol[18] and PA(OCH_3) = 197 kcal/mol[20]). As the proton affinity of the alkene is higher than that of either one of the acidic sites in the boron moiety, the proton in most instances remains with the alkene, and the ion $C_5H_{11}^+$ dominates the product distribution.

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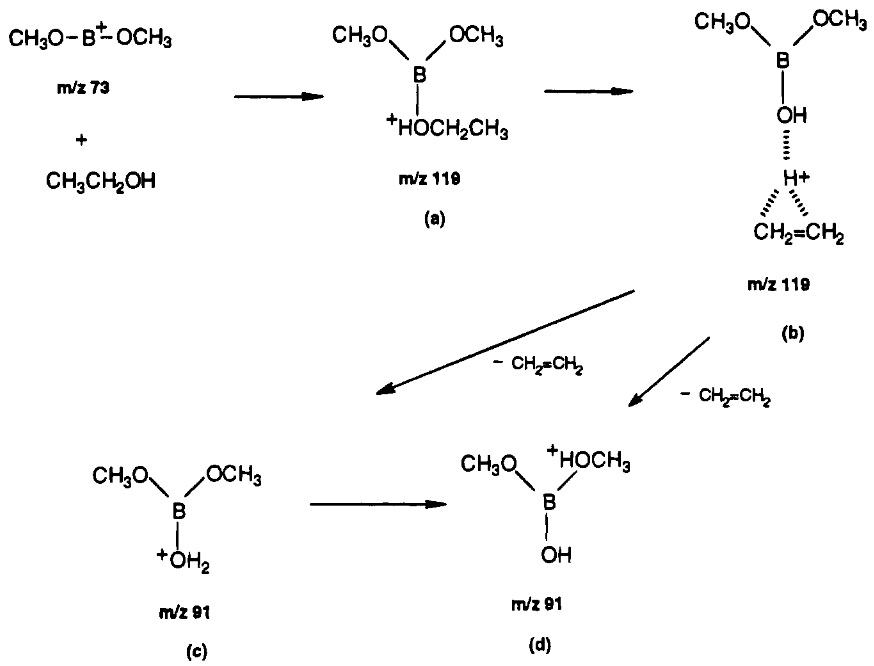
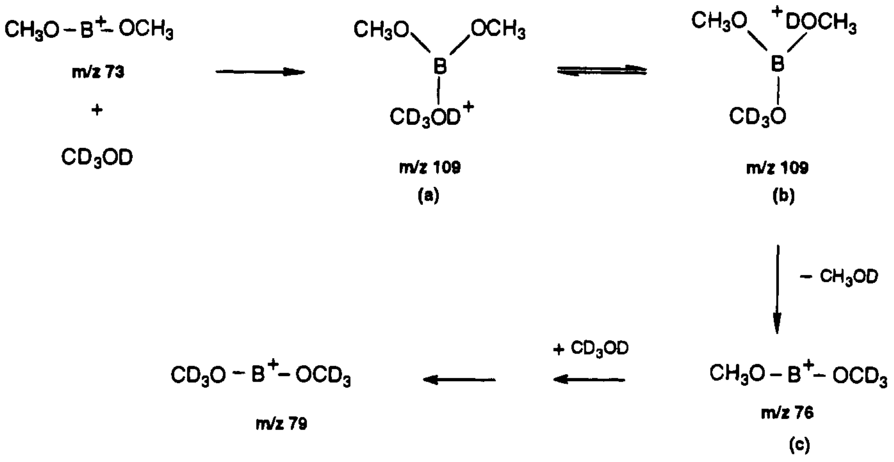
Scheme 1



Scheme 2

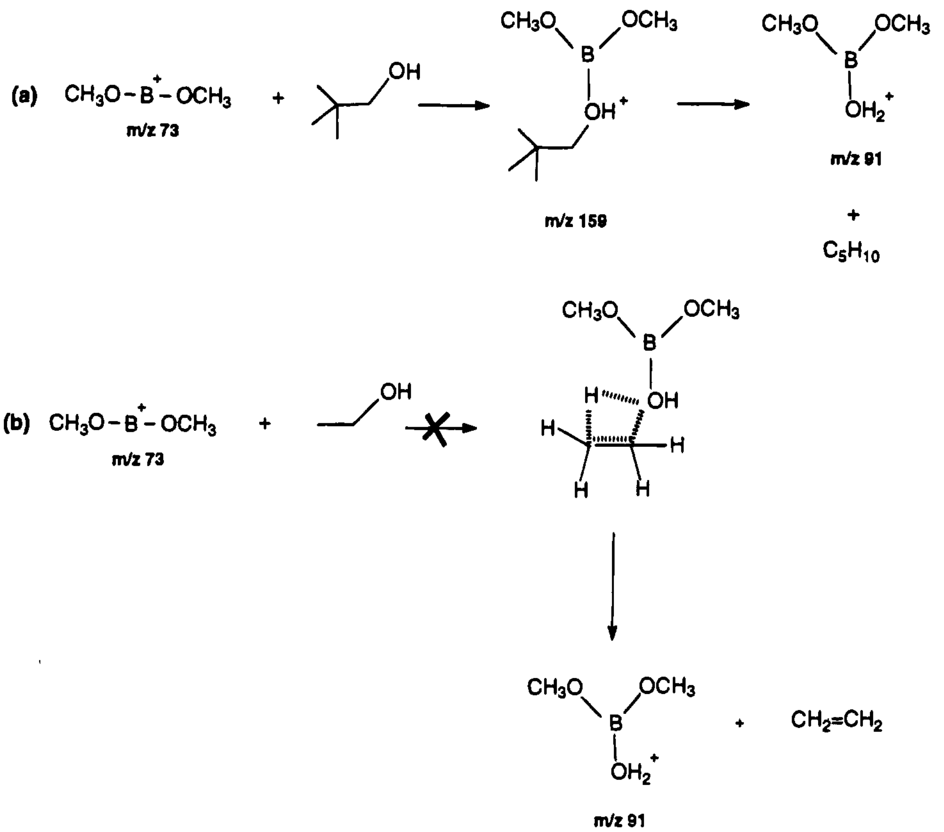


The hydroxyl abstraction channel is more favorable for the boron ion $CH_3BCH_3^+$ than for $CH_3OBOCH_3^+$: the former yields a major hydrocarbon product for 1- and 2-propanol, while the latter reacts with these alcohols by exclusive dehydration. The reasons for this behavior are discussed below in the section on thermochemistry. The generally greater reaction rate for the ion $CH_3BCH_3^+$ as compared to $CH_3OBOCH_3^+$ (Tables 1 and 2; the reaction efficiencies are 0.9 for the reaction of $CH_3BCH_3^+$ with ethanol and 1.1 for the reaction with 2-propanol; the corresponding value for $CH_3OBOCH_3^+$ is 0.6) reflects the greater electron deficiency at boron in the ion $CH_3BCH_3^+$, making this ion a better electrophile. The ion $CH_3OBOCH_3^+$ is stabilized by π-back-bonding to boron by the oxygen lone pairs.

The third boron ion studied, $CH_3(CH_2)_2OBOH^+$, reacts with 1-propanol at a lower rate but yields a similar product distribution as the ion $CH_3BCH_3^+$ (Table 2). This result was surprising, considering the fact that the boron atom in $CH_3(CH_2)_2OBOH^+$ is stabilized by two oxygen atoms and might therefore be expected to behave more like $CH_3OBOCH_3^+$ than $CH_3BCH_3^+$. However, the products arising from $CH_3(CH_2)_2OBOH^+$ are explained by reactions different from those of the other boron cations. This ion is a relatively strong Brönsted acid. Proton transfer is a common reaction for the few acidic dicoordinated borocations studied thus far; e.g., CH_3OBOH^+ transfers a proton to CH_3CHO, CH_3CN, and CH_3COCH_3.[8] The proton affinity of $CH_3(CH_2)_2OB{=}O$ is likely to be close to that of $CH_3OB{=}O$ (183 ± 3 kcal/mol[8]). Hence, $CH_3(CH_2)_2OB{=}O$ is significantly less basic than 1-propanol (PA = 190.8 kcal/mol[19]), and rapid deprotonation is expected to occur for $CH_3(CH_2)_2OBOH^+$ upon collisions with 1-propanol. The so-generated, protonated 1-propanol dissociates by loss of water to yield the major hydrocarbon product ion $C_3H_7^+$. While this product ion may also be formed upon hydroxyl abstraction by the boron ion, the proton transfer pathway is more likely.

The product ion generated upon dehydration of the alcohols by $CH_3OBOCH_3^+$ may rearrange to a more stable form via an intramolecular 1,3-proton transfer (Scheme 1: **c** → **d**). The more stable product ion may also be formed directly from the proton-bound complex if $(CH_3O)_2BOH$ can rotate and bind to the proton via a methoxy group rather than the less basic hydroxyl group. Evidence in support of the formation of the more stable product ions (Scheme 1: **d**) is provided by secondary reactions: replacement of methanol occurs when the product ion (*m/z* 91) reacts with ethanol (*m/z* 105 in Figure 2; see also Scheme 5). The so-generated new product ion (**b**,

Scheme 3



Scheme 5) reacts with ethanol by eliminating another methanol molecule (*m/z* 119, Figure 2; see also Scheme 5). Hence, the proton in ion **b** must have been transferred from the ethoxy group to the less basic methoxy group (**c**, Scheme 5) either through a unimolecular 1,3-proton shift or by a deprotonation/protonation reaction involving ethanol. Reaction of the deuterated ion $CD_3OBOCD_3^+$ with ethanol shows no deuterium incorporation in the final product ion (**d**, Scheme 5; Table 1), demonstrating that both OCD_3 groups are indeed replaced with ethanol molecules during the reaction. The presence of boron in all the product ions was confirmed by comparing the products obtained for $CH_3O^{10}BOCH_3^+$ and $CH_3O^{11}BOCH_3^+$ (Table 1).

A similar reaction sequence was observed also for some of the other alcohols. For example, stepwise replacement of two methanol molecules with two 1-propanol (Figure 3) or 2-propanol molecules occurs in the dehydration product $[(CH_3O)_2BOH]H^+$ upon reaction with 1-propanol and 2-propanol, respectively (Table 1). However, only one methanol is replaced by cyclohexanol (*m/z* 159; Table 1; Scheme 6). The absence of the second replacement may be due to steric crowding as well as the endothermicity for transfer of the proton from the cyclohexyloxy group to the methoxy group. Note that displacement of water does not occur for any of the alcohols. Hence, the predominant reaction between the alcohols and the OH-protonated $(CH_3O)_2BOH$, if formed, must be a deprotonation/protonation reaction that yields the CH_3O-protonated $(CH_3O)_2BOH$. Transfer of the proton back to the hydroxy group in the primary dehydration product and its reaction products is highly unlikely, due to the great endothermicity of this proton transfer (about 21 kcal/mol).[18,20]

Examination of the reactions of deuterated methanol with $CH_3OBOCH_3^+$ provides support for the occurrence of intramolecular 1,3-proton transfers in the adducts of the dicoordinated boron cations and neutral alcohols (Scheme 2). Reaction of $CH_3OBOCH_3^+$ with CD_3OD produces the ion $CH_3OBOCD_3^+$ (*m/z* 76; Table 1) by elimination of CH_3OD. This reaction must occur via a 1,3-deuterium shift as shown in Scheme 2 (**a** → **b**). Further reaction of the so-formed product ion (**c**) with CD_3OD results in replacement of CH_3OD and produces the ion $CD_3OBOCD_3^+$ (*m/z* 79; Table 1), again a reaction that requires a 1,3-deuterium shift in the initially formed adduct.

The dehydration product $(CH_3)_2BOH_2^+$ formed from the ion $CH_3BCH_3^+$ (*m/z* 59; Table 2) reacts further with the alcohols by replacement of water (*m/z* 101, Figure 4). The other observed secondary product, protonated alcohol, is probably formed upon reaction of both the primary product ions (Table 2) with the alcohol.

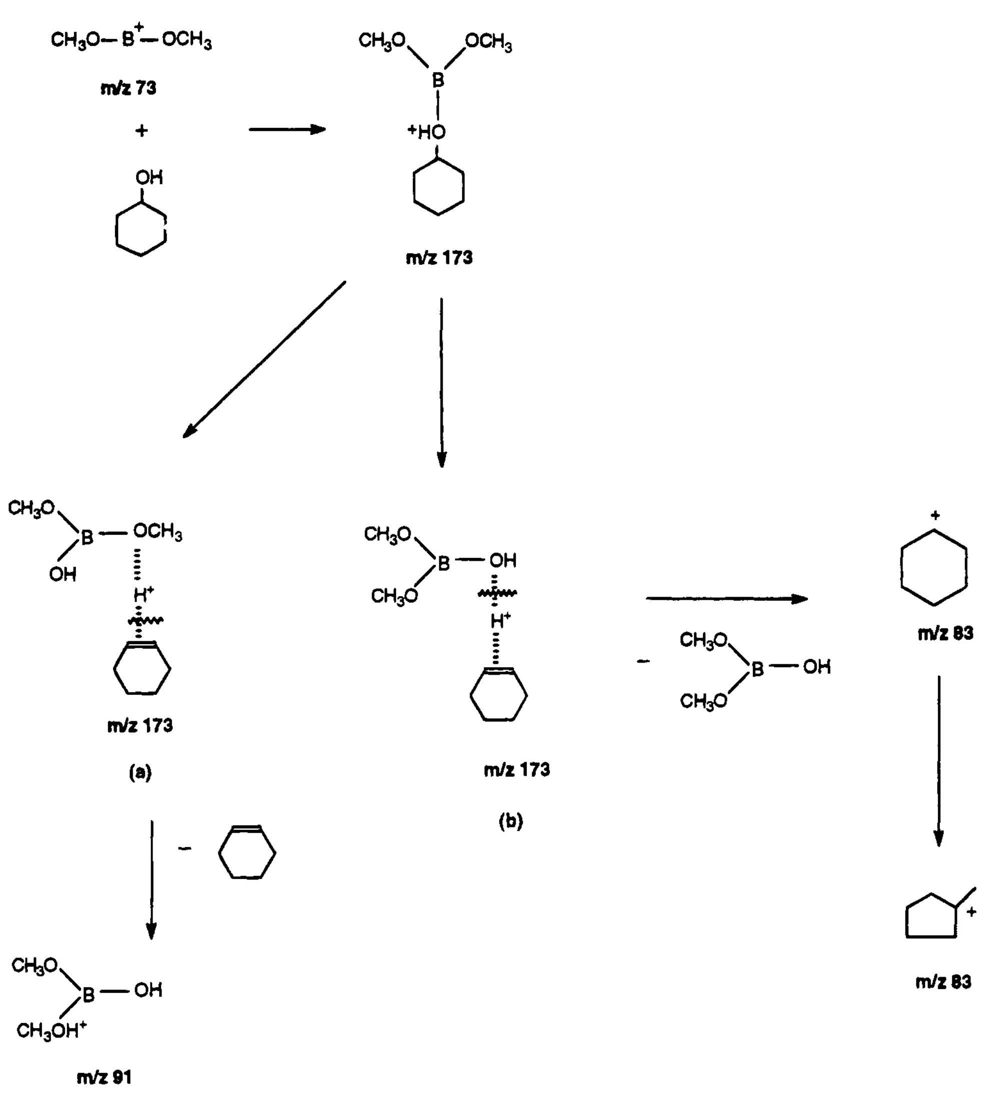
Thermochemistry of the Dehydration Reactions. The exothermicities for the different channels for the reaction of $CH_3OBOCH_3^+$ with ethanol (Figure 5) can be estimated,[21,22] by using the previously reported heat of formation for $CH_3OBOCH_3^+$ ($\Delta H_f^\circ = 41.4$ kcal/mol) and the proton affinities of the two basic sites in $(CH_3O)_2BOH$ (PA of CH_3O is assumed to be the same as PA of $(CH_3O)_3B$, 197 ± 3 kcal/mol,[20] and

---

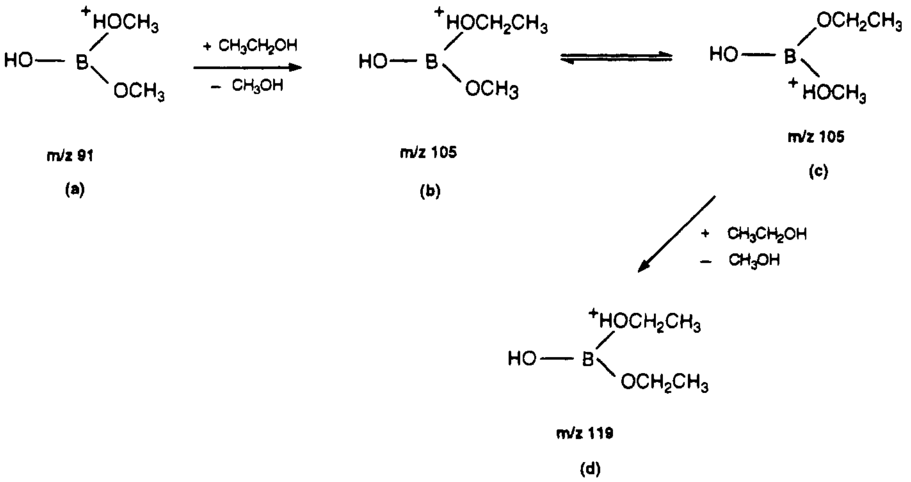
(21) $\Delta H_f[(CH_3O)_2B(OH_2)^+] = -60$ kcal/mol and $\Delta H_f[(CH_3O)(HO)B(HOCH_3)^+] = -83$ kcal/mol were calculated using the equations $\Delta H_f[(CH_3O)_2B(OH_2)^+] = \Delta H_f[(CH_3O)_2B(OH)] - PA[(CH_3O)_2B(OH)$ at $OH] + \Delta H_f(H^+)$ and $\Delta H_f[(CH_3O)(HO)B(HOCH_3)^+] = \Delta H_f[(CH_3O)_2B(OH)] - PA[(CH_3O)_2B(OH)$ at $OCH_3] + \Delta H_f(H^+)$; $\Delta H_f[(CH_3O)_2B(OH)] = -250$ kcal/mol (Benson's method); PA of $(CH_3O)_2BOH$ at OH was approximated with 176 kcal/mol (PA of $(HO)_3B$[19]); PA of $(CH_3O)_2BOH$ on OCH_3 was approximated with 197 kcal/mol (PA of $(CH_3O)_3B$[21]); $\Delta H_f[(CH_3O)_3B] = -215.0$ kcal/mol;[20] $\Delta H_f(H^+) = -365.7$ kcal/mol.[20] $\Delta H_f[(CH_3O)_2B(HOCH_2CH_3)^+] = -57$ kcal/mol was calculated in the same way using the following additional values: PA of $(CH_3O)_2BOCH_2CH_3$ at CH_3CH_2O was assumed to be 4 kcal/mol greater than PA of $(CH_3O)_3B$ ($\Delta PA = 4$ kcal/mol for dimethyl and ethyl methyl ether[20]); $\Delta H_f[(CH_3O)_2BOCH_2CH_3] = -222$ kcal/mol (Benson's method). The association energy for $(CH_3O)(HO)B(HOCH_3)^+$ and ethylene was assumed to be about 20 kcal/mol; the true value is likely smaller.[23]

(22) Keesee, R. G.; Castleman, A. W., Jr. *J. Phys. Chem. Ref. Data* **1986**, *15*, 1048.

Scheme 4



Scheme 5



PA of OH is assumed to be the same as PA of $B(OH)_3$, 176 kcal/mol[18]). Hence, dehydration of ethanol to yield the ion $(CH_3O)_2B(OH_2)^+$ is estimated to be exothermic by about 33 kcal/mol.[21] The enthalpy change for the formation of the more stable product ion $(CH_3O)_2B(HOCH_3)^+$ is about −54 kcal/mol.[21]

Water abstraction from ethanol by $CH_3OBOCH_3^+$ is highly exothermic when compared to hydroxyl abstraction (Scheme 7a). Thus, the reaction proceeds via exclusive water abstraction. For longer chain alcohols, the difference in the enthalpy change between these two reaction channels becomes smaller (Scheme 7a,b) and eventually reverses. Indeed, the reactions with neopentyl alcohol and cyclohexanol proceed by predominant hydroxyl abstraction.

The determination of the heat of formation of the dehydration product of $CH_3BCH_3^+$, the ion $(CH_3)_2BOH_2^+$, requires knowledge of the proton affinity of $(CH_3)_2BOH$. This value was

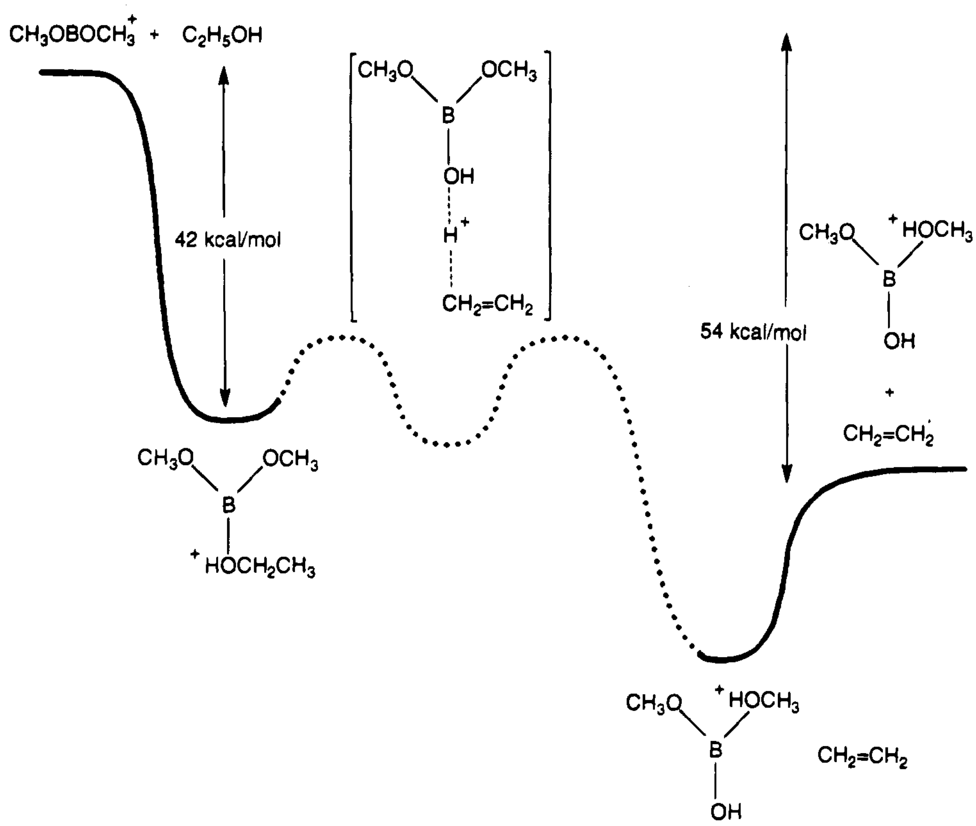
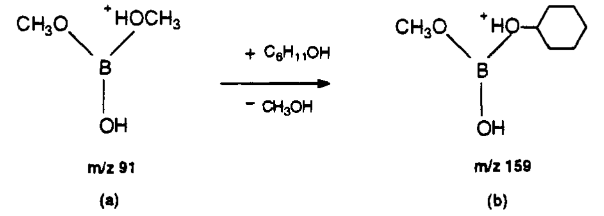


Figure 5. Potential energy surface for the reaction of $CH_3OBOCH_3^+$ with ethanol.

Scheme 6



measured by using bracketing experiments. The ion $(CH_3)_2BOH_2^+$ was allowed to react with several compounds with different proton affinities (Table 3). The occurrence of a facile proton transfer to 4-chlorotoluene (PA = 180.2 kcal/mol) and to other molecules with proton affinities greater than 180.2 kcal/mol and the absence of proton transfer to molecules with proton affinities below 178.6 kcal/mol bracket the proton affinity of $(CH_3)_2BOH$ between 178.6 and 180.2 kcal/mol (179.4 kcal/mol). This value, together with the heat of formation of $CH_3BCH_3^+$ (175 kcal/mol[9]), yields[23] a heat of formation of 85.7 kcal/mol for $(CH_3)_2BOH_2^+$. Hence, the exothermicity for water abstraction by $CH_3BCH_3^+$ from ethanol is about 21 kcal/mol.

Relative to the dehydration reaction, the hydroxyl abstraction channel is thermodynamically more favorable for the ion $CH_3BCH_3^+$ than for $CH_3OBOCH_3^+$ (Schemes 7 and 8). For example, the water and hydroxyl abstraction pathways are estimated to be equally exothermic (about 24 kcal/mol) for the reactions of $CH_3BCH_3^+$ with 1-propanol and 2-propanol. Indeed, both reaction channels are observed for these two alcohols.

Reactions with Ethyl Acetate. The mechanistic rationale provided above for the reactions of the dicoordinated borocations with alcohols can be applied to other reactions, as well. For example, the reactions of these boron cations with ethyl acetate occur via analogous pathways. The ion $CH_3OBOCH_3^+$ reacts with ethyl acetate (Table 1) producing three major products, the ions of *m/z* 43, 119, and 133. As shown in Scheme 9, the formation of all these products can be rationalized on the basis of dissociation of two adducts: **a** and **b** (more stable). In analogy with water abstraction from the alcohols, $CH_3OBOCH_3^+$ abstracts acetic acid (to yield the ion of *m/z* 133) and ethanol (*m/z* 119) from the ester. Abstraction of the ethoxy group (formation of CH_3CO^+, *m/z* 43) is in competition with abstraction of ethanol (elimination of $CH_2{=}C{=}O$), just as hydroxyl and water abstraction reactions compete for the alcohols. The relative proton affinities of $CH_2{=}C{=}O$ (198 kcal/mol[19]) and $(CH_3O)_2BOCH_2CH_3$ (PA 201 kcal/mol[21] at the ethoxy group) suggest that loss of $CH_2{=}C{=}O$ should be the favored reaction channel, which indeed is the case.

The ion $CH_3BCH_3^+$ reacts preferentially by ethoxy rather than ethanol abstraction, i.e., prefers not to form boron-containing products, just as was observed for the alcohols. Further, the secondary reactions for the alcohols and the ester are similar. Specifically, the ethanol and acetic acid abstraction products of $CH_3OBOCH_3^+$ (*m/z* 119 and 133, respectively; Table 1) react with ethyl acetate through replacement of ethanol and acetic acid, respectively (to yield the ion of *m/z* 161; Table 1).

The acidic ion $CH_3(CH_2)_2OBOH^+$ abstracts ethanol and an ethoxy group from ethyl acetate, just like the other two borocations. In addition, proton transfer to ethyl acetate was observed (Table 2).

Dissociation Reactions. Low-energy collision-activated dissociation (CAD) experiments (Table 4) were carried out to obtain information concerning the stability of the ions $CH_3OBOCH_3^+$, $CH_3BCH_3^+$, and $CH_3(CH_2)_2OBOH^+$ toward dissociation. No fragmentation was observed for the ions $CH_3OBOCH_3^+$ and $CH_3BCH_3^+$ even at very high collision energies

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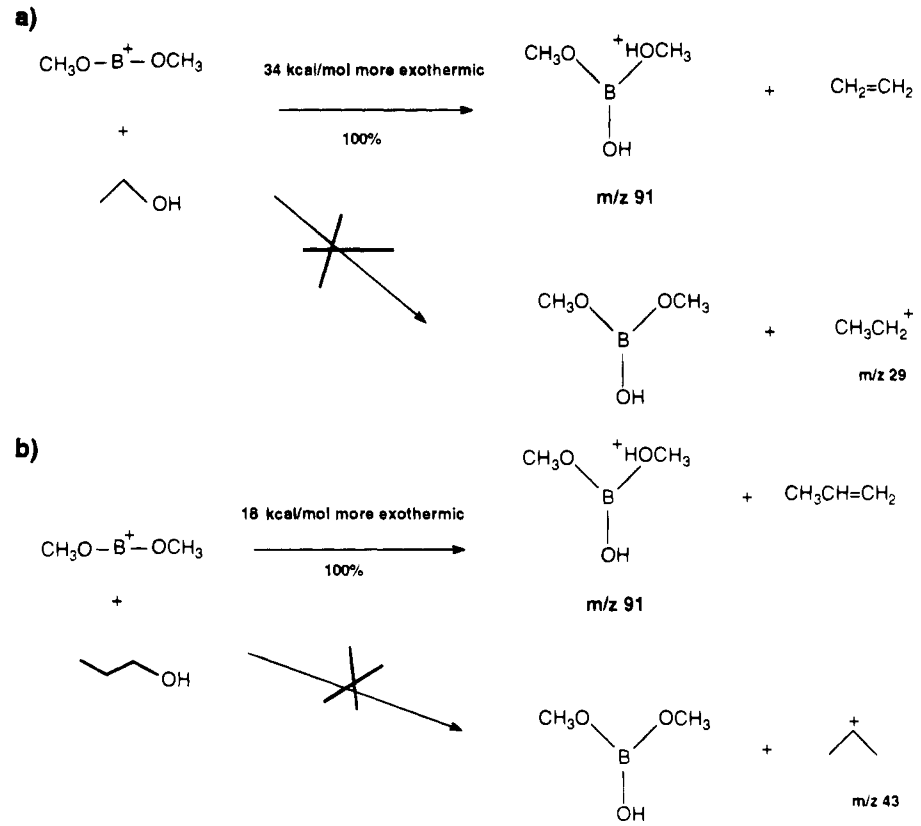
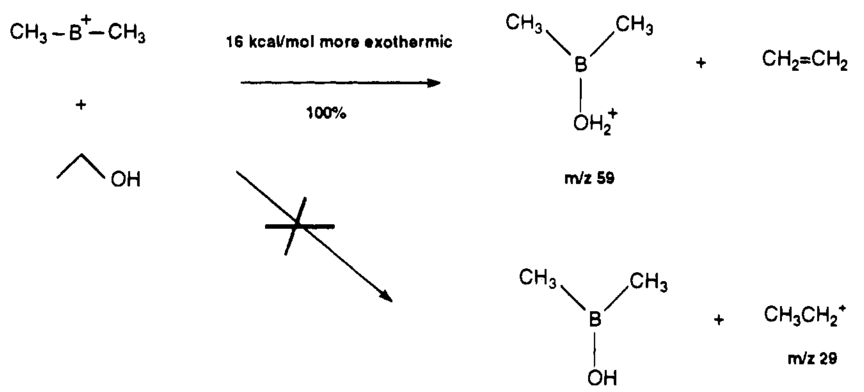
(23) $\Delta H_f[(CH_3)_2BOH_2^+] = 85.7$ kcal/mol was calculated using the equation $\Delta H_f[(CH_3)_2BOH_2^+] = \Delta H_f[(CH_3)_2BOH] - PA[(CH_3)_2BOH] + \Delta H_f(H^+)$; $\Delta H_f[(CH_3)_2BOH] = -101$ kcal/mol (AM1).[24]

(24) Dewar, M. J. S.; Jie, C.; Zoebisch, E. G. *Organometallics* **1988**, *7*, 513.

Scheme 7



Scheme 8



(100 eV). Hence, although these borocations are highly reactive toward neutral molecules, they have very high intrinsic barriers toward unimolecular dissociation.

The ion $CH_3(CH_2)_2OBOH^+$ is less stable toward dissociation than the other two borocations studied. Even at relatively low collision energies, this ion decomposes to yield the fragment ions of *m/z* 43 and 45 (the latter dominates at high energies). In both of these fragmentations, the C—O bond is broken while the two strong B—O bonds remain intact. It is possible that the branching ratio for these two dissociation products is determined by competition for the proton between the two fragments generated by cleavage of the weakest bond, the C—O bond (Scheme 10). This situation resembles those presented in Schemes 4 and 9 to rationalize the competition between the different channels for reactions of the borocations with alcohols and ethyl acetate. The proposed dissociation mechanism is supported by the similar proton affinities of the two neutral fragments: the proton affinity of propylene is 179.5 kcal/mol[19] while that of HO—B═O is likely to be slightly below 183 ± 3 kcal/mol (the proton affinity of CH_3O—B═O).[8] These values suggest that the two fragments should be able to compete nearly equally well for the proton. Hence, it is not surprising that both fragment ions are formed at a high abundance.

Conclusions

The dicoordinated boron cations $CH_3OBOCH_3^+$, $CH_3BCH_3^+$, and $CH_3(CH_2)_2OBOH^+$ readily dehydrate alcohols via alkene elimination. The reaction is initiated by exothermic addition of the alcohol to the borocation. The adduct dissociates in a manner that closely resembles the dissociation of activated, protonated alcohols. For example, the facile dissociation of protonated ethanol to ethylene and H_3O^+ occurs via a proton-bound intermediate of ethylene and water.[25] An analogous intermediate likely occurs during elimination of an alkene from the boron ion/alcohol complex. In addition to dehydration, a competing hydroxyl abstraction was observed in some of the reactions.

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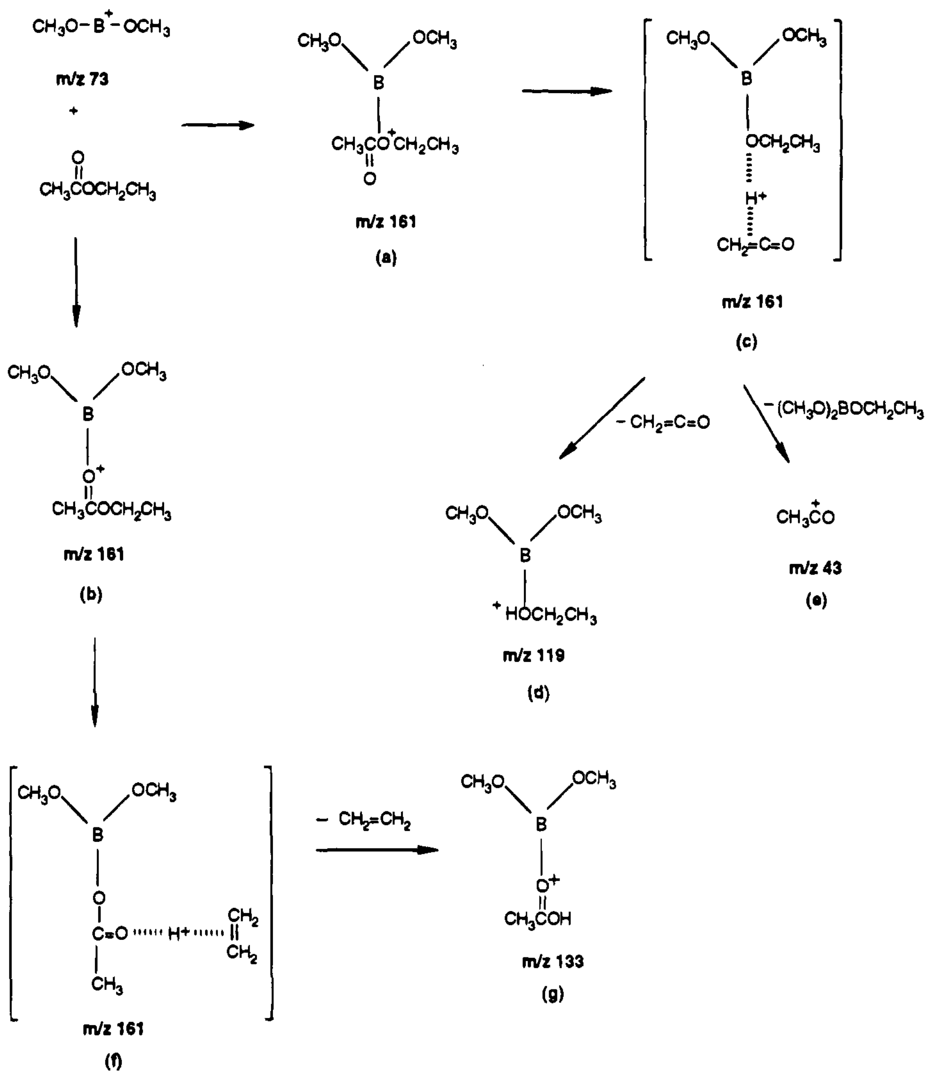
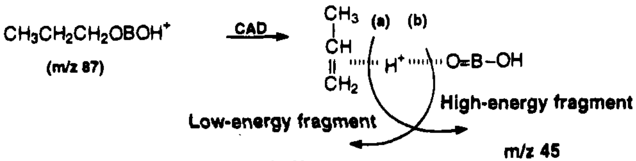
(25) (a) Swanton, D. J.; Marsden, D. C. J.; Radom, L. *Org. Mass Spectrom.* **1991**, *26*, 227. (b) Bouchoux, G.; Yannik, H. *J. Am. Chem. Soc.* **1990**, *112*, 9110.

Scheme 9



Scheme 10



Proton affinity bracketing experiments yielded a proton affinity of 179.4 ± 1 kcal/mol for $(CH_3)_2BOH$. On the basis of this value, the heat of formation of the dehydration product of $CH_3BCH_3^+$, the ion $(CH_3)_2BOH_2^+$, is 86 kcal/mol. Hence, dehydration of ethanol by $CH_3BCH_3^+$ is estimated to be somewhat less exothermic than the corresponding reaction for $CH_3OBOCH_3^+$. Comparison of the enthalpy changes associated with the two competing pathways (water vs hydroxyl abstraction) reveals that the relative extent of the pathways depends on their relative exothermicities. Hence, the hydroxyl abstraction channel dominates for larger alcohols. Further, this reaction is thermodynamically more favorable for the ion $CH_3BCH_3^+$ than for $CH_3OBOCH_3^+$. Hence, the former ion forms hydrocarbon product ions more readily.

The mechanistic rationale provided for the reactions of the borocations with alcohols can also be applied to explain the reactivity of these cations toward ethyl acetate. For example, abstractions of ethanol and an ethoxy group are competing channels upon reaction of $CH_3OBOCH_3^+$ with ethyl acetate, and the relative exothermicity determines which channel dominates.

The driving force for the reactions of the dicoordinated borocations with oxygen-containing organic molecules is the formation of the strong B—O bond. These cations are highly reactive toward neutral molecules with lone electron pairs. However, the simple ions were found to have very high barriers toward unimolecular dissociation.

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