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Disubstituted Boron Cations Cleave Carbonyl Bonds

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Abstract: The disubstituted boron cations $CH_3OBOCH_3^+$ and $CH_3BCH_3^+$ readily cleave $C=O$ and $C-C$ bonds in gaseous long-chain aldehydes and ketones in a dual-cell Fourier transform ion cyclotron resonance mass spectrometer. Abstraction of OH by the borocations yields a hydrocarbon product ion that contains the entire carbon skeleton of the aldehyde or ketone. A competing abstraction of part of the carbonyl compound as a small aldehyde results in a borocation product that is indicative of the location of the carbonyl group in the neutral substrate. The mechanisms of these two reactions likely involve common intermediates formed via 1,2-hydride shifts in an initially formed $B-O=C$ adduct. Both reactions are highly exothermic. The OH abstraction reaction is the thermodynamically favored pathway while aldehyde abstraction is kinetically favored by the smaller carbonyl compounds. The overall enthalpy change associated with the latter reaction is likely to be relatively insensitive to the size of the carbonyl compound. In contrast, the OH abstraction reaction becomes more exothermic as the size of the substrate increases. This results in a predominant hydrocarbon ion product for the larger aldehydes and ketones.

Introduction

Disubstituted boron cations are of interest as intermediates in some solution reactions.[1−3] Unfortunately, condensed-phase studies of their properties are currently limited to species with strongly π-back bonding and bulky substituents that provide electronic stability and that sterically shield the boron center against counterions and solvent molecules. In sharp contrast to solution work, gas-phase experiments allow the detailed investigation of various disubstituted boron cations, including those with no π-back-bonding substituents.[4−13]

Simple gaseous disubstituted borocations have been found to be exceedingly reactive toward oxygen-containing organic molecules. For example, $CH_3BCH_3^+$ and $CH_3OBOCH_3^+$ rapidly abstract water from alcohols and ethers.[12,13] The present study demonstrates that $CH_3BCH_3^+$ and $CH_3OBOCH_3^+$ also readily attack carbonyl compounds, inducing $C=O$ and $C-C$ bond cleavages. These highly exothermic reactions bear some resemblance to unimolecular decomposition of internally excited protonated carbonyl compounds,[14] and they provide a simple chemical means for the structural characterization of unknown carbonyl compounds in mass spectrometry.

Experimental Section

All experiments were carried out in an Extrel FTMS Model 2001 Fourier-transform ion cyclotron mass spectrometer equipped with a 1280 data system. The instrument contains a dual cell consisting of two identical 2-in. cells aligned collinearly with a magnetic field produced by a 3-T superconducting magnet operated at about 2.5 T. The dual cell is differentially pumped with two Balzer's turbomolecular pumps (330 L/s) backed with Alcatel 2012 mechanical pumps. The nominal background pressure in each cell was less than 1×10^{-9} Torr, as indicated by a Bayard−Albert ionization gauge located on each side of the dual cell.

Two Extrel FTMS heated single batch inlet systems equipped with a variable-leak valve were used to introduce the samples into the dual cell. The ions $CH_3BCH_3^+$, $CH_3OBOCH_3^+$, and $CD_3OBOCD_3^+$ were generated by electron ionization of $(CH_3)_2BBr$, $(CH_3O)_3B$, and $(CD_3O)_3B$, respectively, in one side of the dual cell. The ion signal was optimized for each experiment by adjusting the electron energy, filament current, and electron beam time. Undesired ions formed in the other cell by the electron beam were ejected by applying a negative potential (−9.8 V) to the remote trapping plate of this cell for 5−10 ms. After this, the desired ions were transferred into this cell through a 2-mm hole in the middle plate (the conductance limit plate) by grounding the plate for 100−200 μs. The ions were collisionally cooled by pulsing[15a] a high pressure of argon into the cell (1×10^{-5} Torr peak pressure). Subsequently, the desired reactant ions were isolated by ejecting all the unwanted ions from the cell. This was accomplished either by applying several single-frequency pulses and frequency sweeps to the excitation plates of the cell or by using the Stored Waveform Inverse Fourier transform excitation method (Extrel FTMS SWIFT module).[16] All attempts were taken to avoid exciting the ions to be isolated.

The isolated ions were allowed to react with a neutral reagent for a variable period of time. The branching ratios of the different reaction

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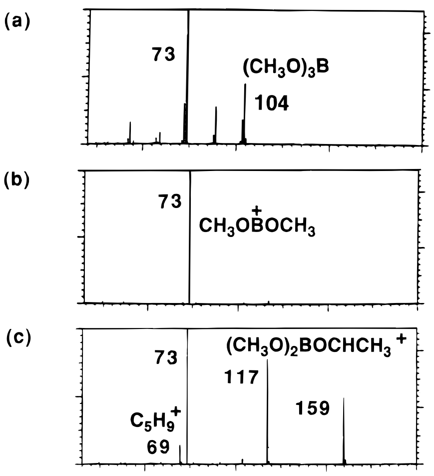

Figure 1. (a) Electron ionization of $(CH_3O)_3B$ (MW 104). (b) Transfer of the ions into the other reaction chamber, followed by isolation of the fragment ion $CH_3OBOCH_3^+$ (*m/z* 73). (c) Reaction of the ion $CH_3OBOCH_3^+$ for 800 ms with 2-pentanone (nominal pressure 1.2×10^{-7} Torr). The primary products were identified as $C_5H_9^+$ (*m/z* 69) and $(CH_3O)_2BOCHCH_3^+$ (*m/z* 117). The only secondary product is $(CH_3O)_2BOC(CH_3)CH_2CH_2CH_3^+$ (*m/z* 159).

channels were derived from the abundance ratios of the corresponding primary product ions. These ratios were constant at short reaction times. The second-order reaction rate constants were determined from the decay of the relative reactant ion abundance as a function of time. For all reactions, nominal sample pressures of 1.0×10^{-7} to 1.2×10^{-7} Torr were maintained in the cell throughout the experiment. The pressure readings were corrected for the sensitivity of the ion gauge[17] toward each neutral reagent. Further, the rates of several exothermic temperature-independent proton transfer and electron transfer reactions with known rate constants were determined to obtain a correction factor for the pressure gradient between the dual cell and the ion gauge, as described previously.[18] The precision of the rate constant measurements is better than 10%; the accuracy is estimated to be better than 50%. All the spectra were acquired at a digitizer rate of 5.4 MHz with use of an excitation sweep with 107 or 124 $V_{(p-p)}$ amplitude, 2.7 MHz bandwidth, and 3.0–3.2 kHz/μs sweep rate. The spectra were recorded as 32K data points and subjected to one zero fill before Fourier transformation.

Collision-activated dissociation was carried out for some of the product ions. In order to cool the ions, they were given a relatively long time period (about 1s) to undergo collisions with the argon present in the cell. The isolated ions were accelerated[15b] by using an excitation pulse with a fixed amplitude (3 or 3.5 V_{p-p}) and then allowed to collide for 100 ms with argon at a static nominal pressure of about 1.2×10^{-7} Torr. Variation of the excitation time led to different final kinetic energies of the accelerated ions. The reported ion kinetic energies are laboratory kinetic energies calculated as recommended by Grosshans and Marshall, *i.e.*, by taking half the value computed according to the infinite parallel plate approximation.[15c]

$(CD_3O)_3B$ was synthesized by a reaction of B_2O_3 with CD_3OD.[19] Hexanal-*2,2-d*$_2$ was prepared by a literature method used to synthesize similar d_2-aldehydes.[20] The purity of the labeled aldehyde was estimated to be about 95% with use of gas chromatography and ^{1}H NMR. All other reagents were obtained from Aldrich without further purification. The purity of the reagents was verified by GC and by mass spectrometry.

Results and Discussion

The ions $CH_3OBOCH_3^+$ and $CH_3BCH_3^+$ were generated by electron ionization (Figure 1a) and transferred into the other side of the dual cell, collisionally cooled, isolated (Figure 1b), and allowed to react with an aldehyde or ketone for a variable period of time (Figure 1c). The measured reaction rate constants and product branching ratios are given in Tables 1 and 2. The boron cations add to small aldehydes and ketones (*i.e.*, acetaldehyde, propanal, acetone, and 2-butanone), yielding a stable adduct as the only product. Abstraction of a small aldehyde and/or OH by the boron cation predominates for the longer chain aldehydes and ketones. The mechanisms of these reactions are discussed below, with the focus on the reactions of $CH_3OBOCH_3^+$.

Aldehyde Abstraction Pathway. Abstraction of a small aldehyde by $CH_3OBOCH_3^+$ dominates the reaction of this ion with the medium-sized carbonyl compounds studied (four to five carbon chain for the aldehydes; five to nine carbon chain for the ketones). For example, the reaction of 2-pentanone yields a major product ion (*m/z* 117; Figures 1 and 2) arising from abstraction of CH_3CHO. The identity of this product ion was probed by using different approaches. For example, its exact mass value was determined and found to correspond to the elemental composition $C_4H_{10}BO_3$. Reaction of 2-pentanone with the ^{10}B-containing ion $CH_3O^{10}BOCH_3^+$ (instead of the more abundant $CH_3O^{11}BOCH_3^+$ (*m/z* 73) used in all other experiments) results in an ion with one unit lower *m/z* ratio, further confirming the presence of boron in the product ion. Hence, the product ion arises via elimination of C_3H_6 (most likely propene) from the collision complex. The structure of the product ion of *m/z* 117 was examined by collision-activated dissociation. The ion yields only two fragment ions, CH_3OBH^+ (*m/z* 43) and $CH_3OBOCH_3^+$ (*m/z* 73; Figure 3a). The same fragment ions, with the same relative abundances, were obtained for a reference ion $(CH_3O)_2BOCHCH_3^+$ (*m/z* 117) generated upon reaction of $CH_3OBOCH_3^+$ with CH_3CHO (Figure 3b). Hence, the ion of *m/z* 117 is concluded to have the structure $(CH_3O)_2BOCHCH_3^+$.

The effects of the size of the neutral substrate and the location of the carbonyl functionality were examined by allowing $CH_3OBOCH_3^+$ to react with different carbonyl compounds (Tables 1 and 2). The ion was found to abstract an aldehyde from compounds with a propyl or a longer alkyl group attached to the carbonyl carbon, but not from compounds with only short alkyl groups. The nature of the abstracted aldehyde depends on the location of the carbonyl functionality. For example, CH_2O is abstracted from all aldehydes, CH_3CHO from all 2-ketones, and CH_3CH_2CHO from all 3-ketones.

The deuterium labeled borocation $CD_3OBOCD_3^+$ reacts with 2-pentanone to yield a product ion of *m/z* 123, corresponding to $(CD_3O)_2BOCHCH_3^+$. No H/D scrambling was observed in this reaction. Hence, the hydrogen atoms in the borocation do not undergo exchange with the hydrogen atoms in the carbonyl compound during the reaction. Further, the presence of oxygen atoms in the reactant ion is not crucial for the reaction since $CH_3BCH_3^+$ reacts with 2-pentanone to yield the analogous aldehyde abstraction product $(CH_3)_2BOCHCH_3^+$ (*m/z* 85).

All the above evidence suggests that the aldehyde abstraction reaction occurs via a mechanism similar to that proposed earlier for acid or methyl cation catalyzed loss of an alkene from protonated carbonyl compounds.[21-25] Hence, the mechanism is likely to involve two 1,2-hydride shifts (**a** and **b** in Scheme

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Table 1. Rate Constants and Product Distributions Obtained for Ion−Molecule Reactions of $CH_3OBOCH_3^+$ (*m/z* 73), $CD_3OBOCD_3^+$ (*m/z* 79), and $CH_3BCH_3^+$ (*m/z* 41) with Aldehydes

reactant ion (*m/z*)	neutral reagent (MW)	ionic product (*m/z*)[a]	branching ratio (%)[b]	k_{exp}[c]	k_{col}[d]	k_{exp}/k_{coll}
$CH_3OBOCH_3^+$ (73)	CH_3CHO (44)	$(CH_3O)_2BOCHCH_3$ (117)[e]	100	f	2.6	
	CH_3CH_2CHO (58)	$(CH_3O)_2BOCHCH_2CH_3^+$ (131)[e]	100	f	2.3	
	$CH_3(CH_2)_2CHO$ (72)	$C_4H_7^+$ (55)[e]	16	0.5	2.8	0.2
		$(CH_3O)_2BOCH_2^+$ (103)[e]	84			
		$(CH_3O)_2BOCH(CH_2)_2CH_3^+$ (145)				
	$CH_3CH_2CH(CH_3)CHO$ (86)	$C_5H_9^+$ (69)[e]	23	1.8	2.4	0.8
		$(CH_3O)_2BOCH_2^+$ (103)[e]	18			
		$(CH_3O)_2BOCHCH_3^+$ (117)[e]	59			
		$(CH_3O)_2BOCHCH(CH_3)CH_2CH_3^+$ (159)				
	$CH_3CH(CH_3)CH_2CHO$ (86)	$C_5H_9^+$ (69)[e]	75	2.1	2.4	0.9
		$(CH_3O)_2BOCH_2^+$ (103)[e]	25			
		$(CH_3O)_2BOCH(CH_3)CH(CH_3)CH_3^+$ (159)				
	$CH_3(CH_2)_3CHO$ (86)	$C_5H_9^+$ (69)[e]	80	1.9	2.3	0.8
		$(CH_3O)_2BOCH_2^+$ (103)[e]	20			
		$(CH_3O)_2BOCH(CH_2)_3CH_3^+$ (159)				
	$CH_3(CH_2)_4CHO$ (100)	$C_4H_7^+$ (55)[e]	12	2.4	2.4	1.0
		$C_6H_{11}^+$ (83)[e]	79			
		$CH_3(CH_2)_4CHOH^+$ (101)				
		$(CH_3O)_2BOCH_2^+$ (103)[e]	9			
		$(CH_3O)_2BOCH(CH_2)_4CH_3^+$ (173)				
	$CH_3(CH_2)_3CD_2CHO$ (102)	$C_4H_6D^+$ (56)[e,g]	10	2.0	2.4	0.8
		$C_6H_{10}D^+$ (84)[e]	21			
		$C_6H_9D_2^+$ (85)[e]	59			
		$CH_3(CH_2)_3CD_2CHOH^+$ (103)				
		$(CH_3O)_2BOCDH^+$ (104)[e]	10			
		$(CH_3O)_2BOCHCD_2(CH_2)_3CH_3^+$ (175)				
	$CH_3(CH_2)_5CHO$ (114)	$C_5H_9^+$ (69)[e]	47	1.3	2.1	0.6
		$C_7H_{13}^+$ (97)[e]	50			
		$CH_3(CH_2)_5CHOH^+$ (115)				
		$(CH_3O)_2BOCH(CH_2)_5CH_3^+$ (187)[e]	3			
$CD_3OBOCD_3^+$ (79)	$CH_3(CH_2)_3CHO$ (86)	$C_5H_9^+$ (69)[e]	87	1.7	2.3	0.7
		$(CD_3O)_2BOCH_2^+$ (109)[e]	13			
		$(CD_3O)_2BOCH(CH_2)_3CH_3^+$ (165)				
	$CH_3(CH_2)_4CHO$ (100)	$C_4H_7^+$ (55)[e]	3	2.5	2.9	0.9
		$C_6H_{11}^+$ (83)[e]	93			
		$CH_3(CH_2)_4CHOH^+$ (101)				
		$(CD_3O)_2BOCH_2^+$ (109)[e]	4			
		$(CD_3O)_2BOCH(CH_2)_4CH_3^+$ (179)				
$CH_3BCH_3^+$ (41)	$CH_3(CH_2)_4CHO$ (100)	$C_4H_7^+$ (55)[e]	50	2.3	1.9	1.2
		$C_6H_{11}^+$ (83)[e]	50			
		$CH_3(CH_2)_4CHOH^+$ (101)				

[a] The most likely structure is shown. [b] Branching ratios are for primary products only. [c] k_{exp} is given in units of $\times 10^{-9}$ cm^3 molecule^{-1}. [d] k_{coll} is the collision rate constant given in units of $\times 10^{-9}$cm^3 molecule^{-1}. [e] Denotes primary products. [f] Rate too slow to measure. [g] Ions corresponding to *m/z* 55 and 57 are also present in very small amounts.

1) in an initially formed B−O═C adduct, yielding the intermediate ion **c** (Scheme 1). Cleavage of a C−C bond in this intermediate results in the formation of the aldehyde abstraction product. The use of hexanal-*2,2-d*$_2$ as the neutral substrate leads to incorporation of one deuterium atom in the aldehyde abstraction product (deuterium labeling does not affect the reaction rate constant or the product branching ratios). This finding provides support for the occurrence of a 1,2-hydride shift to the carbonyl group (Scheme 2, path a; also see **a** in Scheme 1). The second hydride shift (**b** in Scheme 1) cannot take place for aldehydes and ketones with only methyl groups attached to the carbonyl carbon. Further, this shift would yield a high-energy intermediate, a primary carbocation, for compounds wherein ethyl is the longest alkyl group. The fact that no aldehyde abstraction product is generated for acetaldehyde, propanal, acetone, and 2-butanone, but the product is observed for all compounds with propyl or longer alkyl groups, provides strong support for the occurrence of the second hydride shift during the reaction.

Examination of reactions of $CH_3OBOCH_3^+$ with branched aldehydes reveals that not only hydrogen atoms but also methyl groups can undergo a 1,2-shift to an adjacent carbonyl carbon. For example, 2-methylbutanal yields two product ions, the expected ion of *m/z* 103 formed by a 1,2-hydride shift followed by CH_2O abstraction, and an ion of *m/z* 117 formed by a 1,2-methyl shift followed by CH_3CHO abstraction (Scheme 3a). An analogous pinacolic−retro-pinacolic rearrangement has been reported[26] earlier for the adduct of $(CH_3)_3Si^+$ with C_6-ketones during elimination of an alkene molecule.[26] In contrast to 2-methylbutanal, the reaction of $CH_3OBOCH_3^+$ with 3-methylbutanal produces only the expected CH_2O abstraction product $(CH_3O)_2BOCH_2^+$ (*m/z* 103; Scheme 3b). Hence, remote methyl groups are not transferred to the carbonyl carbon.

Formation of the initial B−O═C adduct (**a** in Scheme 1) between the boron cation and the carbonyl compound is estimated to be exothermic by at least 40 kcal/mol.[27] On the basis of this value, the heat of formation of the aldehyde abstraction product $(CH_3O)_2BOCHCH_3^+$ is concluded to be ≤ -38 kcal/mol.[27,28] Hence, CH_3CHO abstraction from 2-pentanone is exothermic by at least 13 kcal/mol.[29] The overall enthalpy change associated with aldehyde abstraction by $CH_3OBOCH_3^+$ from different carbonyl compounds is likely to be fairly unaffected by the size of the carbonyl compound. For example, the exothermicity of the generation of $(CH_3O)_2$-

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Table 2. Rate Constants and Product Distributions Obtained for Ion−Molecule Reactions of $CH_3OBOCH_3^+$ (*m/z* 73), $CD_3OBOCD_3^+$ (*m/z* 79), and $CH_3BCH_3^+$ (*m/z* 41) with Ketones

reactant ion (*m/z*)	neutral reagent (MW)	ionic product (*m/z*)[a]	branching ratios[b] (%)	k_{exp}[c]	k_{coll}[d]	k_{exp}/k_{coll}
$CH_3OBOCH_3^+$ (73)	$CH_3C(O)CH_3$ (58)	$(CH_3O)_2BOC(CH_3)_2^+$ (131)[e]	100	0.4	1.1	0.4
	$CH_3CH_2C(O)CH_3$ (72)	$(CH_3O)_2BOC(CH_3)CH_2CH_3^+$ (145)[e]	100	1.2	2.8	0.4
	$CH_3(CH_2)_2C(O)CH_3$ (86)	$C_5H_9^+$ (69)[e]	12	1.7	2.4	0.7
		$CH_3CH_2CH_2C(OH)CH_3^+$ (87)				
		$(CH_3O)_2BOCHCH_3^+$ (117)[e]	88		88	
		$(CH_3O)_2BOC(CH_3)CH_2CH_2CH_3^+$ (159)				
	$CH_3(CH_2)_3C(O)CH_3$ (100)	$C_6H_{11}^+$ (83)[e]	27	2.4	2.4	1.0
		$CH_3(CH_2)_3C(OH)CH_3^+$ (101)				
		$(CH_3O)_2BOCHCH_3^+$ (117)[e]	69			
		$(CH_3O)_2BOCHCH_2CH_3^+$ (131)	4			
		$(CH_3O)_2BOC(CH_3)(CH_2)_3CH_3^+$ (173)				
	$CH_3(CH_2)_4C(O)CH_3$ (114)	$C_7H_{13}^+$ (97)[e]	39	2.9	2.3	1.3
		$CH_3(CH_2)_4C(OH)CH_3^+$ (115)				
		$(CH_3O)_2BOCHCH_3^+$ (117)[e]	61			
		$(CH_3O)_2BOC(CH_3)(CH_2)_4CH_3^+$ (187)				
	$CH_3(CH_2)_3C(O)CH_2CH_3$ (114)	$C_7H_{13}^+$ (97)[e]	27	2.1	2.4	0.9
		$(CH_3O)_2BOCHCH_3^+$ (117)[e]	12			
		$(CH_3O)_2BOCHCH_2CH_3^+$ (131)[e]	52			
		$(CH_3O)_2BOCHCH_2CH_2CH_3^+$ (145)	6			
		$(CH_3O)_2BOC(CH_2CH_3)(CH_2)_3CH_3^+$ (187)				
	$CH_3(CH_2)_2C(O)(CH_2)_2CH_3$ (114)	$C_7H_{13}^+$ (97)[e]	28	2.9	2.3	1.3
		$(CH_3O)_2BOCHC_2H_5^+$ (131)[e]	35	35		
		$(CH_3O)_2BOCHCH_2CH_2CH_3^+$ (145)[e]	37	37		
		$(CH_3O)_2BOC[(CH_2)_2CH_3]_2^+$ (187)				
	$CH_3(CH_2)_5C(O)CH_2CH_3$ (142)	$C_5H_9^+$ (69)[e]	25	3.5	2.3	1.5
		$C_6H_{11}^+$ (83)[e]	14			
		$(CH_3O)_2BOCHCH_2CH_3^+$ (131)[e]	61			
		$CH_3(CH_2)_5C(OH)CH_2CH_3^+$ (143)				
		$(CH_3O)_2BOC(CH_2CH_3)(CH_2)_5CH_3^+$ (215)				
	$CH_3(CH_2)_3C(O)(CH_2)_3CH_3$ (142)	$C_6H_9^+$ (69)[e]	33	2.6	2.3	1.1
		$C_6H_{11}^+$ (83)[e]	11			
		$(CH_3O)_2BOCHCH_2CH_2CH_3^+$ (145)[e]	22			
		$(CH_3O)_2BOCH(CH_2)_3CH_3^+$ (159)[e]	34			
		$(CH_3O)_2BOC[(CH_2)_3CH_3]_2^+$ (215)				
$CD_3OBOCD_3^+$ (79)	$CH_3(CH_2)_2C(O)CH_3$ (86)	$C_6H_9^+$ (69)[e]	13	1.6	2.4	0.7
		$CH_3(CH_2)_2C(OH)CH_3^+$ (87)				
		$(CD_3O)_2BOCHCH_3^+$ (123)[e]	87			
		$(CD_3O)_2BOC(CH_3)(CH_2)_2CH_3^+$ (165)				
$CH_3BCH_3^+$ (41)	$CH_3(CH_2)_2C(O)CH_3$ (86)	$C_3H_7^+$ (43)[e]	78	2.3	2.7	0.9
		$C_6H_9^+$ (69)[e]	15			
		$(CH_3)_2BOCHCH_3^+$ (85)[e]	7			
		$CH_3(CH_2)_2C(OH)CH_3^+$ (87)				
		$(CH_3)_2BOC(CH_3)(CH_2)_2CH_3^+$ (127)				

[a] The most likely structure is shown. [b] Branching ratios are for primary products only. [c] k_{exp} is given in units of $\times 10^{-9}$ cm^3 molecule s^{-1}. [d] k_{coll} is the collision rate constant given in units of $\times 10^{-9}$ cm^3 molecule. [e] Denotes primary products.

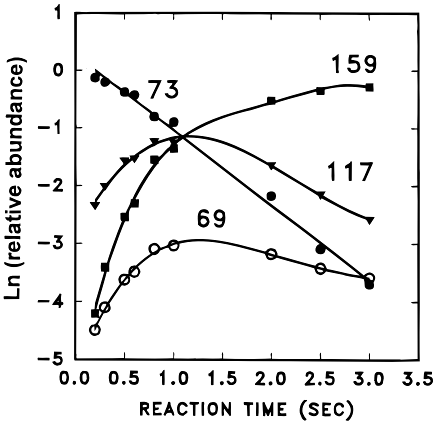


Figure 2. Temporal variation of the ion abundances for the reaction of $CH_3OBOCH_3^+$ (*m/z* 73) with 2-pentanone (nominal pressure 1.2 × 10^{-7} Torr). The nature of the products is explained in Figure 1.

$BOCHCH_3^+$ from 2-hexanone and from 2-heptanone is estimated to be −14 and −13 kcal/mol, respectively.[29]

The highly exothermic initial addition permits the adduct (**a**, Scheme 1) to overcome high-energy barriers before dissociation of the collision complex. The first hydride shift shown in Scheme 1 (**a**) is likely to be the most endothermic step in the reaction sequence (the second hydride shift is exothermic). The enthalpy changes of analogous 1,2-hydride shifts in protonated carbonyl compounds have been estimated to be 30−36 kcal/mol.[28,30−33] Hence, the energy released upon adduct formation

---

(27) The heterolytic B−O bond dissociation energy for $(CH_3O)_2B^+{-}OCHCH_3$ is likely to be somewhat greater than that in $(CH_3O)_2B^+{-}O(H)CH_3$ (39.5 kcal/mol, ref 11a; the assumption is based on the similar binding energy of CH_3CHO and CH_3OH to the methyl cation: 87.7 and 83.1 kcal/mol, respectively; ref 28). This bond energy, together with the known values of heat of formation for CH_3CHO (−39.6 kcal/mol; ref 28) and $CH_3OBOCH_3^+$ (41.4 kcal/mol; ref 11a), was used to calculate $\Delta H_f[(CH_3O)_2BOCHCH_3^+] \leq -37.7$ kcal/mol.

(28) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, G. J. *Phys. Chem. Ref. Data, Suppl. 1* **1988**, 17.

(29) The exothermicity of the reaction of 2-pentanone (−13 kcal/mol) was calculated by using the values: $\Delta H_f[CH_3OBOCH_3^+] = 41.4$ kcal/mol (ref 11a); $\Delta H_f[(CH_3O)_2BOCHCH_3^+] = -38$ kcal/mol (ref 27); $\Delta H_f[CH_3(CH_2)_2C(O)CH_3] = -61.9$ kcal/mol (ref 28), $\Delta H_f[CH_3CH{=}CH_2] = 4.8$ kcal/mol (ref 28). Calculations for the other ketones were carried out in the same manner by using the following additional values: $\Delta H_f[CH_3(CH_2)_3C(O)CH_3] = -66$ kcal/mol, $\Delta H_f[CH_3(CH_2)_4C(O)CH_3] = -72$ kcal/mol, $\Delta H_f[CH_3CH_2CH{=}CH_2] = -0.1$ kcal/mol, and $\Delta H_f[CH_3CH_2CH_2CH{=}CH_2] = -5.1$ kcal/mol (ref 28).

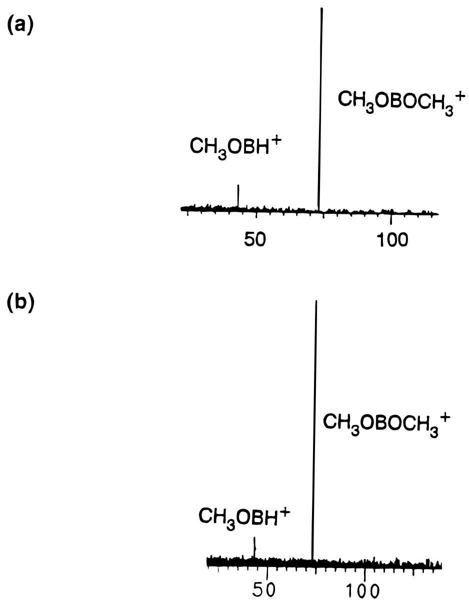
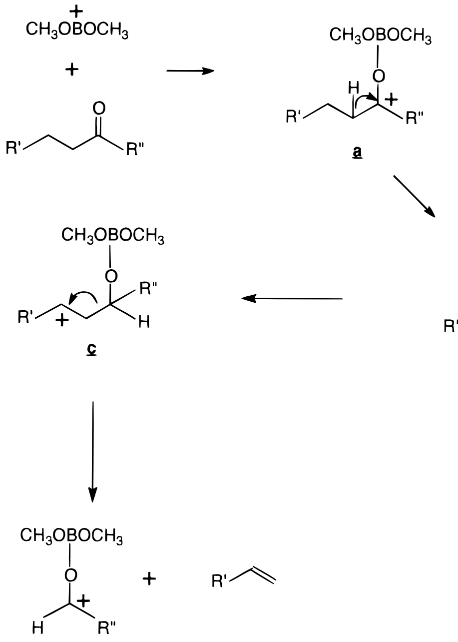


Figure 3. (a) Collision-activated dissociation of the ion of *m/z* 117 obtained from the reaction of $CH_3OBOCH_3^+$ (*m/z* 73) with 2-pentanone. (b) Collision-activated dissociation of the adduct (*m/z* 117) of $CH_3OBOCH_3^+$ and acetaldehyde.

Scheme 1

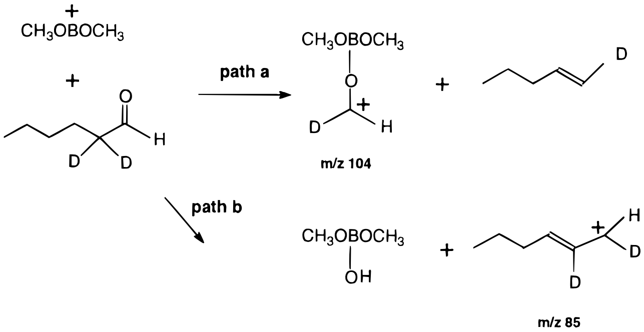


(≥40 kcal/mol) should be enough to overcome this energy barrier, as indicated in Figure 4.

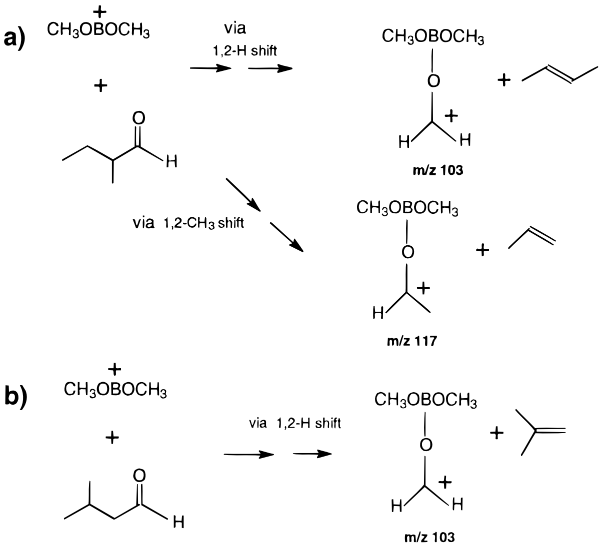
OH Abstraction Pathway. The borocation $CH_3OBOCH_3^+$ reacts with long-chain aldehydes and ketones (at least a four-carbon chain for aldehydes and at least a five-carbon chain for ketones) not only by aldehyde abstraction but also by OH abstraction. For example, the reaction with 2-hexanone yields the aldehyde abstraction product of *m/z* 117 and a product ion of *m/z* 83. The mass value of the latter product corresponds to the entire hydrocarbon skeleton of 2-hexanone minus one hydrogen atom, *i.e.*, $C_6H_{11}^+$. Analogous products are formed from all aldehydes and ketones with four or more carbon atoms (Tables 1 and 2).

The OH abstraction product obtained upon the reaction of $CH_3OBOCH_3^+$ with 2-hexanone was verified by exact mass measurements to have the elemental composition C_6H_{11}. All the hydrogen atoms in the product ion originate from the hydrocarbon skeleton of 2-pentanone, as demonstrated by no deuterium incorporation in the product ion (*m/z* 69; Table 2) formed upon reaction of $CD_3OBOCD_3^+$ with 2-pentanone. Reaction of $CH_3BCH_3^+$ with 2-pentanone produces the same product ion (*m/z* 69; Table 2) as the reaction of $CH_3OBOCH_3^+$ and $CD_3OBOCD_3^+$, indicating that the oxygen atoms in $CH_3OBOCH_3^+$ do not play a crucial role in formation of this product ion.

Scheme 2



Scheme 3



The OH abstraction reaction can be rationalized based on the same initial steps (Figure 4) that are thought to occur during the aldehyde abstraction reaction, addition followed by a 1,2-hydride transfer to form the high-energy intermediate **b** (Scheme 4). Rearrangement of this intermediate by proton transfer (pathway **b** in Scheme 4; pathway **a** leads to aldehyde abstraction) would readily yield the observed hydrocarbon product ion and a neutral borate. This mechanism is analogous to that proposed earlier for dissociation of protonated carbonyl compounds to water and an allyl cation.[31,34] It should also be mentioned that the ion $(CH_3)_3Si^+$ has been reported to react with C_6-ketones by OH abstraction.[26]

The origin of the hydrogen atom abstracted as part of the OH group was probed by examining the reaction of $CH_3OBOCH_3^+$ with hexanal-*2,2-d*$_2$ (Scheme 2, path b). Two deuterium atoms are incorporated in the hydrocarbon product

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[30] Heinrich, N.; Wolfschutz, R.; Frenking, G.; Schwarz, H. *Int. J. Mass Spectrom. Ion Phys.* **1982**, *44*, 81.

[31] Bowen, R. D.; Williams, D. H.; Hvistendahl, G.; Kalman, J. R. *Org. Mass Spectrom.* **1978**, *13*, 721.

[32] Audier, H. E.; Milliet, C.; Perret, A.; Varenne, P. *Org. Mass Spectrom.* **1979**, *14*, 129.

[33] Nobes, R. H.; Radom, L. *Org. Mass Spectrom.* **1984**, *19*, 385.

[34] Bowen, R. D.; Harrison, A. G. *Org. Mass Spectrom.* **1981**, *15*, 159.

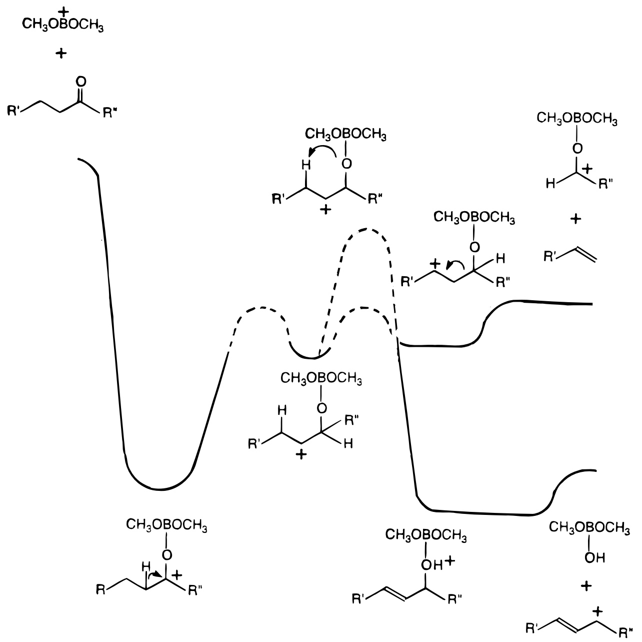
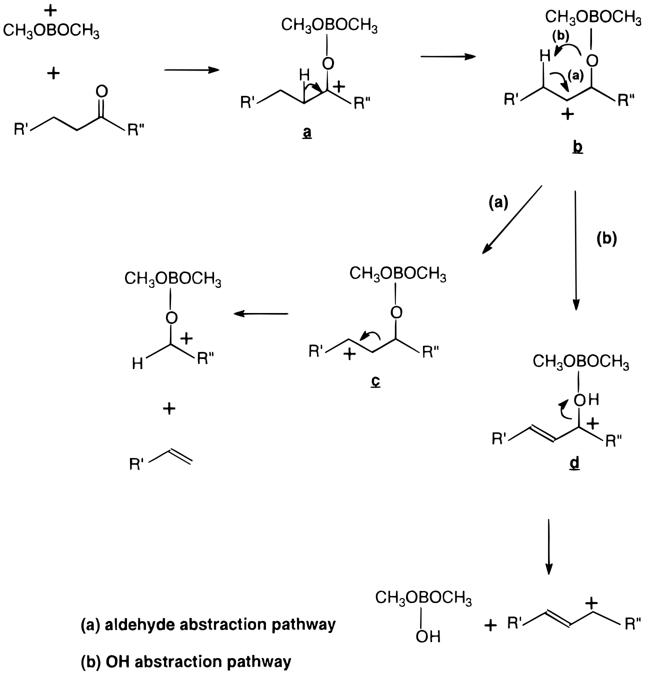
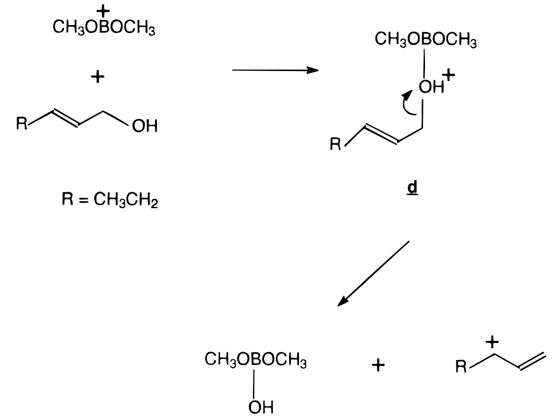


Figure 4. A schematic potential energy surface[37] for the reaction of the ion $CH_3OBOCH_3^+$ with carbonyl compounds.

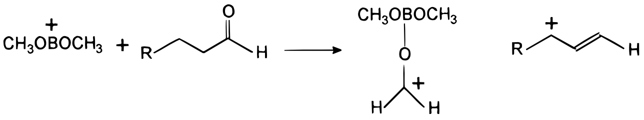
Scheme 4



Scheme 5



Scheme 6



R = H	None	None
R = CH_3	84%	16%
R = CH_3CH_2	20%	80%
R = $CH_3(CH_2)_2$	10%	90%

ion. Hence, the hydrogen atom in OH must originate from a carbon other than that adjacent to the carbonyl group, in agreement with the proposed mechanism. The mechanism is further supported by the results obtained for the reaction of $CH_3OBOCH_3^+$ with crotyl alcohol (Scheme 5). Addition of crotyl alcohol to $CH_3OBOCH_3^+$ yields the intermediate ion **d** (Scheme 4; R = CH_3CH_2). This adduct decomposes as proposed in Scheme 4, yielding a hydrocarbon ion that corresponds to the entire hydrocarbon skeleton of the reactant alcohol (Scheme 5).

The OH abstraction reaction is highly exothermic (see Figure 4 for an approximate potential energy surface). For example, the enthalpy change for OH abstraction from 2-pentanone by $CH_3OBOCH_3^+$ to yield $(CH_3O)_2BOH$ and $CH_3CH{=}CHCH^+CH_3$ is calculated to be about -48 kcal/mol.[35] The critical step in the reaction involves proton transfer *via* a five-membered transition state (**b** → **d**, Scheme 4). This step is likely to be associated with a substantial energy barrier (10 kcal/mol has been estimated[31] earlier for similar reactions) since the OH abstraction pathway is not favored by the smaller carbonyl compounds inspite of a great exothermicity. The reaction becomes more exothermic and hence more competitive as the size of the carbonyl compound increases. For example, the energy released upon OH abstraction is estimated to be about 4 kcal/mol greater for pentanal than for butanal.[35]

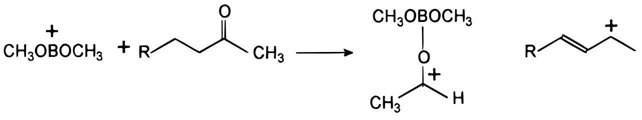
Competition between the Two Reaction Channels. The aldehyde and the OH abstraction pathways are competitive, and their relative extent is strongly dependent on the size of the carbonyl compound (Schemes 6 and 7). Abstraction of OH is the thermodynamically favored pathway. For example, OH abstraction is about 35 kcal/mol more exothermic than CH_3CHO abstraction for the reaction of 2-pentanone with $CH_3OBOCH_3^+$.[29] However, as mentioned above, OH abstraction

---

(35) The enhalpy change for OH abstraction from 2-pentanone was estimated to be -47.5 kcal/mol based on the values given above, as well as the following values: $\Delta H_f[(CH_3O)_2B{-}OH] = -250$ kcal/mol (obtained by using Benson's rules) and $\Delta H_f[CH_3CH{=}CHCH^+CH_3] = 182$ kcal/mol (ref 28). The enhalpy change for OH abstraction was estimated to be -39.8 kcal/mol from butanal and -43.3 kcal/mol from pentanal, based on the values given above and the following values: $\Delta H_f[CH_3CH{=}CHCH_2^+] = 202$ kcal/mol (ref 28), $\Delta H_f[CH_3CH_2CH{=}CHCH_2^+] = 193$ kcal/mol (ref 28), $\Delta H_f[CH_3CH_2CH_2CHO] = -49.6$ kcal/mol (ref 28), and $\Delta H_f[CH_3CH_2CH_2CH_2CHO] = -55.1$ kcal/mol (ref 28). The enhalpy change for CH_2O abstraction was estimated to be ≥ -11 kcal/mol from butanal and ≥ -10.4 kcal/mol from pentanal, based on the values given above and the following values: $\Delta H_f[CH_3CH{=}CH_2] = 4.8$ kcal/mol (ref 28), $\Delta H_f[CH_3CH_2CH{=}CH_2] = -0.1$ kcal/mol (ref 28), and $\Delta H_f[(CH_3O)BOCH_2^+] \geq 24$ kcal/mol (estimated in the same way as $\Delta H_f[(CH_3O)_2BOCHCH_3^+]$; see refs 27 and 36).

(36) The heterolytic bond dissociation energy for $(CH_3O)_2B^+{-}OCH_2$ is likely to be somewhat less than that in $(CH_3O)_2B^+{-}O(H)CH_3$ (39.5 kcal/mol, ref 11a; the assumption is based on the binding energy of CH_2O and CH_3OH to the methyl cation: 78 and 83.1 kcal/mol, respectively; ref 28). This bond energy, together with the known values of heat of formation for CH_2O (-26 kcal/mol; ref 28) and $CH_3OBOCH_3^+$ (41.4 kcal/mol; ref 11a), yields $\Delta H_f[(CH_3O)_2BOCH_2^+] \geq -24$ kcal/mol.

Scheme 7



R = H	None	None
R = CH_3	88%	12%
R = CH_3CH_2	72%	28%
R = $CH_3(CH_2)_2$	39%	61%

is likely to be associated with a substantial energy barrier (Figure 4).[31] In contrast, the 1,2-hydride shifts required for the aldehyde abstraction reaction probably take place with low or no barriers and hence can occur readily if the energy of the products is not above the energy of the separated reactants. Indeed, aldehyde abstraction dominates for the short-chain carbonyl compounds.

As the chain length of the carbonyl compound increases, the efficiency of the OH abstraction reaction increases. This finding may be explained by the increasing reaction exothermicity since this is often associated with a lowering of the barrier height for a series of similar reactions. Since the enthalpy change of the aldehyde abstraction reaction is fairly unaffected by the size of the carbonyl compound, this reaction becomes less competitive as the size of the compound increases. Indeed, the OH abstraction reaction dominates over aldehyde abstraction for all aldehydes and ketones with at least seven carbon atoms (Schemes 6 and 7).

The ion $CH_3BCH_3^+$ yields similar products as $CH_3OBOCH_3^+$. However, the former ion shows a greater preference for the OH than the aldehyde abstraction pathway. A similar preference for OH abstraction to form a hydrocarbon ion rather than H_2O abstraction to form a borocation was observed earlier for $CH_3BCH_3^+$ upon reactions with alcohols.[13] Many of the hydrocarbon product ions initially formed upon the reactions of $CH_3BCH_3^+$ fragment to yield other hydrocarbon ions. This was not observed for $CH_3OBOCH_3^+$, which suggests that the reactions of this ion are generally less exothermic than those of $CH_3BCH_3^+$.

The aldehyde and OH abstraction reactions may prove to be useful in the identification of unknown carbonyl compounds by using mass spectrometry. The hydrocarbon product ion can be used to identify the chain length of the aldehyde or ketone. For example, $C_5H_9^+$ is formed from all C_5-aldehydes and ketones, $C_6H_{11}^+$ from all C_6-aldehydes and ketones, and $C_7H_{13}^+$ from all C_7-aldehydes and ketones. Isomeric compounds yield different aldehyde abstraction products that are characteristic of the location of the carbonyl group. For example, 2-heptanone, 3-heptanone, and 4-heptanone produce $(CH_3O)_2BOCHCH_3^+$ (*m/z* 117), $(CH_3O)_2BOCHCH_2CH_3^+$ (*m/z* 131), and $(CH_3O)_2BOCHCH_2CH_2CH_3^+$ (*m/z* 145), respectively (Figure 5). In addition to these structurally characteristic products, the 3- and 4-heptanones also yield $(CH_3O)_2BOCHCH_3^+$ (*m/z* 117) and $(CH_3O)_2BOCHCH_2CH_3^+$ (*m/z* 131), respectively, although in smaller abundance. These ions most likely arise via a skeletal rearrangement similar to that reported for the adduct of $(CH_3)_3Si^+$ with C_6-ketones and for protonated carbonyl compounds.[14,22,26]

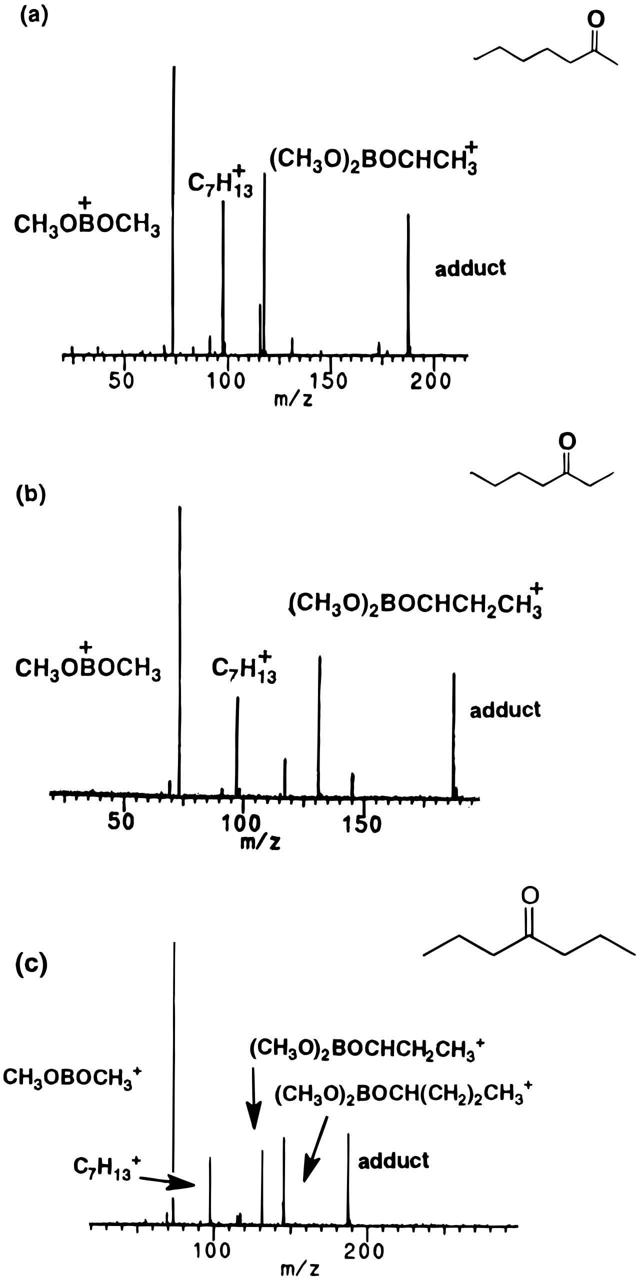


Figure 5. Reaction of $CH_3OBOCH_3^+$ for 500 ms with (a) 2-heptanone, (b) 3-heptanone, and (c) 4-heptanone.

Formation of the Secondary Product Ions. In addition to the aldehyde and OH abstraction products, some secondary products are formed upon reaction of the boron cations with the aldehydes and ketones. Some of the hydrocarbon ions formed upon OH abstraction protonate the neutral carbonyl compund. Further, the aldehyde abstraction products react with the neutral carbonyl compound by displacement of the abstracted aldehyde (Tables 1 and 2). For example, an abundant secondary product ion of *m/z* 159 is formed in the reaction of $CH_3OBOCH_3^+$ with 2-pentanone. This ion arises from displacement of CH_3CHO in the primary product, $(CH_3O)_2BOCHCH_3^+$ (*m/z* 117), with a 2-pentanone molecule (see the rate plot in Figure 2). This reaction pathway was verified by isolating the ion $(CH_3O)_2BOCHCH_3^+$ and allowing it to react with 2-pentanone. The only product observed was the ion of *m/z* 159. Collision-activated dissociation of the ion of *m/z* 159 yields $(CH_3O)_2BOCHCH_3^+$ (*m/z* 117) and $CH_3OBOCH_3^+$ (*m/z* 73) at low energies. The fragment ion $(CH_3O)_2BOCHCH_3^+$ dissociates further to yield CH_3OBH^+ (*m/z* 43) at higher energies (Figure

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[37] The approximate thermochemical values associated with the reactions of butanal were used to construct the schematic potential energy surface. $\Delta H_f[(CH_3O)_2BO(H)CH_2CH{=}CHCH_3^+] \leq -35$ kcal/mol was estimated by using heterolytic bond dissociation energy of $\geq$39.5 kcal/mol for $(CH_3O)_2B{-}O(CH_2CH{=}CHCH_3)$ (ref 27) and $\Delta H_f[CH_3CH{=}CHCH_2\text{-}OH] = -37$ kcal/mol (ref 28).

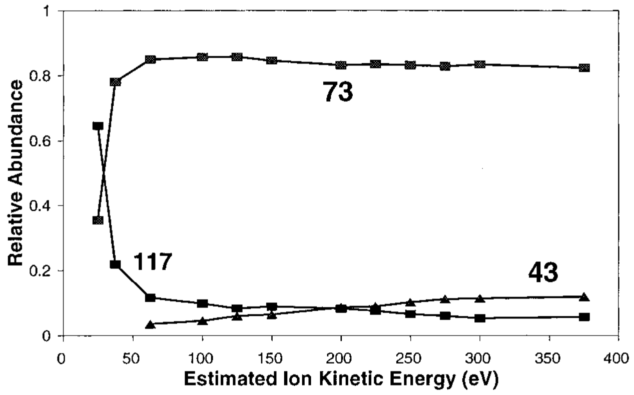

Figure 6. Energy-resolved collision-activated dissociation of the product ion of *m/z* 159 obtained from the reaction of $CH_3OBOCH_3^+$ with 2-pentanone.

6; see also Figure 3). These findings suggest that the structure of the ion of *m/z* 159 is $(CH_3O)_2BOC(CH_3)CH_2CH_2CH_3^+$, as expected.

Conclusions

The boron cations $CH_3OBOCH_3^+$ and $CH_3BCH_3^+$ are highly reactive toward carbonyl compounds. Two dominant reaction pathways were observed. Abstraction of a small aldehyde by the boron cation leads to elimination of a carbonyl bonded alkyl group as a neutral alkene, yielding an ionic product that is indicative of the location of the carbonyl group in the neutral substrate. Abstraction of a OH group yields a dominant hydrocarbon ion that contains the entire carbon skeleton of the neutral substrate. These two reaction pathways are competitive and involve common reaction intermediates. The OH abstraction reaction is the thermodynamically favored pathway. Aldehyde abstraction is kinetically favored for the shorter chain substrates. This is not true for the longer chain carbonyl compounds, possibly because the increasing exothermicity of the OH abstraction reaction associated with the increasing size of the carbonyl compound results in lowering of the energy barrier associated with this reaction. Hence, the longer chain carbonyl compounds predominantly form the hydrocarbon product ion.

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