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Generation and characterization of ionic and neutral $(CH_3OBH)^{+/\cdot}$ and $(CH_3BOH)^{+/\cdot}$ in the gas phase by tandem mass spectrometry

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Abstract

The isomeric dicoordinated borinium ions $CH_3O–B–H^+$ and $CH_3–B–OH^+$ are generated upon electron ionization of trimethylborate and methyl boronic acid, respectively. The connectivity of the ions is confirmed by collision-induced dissociation experiments on magnetic deflection type tandem mass spectrometers. Neutralization–reionization experiments on these structurally characterized ions indicate that the neutral radicals $CH_3O–B–H^\cdot$ and $CH_3–B–OH^\cdot$ are viable species in the gas phase. Calculations at the G2 level of theory were performed to obtain thermochemical data on the title isomers and their main dissociation products. The calculations also provide a rationale for the moderate yield of the neutrals generated in the experiments: the vertical electron transfer processes for both systems are associated with particularly unfavourable Franck-Condon factors. (Int J Mass Spectrom 202 (2000) 315–322) © 2000 Elsevier Science B.V.

Keywords: Borinium ions; Electron transfer; G2 calculations; Mass spectrometry

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1. Introduction

Dicoordinated boron molecules are important intermediates in organoboron chemistry, not in the least because of their role in the combustion of boron compounds in aerospace systems [1,2]. However, so far not many of such subvalent boron species have been experimentally identified. One reason is their high reactivity which has been attributed to the electrophilicity induced by the two empty *p* orbitals on boron.

In contrast, their ionic counterparts, borinium ions are readily generated as stable species in a mass spectrometer by either dissociative ionization of simple boron containing compounds or ion molecule reactions [3]. The chemical reactivity of various borinium ions toward different organic substrates has been thoroughly investigated by Kenttamäa and coworkers using a dual cell Fourier transform ion cyclotron resonance (FTICR) mass spectrometer [4]. The group of Brodbelt extended these studies and has demonstrated that borinium ions are useful reagents in the analysis of drugs by chemical ionization [5].

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the dilute gas phase may therefore be an attractive route to generate their highly reactive counterparts. This process represents the first step in neutralization–reionization (NR) mass spectrometry which has developed over the years into a powerful method for the study of elusive neutral species [6]. Using this technique, we have recently demonstrated that neutral $B(OH)_2^{\cdot}$ is a stable species in the gas phase [7]. Here we report on the use of the NR methodology to study the generation of $CH_3OBH^{\cdot}$ and $CH_3BOH^{\cdot}$ from their ionic counterparts.

2. Experimental and computational methods

The mass spectrometric experiments described in this work were performed on a VG Autospec-M mass spectrometer of EBE geometry (E stands for electric sector and B for magnetic sector), a ZAB/HF/AMD 604 four-sector mass spectrometer of BEBE configuration, and a VG-analytical ZAB-R instrument of BEE geometry. Detailed information about these instruments has been previously reported [8]. The collision-induced dissociation (CID) and related MS/MS/MS spectra were obtained with the ZAB-R instrument and for reasons of uniformity the other spectra presented in this article were also recorded on this instrument.

CID mass spectra were recorded in the second and third field-free regions (ffr) using oxygen as collision gas (transmittance $T = 70\%$). Neutralization–reionization spectra were recorded in the 2ffr using N,N-dimethylaniline (NDMA) or xenon as reducing agents and oxygen gas for reionization. The spectra were recorded using a small PC-based data system developed by Mommers Technologies Inc. (Ottowa, Ontario).

Trimethylborate and methyl boronic acid were of research grade (Aldrich) and used without further purification. The D-labeled isotopomer of trimethylborate $^{10}B(OCD_3)_3$ was prepared on a milligram scale by reacting 50 mg of $^{10}B(OH)_3$ with 150 μL of CD_3OD at room temperature for ~15 min. The resulting solution was used without further purification. The compounds were introduced to the ion chamber (kept at 100 °C) by means of an all-glass heated inlet system equipped with a leak valve or a direct insertion-type wide-bore quartz probe whose sample reservoir was at or below ambient temperature. Methyl boronic acid has a tendency to trimerize during the introduction of the sample. The mass spectrum of the resulting trimethylboroxine [9] is characterized by signals at *m/z* 126, 111, 69, and 41; a peak at *m/z* 43 is not present, thus, the trimerization does not cause interference in this study.

The Gaussian series of programs [10,11] was used to perform G2 calculations [12] on the ionic and neutral CH_4BO isomers and their main dissociation products. Geometry optimizations for $CH_4BO^{+/\cdot}$ were performed at the MP2/6-311+G(3*df*,2*p*) level of theory. Optimized geometries of the dissociation products were obtained at the standard MP2(full)/6-31G(*d*) level of theory used in the G2 set. This approach is expected to yield accurate energetics, with in ±2 kcal/mol in all but a few notorious cases [12–15]. The energetics of vertical electron-transfer processes of interest were obtained by using the optimized geometry of the species in question and subsequently performing the G2 series of single-point calculations on the neutralized or ionized species, respectively, incorporating the so-called higher level corrections of the G2 method, but no zero-point vibrational energies.

3. Results and discussions

3.1. Trimethylborate

The 70 eV electron ionization (EI) mass spectrum of trimethylborate (**I**) displays an intense molecular ion at *m/z* 104 (55%, ^{11}B isotope) and prominent fragment ions at *m/z* 73 (base peak, loss of $CH_3O^{\cdot}$), *m/z* 43 (27%), *m/z* 15 (12%, CH_3^+). Early experimental work [16] suggested that the *m/z* 43 ion would correspond to $^{11}BO_2^+$ generated by loss of C_2H_6 from the *m/z* 73 ion. However, in subsequent experiments Hettich et al. [17] showed that the ion has the elemental composition $CH_4^{11}BO$ and that it is exclusively generated by loss of $CH_2{=}O$ from the *m/z* 73

Table 1
Calculated G2 energies E_{tot} (hartrees) and relative energies E_{rel} (kcal/mol) of possible fragmentation channels of (a) the CH_3OBH^+ cation[a] and (b) the $CH_3OBH^{\cdot}$ radical[b] at 0 K

	E_{tot} (G2)	E_{rel}
(a)		
CH_3OBH^+ (**1**$^+$)	−140.054 961	0.0
$CH_3O(H)B^+$ (**1a**$^+$)	−139.958 120	60.8
$CH_2O(H)BH^+$ (**1b**$^+$)	−140.012 745	26.5
$CH_2OBH^{\cdot+} + H^{\cdot}$	−139.881 234	109.0
$CH_3OB^{\cdot+} + H^{\cdot}$	−139.867 196	117.8
$CH_2OB^+ + H_2$	−139.890 957	102.9
$HBO^{\cdot+} + CH_3^{\cdot}$	−139.755 740	188.0
$BOH^{\cdot+} + CH_3^{\cdot}$	−139.880 649	109.4
$HBO + CH_3^+$	−139.951 958	65.0
$BOH + CH_3^+$	−139.880 442	109.5
(b)		
$CH_3OBH^{\cdot}$ (**1**$^{\cdot}$)	−140.300 013	0.0
$CH_3O(H)B^{\cdot}$ (**1a**$^{\cdot}$)	−140.238 254	38.8
$CH_2OBH + H^{\cdot}$	−140.227 356	45.6
$CH_3OB + H^{\cdot}$	−140.201 023	62.1
$CH_2OB^{\cdot} + H_2$	−140.209 257	57.0
$HBO + CH_3^{\cdot}$	−140.311 472	−7.2
$BOH + CH_3^{\cdot}$	−140.239 956	37.7

[a] The difference of the total energies yields IE_a (CH_3OBH) = 6.67 eV, and combined with $\Delta H_{f,0}$ (CH_3OBH) = −16.4 kcal/mol (b), $\Delta H_{f,0}$ (CH_3OBH^+) = 137.4 kcal/mol is predicted.

[b] The G2 atomization method using experimental values for the heats of formation of the atoms predicts $\Delta H_{f,0}(CH_3OBH) = -16.4$ kcal/mol, $\Delta H_{f,298}(CH_3OBH) = -19.9$ kcal/mol is predicted using the calculated thermal corrections.

$CH_3O^{11}BOCH_3^+$ ion. On this basis, the connectivity CH_3OBH^+ (**1**$^+$) was proposed for the *m/z* 43 ions, implying that the loss of CH_2=O involves a 1,3-H shift. An alternative route for this rearrangement would involve a 1,4-H shift leading to the isomer CH_3–O(H)–B^+. However, see the computational results in Table 1(a), this species lies c. 60 kcal/mol higher in energy than **1**$^+$ and thus is unlikely to be (co-)generated.

That the $CH_4^{11}BO$ ions represent a single structure follows from a comparison of the CID spectra of the source generated *m/z* 43 ions and the low energy ions generated from metastable *m/z* 73 precursor ions, which, see Fig. 1(a) and (b), are virtually identical. The (weak) metastable ion (MI) spectrum of source generated ions is dominated by a CH_3^+ signal at *m/z* 15 and, see Table 1(a), this is indeed the reaction of lowest energy requirement for *m/z* 43 ions having the

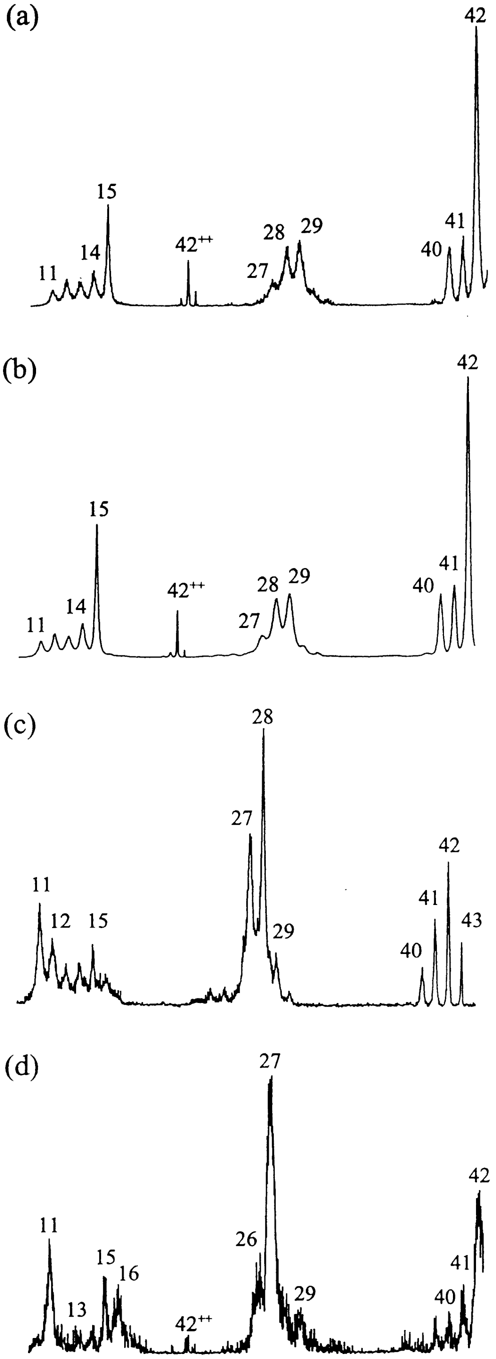
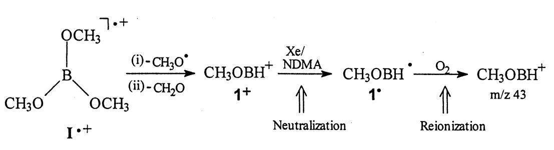


Fig. 1. Collision-induced dissociation mass spectra of (a) *m/z* 43 CH_3O–B–H^+ ions generated from 10 keV metastable $CH_3OBOCH_3^+$ ions, 3ffr; (b) source generated *m/z* 43 CH_3O–B–H^+ ions having 6 keV translational energy, 3ffr; (c) neutralization–reionization mass spectrum of 8 keV CH_3O–B–H^+ ions, 2ffr; (d) CID mass spectrum of 8 keV *m/z* 43 survivor ions, 3ffr.

connectivity $CH_3O–B–H^+$. The *m/z* 15 peak also features prominently in the CID spectrum. However, the spectrum is dominated by a more energy demanding, see Table 1(a), loss of $H^{\cdot}$ from either the CH_3O or the BH moiety yielding stable *m/z* 42 product ins of structure $CH_2OBH^{\cdot+}$ and $CH_3OB^{\cdot+}$, respectively. The spectrum also shows an intense structure characteristic charge stripping peak at *m/z* 21 which may represent ions of structure $^+H_2CO–B–H^+$ generated by loss of $H^{\cdot}$ from the weak *m/z* 21.5 ions of structure $CH_3O–B–H^{++}$. Finally, a cluster of ions is observed at *m/z* 27–29. From a comparison with the spectrum of the ^{10}B isotopomer at *m/z* 42, it follows that these ions represent $^{11}BO^+$, $H^{11}BO^{\cdot+}$, and HCO^+, respectively, the latter ion being characteristic of the CH_3O moiety.

Collisional neutralization of $\mathbf{1}^+$ followed by reionization and mass spectrometric analysis, see Scheme 1, yields the NR spectrum shown in Fig. 1(c). The spectrum shows a substantial "survivor" signal at *m/z* 43 which seems to suggest that a sizeable fraction of the ions subjected to the NR process has remained intact. However, the fragment ion distribution in the NR spectrum is considerably different from that in the CID spectrum: ions at *m/z* 15 and *m/z* 42 are still present in the NR spectrum but it is dominated by *m/z* 28 ions. From the results presented in Table 1(b), which lists calculated minimum energy requirements for various dissociations of neutral $CH_3O–B–H^{\cdot}$, it follows that dissociation into H–B=O and $CH_3^{\cdot}$ may well be facile and thus the *m/z* 28 ions and (part of) the *m/z* 15 ions in the NR spectrum are likely to originate from collisional ionization. In this context we note that the slight exothermicity calculated for the dissociation of $\mathbf{1}^{\cdot}$ into H–B=O does not necessarily imply that $CH_3O–B–H^{\cdot}$ cannot be a viable species in the gas phase. A case in point is the experimentally characterized $CH_3O–C=O^{\cdot}$ radical which lies 19 kcal/mol higher in energy than its dissociation products $CH_3^{\cdot} + CO_2$ but which is prevented to dissociate by a sizable barrier of 27 kcal/mol [18]. On the other hand, the computations discussed below indicate that, analogous to the $B(OH)_2^{+/\cdot}$ system [7], the NR process for $CH_3O–B–H^{+/\cdot}$ is associated with unfavorable Franck-Condon factors. Moreover, it is well known that neutralization–(collisional) reionization efficiencies of isobaric and even isomeric species can easily differ by factor of 100 [6]. We therefore decided to try to verify the identity of the mass selected survivor ions by obtaining their CID spectra [19]. The result for the ^{11}B isotopomer is shown in Fig. 1(d). Signals at *m/z* 42, 41, 29, 21, and 15 characteristic of $\mathbf{1}^+$ are clearly present, implying that neutralization of $\mathbf{1}^+$ does yield stable species $CH_3O–B–H^{\cdot}$ that retain their structural identity. The spectrum also displays peaks of sizable intensity at *m/z* 27 *m/z* (BO^+), 16 (O^+), and 11 (B^+). These signals point to the contribution of a species [20] isobaric to the survivor signal, viz. $^{11}BO_2^+$. These $^{11}BO_2^+$ ions only contribute to a minor extent to the CID spectrum of the source generated *m/z* 43 ions (they could account for part of the weak *m/z* 27 signal) but apparently their neutralization–reionization efficiency is far greater than that of $CH_3O–B–H^+$. From the NR characteristics of BO_2^+, its contribution to the recovery signal at *m/z* 43 could easily be estimated. Unfortunately, however, a precursor molecule providing an intense beam of pure BO_2^+ ions was not available. We therefore decided to examine a sample of the $^{10}B/D$ labeled trimethyl borate isotopomer $^{10}B(OCD_3)_3$ whose *m/z* 46 $CD_3O–^{10}B–D^+$ ions produce a NR spectrum which does not suffer from BO_2^+ interference [21]. From the intensity of the survivor ion in this spectrum (10% of the base peak at *m/z* 28 $D–^{10}B=O^{\cdot+}$) it follows that ~45% of the recovery signal in Fig. 1(c) accounts for the stable $CH_3O–B–H^{\cdot}$ radical.

That NR of the $CH_3O–B–H^{+/\cdot}$ system suffers from unfavourable Franck-condon factors—the survivor ion yield is only $1:10^5$—can be seen from the computational results presented in Figs. 2 and 3. From Fig. 2, it follows that there are large geometry differences between the ion and the neutral: the COB moiety is almost linear in the cation, but bent in the



Scheme 1.

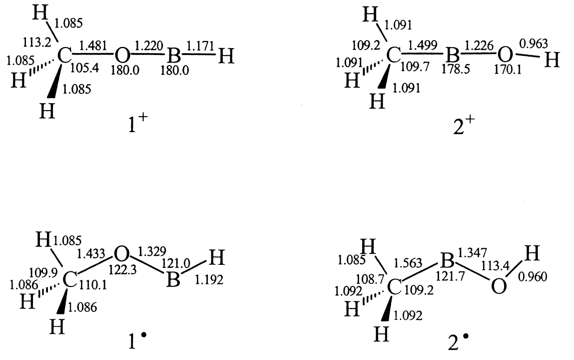
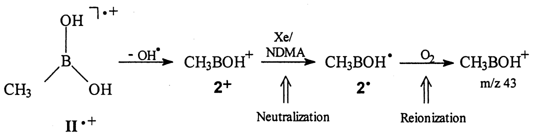


Fig. 2. MP2/6-311+G(3*df*,2*p*) optimized geometries of $\mathrm{CH_4BO}$ isomers, bond lengths in angstrom, bond angles in degrees.

radical. To a first approximation electron transfers in neutralization–reionization experiments occur vertically and thus the vertical recombination energy (RE_v) of the cation and the vertical ionization energy (IE_v) of the neutral need to be considered as well. The G2 results presented in Table 2 predict that $\mathrm{RE}_a = \mathrm{IE}_a = 6.68$ eV. Further, vertical ionization of the neutral ($\mathrm{IE}_v = 7.94$ eV) requires 1.3 eV more than the adiabatic process and it is therefore associated with unfavourable Franck-Condon factors see Fig. 3(a). Similarly, vertical neutralization of thermalized $\mathrm{CH_3O{-}B{-}H^+}$ differs by almost 2 eV from adiabatic process. It yields $\mathrm{CH_3OBH^{\cdot}}$ radicals with a highly nonrelaxed geometry which are prone to dissociate. This effect may account for the enhanced *m/z* 28 ($\mathrm{H{-}B{=}O^{\cdot+}}$) peak in the NR spectrum as well as the weak but discrete survivor signal for $\mathrm{CH_3O{-}B{-}H^+}$.

3.2. Methyl boronic acid

Another interesting $\mathrm{CH_4BO}$ isomer is $\mathrm{CH_3{-}B{-}OH}$ (**2**$^+$), which can be envisaged to be generated by a direct bond cleavage from ionized methyl boronic acid, (**II**), see Scheme 2. The 70 eV EI mass spectrum of **II** indeed yields *m/z* 43 ions which comprise 24% of the base peak at *m/z* 45, the $^{11}\mathrm{B(OH)}_2^+$ ion generated by loss of $\mathrm{CH_3^{\cdot}}$ [7]. The mass spectrum also displays a peak at *m/z* 44 (39%) which represents a mixture of $^{10}\mathrm{B(OH)}_2^+$ and $\mathrm{HO{-}{}^{11}B{=}O^{\cdot+}}$. Considering that the $^{11}\mathrm{B}/^{10}\mathrm{B}$ natural abundance is 81:19, it follows that the *m/z* 43 $\mathrm{CH_4^{11}BO^+}$ ions are contaminated with ~15% isobaric $\mathrm{HO{-}{}^{10}B{=}O^{\cdot+}}$ ions. The presence of these ions does not significantly compromise the CID spectrum of the *m/z* 43 ions, but as we shall see this does not hold true for the NR spectrum and particularly the abundance of the recovery signal therein.



Scheme 2.

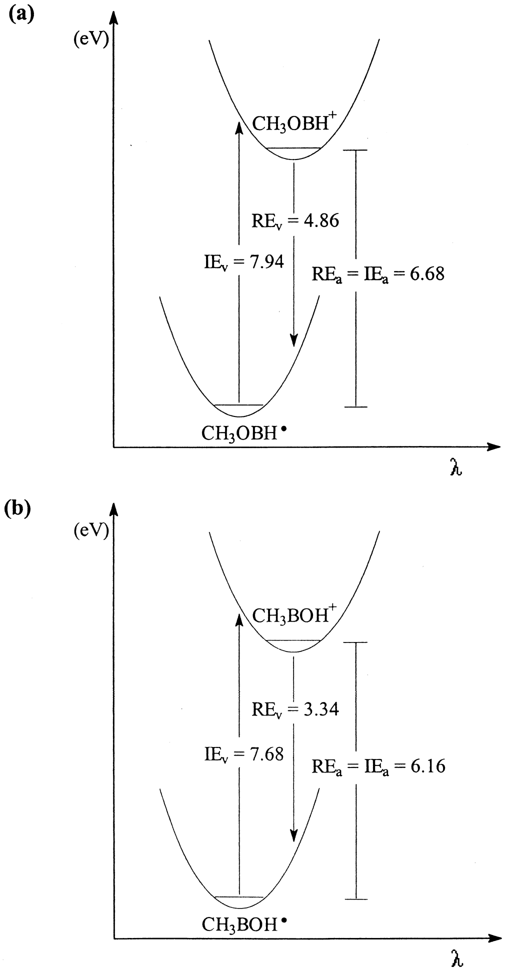


Fig. 3. Schematic G2 potential-energy surfaces for the sequential electron transfer during the NR sequence (a) $\mathrm{CH_3O{-}B{-}H^+} \rightarrow \mathrm{CH_3O{-}B{-}H^{\cdot}} \rightarrow \mathrm{CH_3O{-}B{-}H^+}$ and (b) $\mathrm{CH_3{-}B{-}OH^+} \rightarrow \mathrm{CH_3{-}B{-}OH^{\cdot}} \rightarrow \mathrm{CH_3{-}B{-}OH^+}$.

Table 2
Calculated G2 energies E_{tot} (hartrees) and relative energies E_{rel} (kcal/mol) of neutral and ionic CH_3OBH^+ and CH_3BOH^+ at 0 K

Species	G2 0 K	Relative energy (kcal/mol)
$CH_3BOH^{\cdot}$	−140.336 728	0
$CH_3BOH^{\cdot a}$	−140.232 630	65
CH_3BOH^+	−140.109 833	142
CH_3BOH^{+b}	−140.055 023	177
$CH_3OBH^{\cdot}$	−140.300 013	23
$CH_3OBH^{\cdot a}$	−140.232 573	65
CH_3OBH^+	−140.054 961	177
CH_3OBH^{+b}	−140.007 402	206

[a] Using the fixed optimized geometry of the ion to evaluate the vertical neutralization energy.

[b] Using the fixed optimized geometry of the neutral to evaluate the vertical ionization energy.

The CID spectrum of the *m/z* 43 ions is shown Fig. 4(a). The spectrum resembles that of isomer **1**$^+$ as far the major dissociations leading to *m/z* 15, 28, 29, and 40−42 are concerned. This is not unexpected in light of the calculated minimum energy requirements for dissociation listed in Table 3(a). Nevertheless, telltale peaks at *m/z* 23–26 (BCH_n; $n = 0–3$) reveal that the ions have the B–C connectivity associated with the proposed CH_3–B–OH^+ structure **2**$^+$. In this context we further note that interconversion between **1**$^+$ and **2**$^+$ is unlikely since a key intermediate, $CH_3O(H)B^+$, lies 60 kcal/mol higher in energy than **1**$^+$ [see Table 1(a)].

The NR spectrum of the *m/z* 43 ions is shown in Fig. 4(b). It is seen that the signals characteristic of CH_3–B–OH^+ are still clearly present in the NR spectrum but the peaks at *m/z* 27 and 28 have become much more prominent. Moreover, the spectrum shows an abundant recovery signal. This is surprising in view of our calculations which—analogous to the behavior of ionic and neutral **1**$^{\cdot}$—indicate that in the neutralization step energetic neutral are generated with distorted geometries. As shown in Fig. 2, radical **2**$^{\cdot}$ exhibits a structure with $\alpha_{CBO} = 122$ °, whereas an

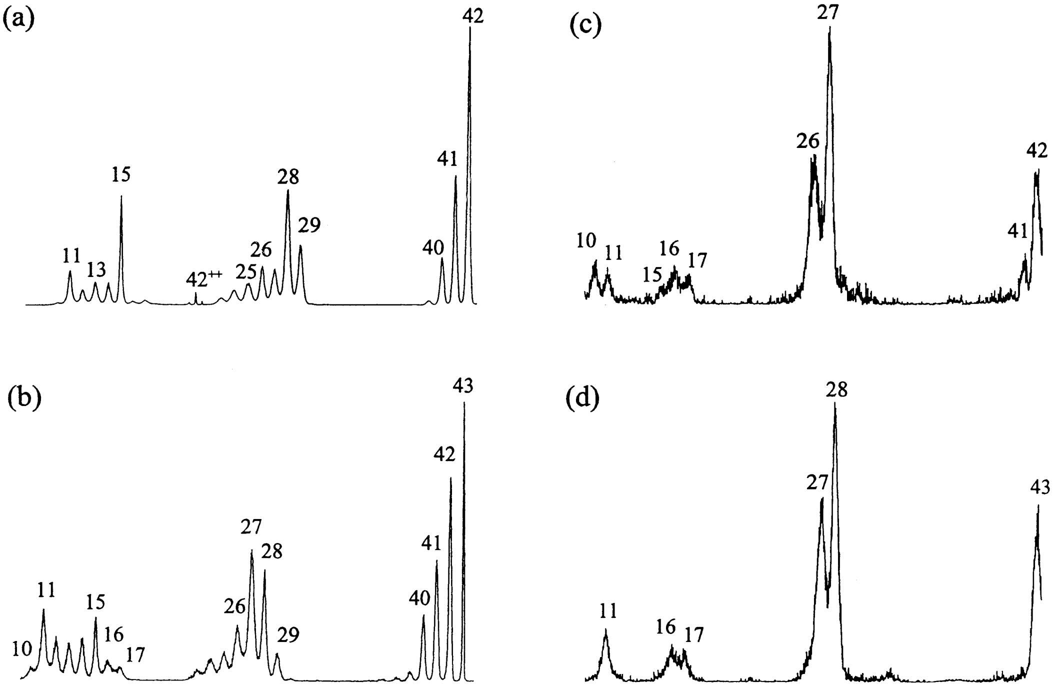


Fig. 4. (a) Collision-induced dissociation mass spectrum of 8 keV *m/z* 43 CH_3–B–OH^+ ions, 2ffr; (b) neutralization–reionization mass spectrum of 8 keV *m/z* 43 CH_3–B–OH^+ ions, 2ffr; (c) CID mass spectrum of 8 keV *m/z* 43 survivor ions in the NR spectrum, 3ffr; (d) CID mass spectrum of 8 keV *m/z* 44 survivor ions in the NR spectrum of $HO^{11}B{=}O$, 3ffr.

Table 3
Calculated G2 energies E_{tot} (hartrees) and relative energies E_{rel} (kcal/mol) of possible fragmentation channels of (a) the CH_3BOH^+ cation[a] and the CH_3BOH radical[b] at 0 K

	E_{tot} (G2)	E_{rel}
(a)		
CH_3BOH^+ (**2^+**)	−140.109 833	0.0
CH_2BHOH^+ (**$2a^+$**)		[c]
$CH_2BOH^{\cdot+} + H^{\cdot}$	−139.931 362	112.0
$CH_3BO^{\cdot+} + H^{\cdot}$	−139.971 455	199.8
$CH_2BO^+ + H_2$	−139.931 298	112.0
$CH_3B^{\cdot+} + OH^{\cdot}$	−139.806 019	190.6
$BOH^{\cdot+} + CH_3^{\cdot}$	−139.880 649	143.8
$HBO^{\cdot+} + CH_3^{\cdot}$	−139.755 740	222.2
$BOH + CH_3^+$	−139.880 442	143.9
$HBO + CH_3^+$	−139.951 958	99.0
(b)		
$CH_3BOH^{\cdot}$ (**$2^{\cdot}$**)	−140.336 728	0.0
$CH_2BHOH^{\cdot}$ (**$2a^{\cdot}$**)		[c]
$CH_2BOH + H^{\cdot}$	−140.240 022	60.7
$CH_3BO + H^{\cdot}$	−140.312 888	15.0
$CH_2BO^{\cdot} + H_2$	−140.320 945	9.9
$BOH + CH_3^{\cdot}$	−140.239 956	60.7
$HBO + CH_3^{\cdot}$	−140.311 472	15.8

[a] The difference of the total energies yields IE_a (CH_3BOH) = 6.17 eV, and combined with $\Delta H_{f,0}$ (CH_3OBH) = −39.5 kcal/mol (b), $\Delta H_{f,0}$ (CH_3BOH^+) = 102.8 kcal/mol is predicted.

[b] The G2 atomization method using experimental values for the heats of formation of the atoms predicts $\Delta H_{f,0}(CH_3BOH) = -39.5$ kcal/mol, $\Delta H_{f,298}(CH_3BOH) = -42.9$ kcal/mol is predicted using the calculated thermal corrections.

[c] All attempts to optimize the geometry of **$2a^+$** and **$2a^{\cdot}$** failed and led to the isomeric structures **2^+** and **$2^{\cdot}$**, respectively.

almost linear CBO unit is found for the cation. Upon vertical neutralization of low energy ions, therefore, energy rich neutrals with bent CBO moieties may be generated and these may dissociate via the routs listed in Table 3(b) which all have fairly low energy requirements.

A satisfactory explanation for both the seemingly intense recovery signal and the enhanced *m/z* 27 and 28 peak intensities comes from an analysis of the *m/z* 43, 44, and 45 recovery signals in the NR spectra. Their relative intensities were found to be 30:100:21 whereas the corresponding source generated ions yield 24:39:100. Knowing the isobaric species contributing to these three peaks, it becomes clear that $HO–B{=}O^{\cdot+}$ ions have a much higher probability of surviving the NR process than either $B(OH)_2^+$ or $CH_3–B–OH^+$. As a result the estimated 15% isobaric $HO–^{10}B{=}O^{\cdot+}$ contamination of the *m/z* 43 ions manifests itself in the NR spectrum by contributing to ~85% of the survivor ion signal. Thus only ~15% of the survivor signal stems from $CH_3–B–OH^{\cdot}$, in line with the theoretical considerations discussed above.

That neutrals **2^+** are stable under NR conditions but only marginally so, is further confirmed by the CID spectrum of the *m/z* 43 survivor ions displayed in Fig. 4(c). The spectrum is dominated by fragment ions characteristic of $HO–^{10}B{=}O^{\cdot+}$, compare Fig. 4(d), including the intense peaks at *m/z* 27 ($H–^{10}B{=}O^{\cdot+}$) and 26 ($^{10}BO^+$) but the weak signal at *m/z* 15 does attest to the presence of $CH_3–B–OH^+$.

4. Conclusions

High energy collision experiments on magnetic deflection type tandem mass spectrometers show that stable *m/z* 43 ions of structure $CH_3O–B–H^+$ and $CH_3–B–OH^+$ are generated by electron-ionization of trimethylborte and methyl boronic acid, respectively.

Neutralization–reionization experiments indicate that the neutral counterparts of both cations, $CH_3O–B–H^{\cdot}$ and $CH_3–B–OH^{\cdot}$ are viable species in the gas phase. However, when contributions from isobaric impurities to the recovery signals in the NR spectra are considered, both species appear to display survivor ion signals of only moderate intensity. Theoretical calculations at the G2 level of theory provide a rationale for these observations. The calculations show (1) that unfavourable Franck-Condon factors [7] govern the NR process of both systems and (2) that fairly low lying dissociation channels are accessible to the incipient neutrals.

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[20] The spectrum also displays weak signals at *m/z* 10 ($^{10}B^+$) and *m/z* 26 ($^{10}BO^+$) which point to the presence of HO–^{10}B=O$^{\cdot+}$ as a minor component in the initial ion beam.

[21] The *m/z* 46 ions actually consist of a 9:1 mixture of CD_3O–^{10}B–D$^+$ and DO–^{10}B–OD$^+$. However, from reference NR spectra of $B(OH)_2^+$, see Ref. [7], we derive that the contribution of DO–^{10}B–OD$^+$ to the recovery signal is not more than ~10% of the *m/z* 46 survivor ion yield.