Can the CH_2BH_2 and CH_3BH radicals, cations and anions be observed by experiment?

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Abstract

The structure, thermochemistry, isomerization and dissociation of the CH_2BH_2 and CH_3BH radicals, cations and anions have been explored with a wide range of ab initio levels of computational theory and their formation has been probed by tandem mass spectrometry and RRKM kinetic theory. Calculations predict that $CH_2BH_2^{]+}$ is not an equilibrium structure on the potential energy surface. The $CH_3BH^{]+}$ was characterized by its collision-induced dissociation mass spectrum and neutralization–reionization (NR) mass spectrometry was used to generate the $CH_3BH^{]\bullet}$ radical. While both $CH_2BH_2^{]\bullet}$ and $CH_3BH^{]\bullet}$ are stable with respect to isomerization and dissociation, a relatively low barrier to the 1,2-hydrogen shift means that pure $CH_3BH^{]\bullet}$ can only be made cold, and so the above NR experiment likely produces a mixture of neutrals, of which only $CH_3BH^{]\bullet}$ can be reionized. Vertical electron attachment to $CH_3BH^{]\bullet}$ is endothermic which means the $CH_3BH^{]-}$ anion is unlikely to be made from the cation or radical. In addition, the anion lies in a shallow well of only 48 kJ mol^{-1} and will undergo fast isomerization to $CH_2BH_2^{]-}$ below the dissociation limit.
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1. Introduction

Boron is the only element in group IIIA that is a non-metal. It forms compounds that are isoelectronic with carbon compounds (i.e., R_3B and R_3C^+, R_4B^- and R_4C, boron nitride and carbon (BN equivalent to CC), etc.). Boron is unique in that it forms $3sp^2$ hybrid orbitals and has an empty pure 2p orbital allowing it to form three coordinate (planar) neutral complexes or four coordinate (tetrahedral) negatively charged complexes. The system of radicals, cations and anions of composition CH_4B are isoelectronic with derivatives of ethene. Isomers $CH_2BH_2^{]\bullet}$ and $CH_3BH^{]\bullet}$ are isoelectronic with $CH_2CH_2^{]+\bullet}$ and $CH_3CH^{]+\bullet}$. As will be seen, while $CH_3BH^{]\bullet}$ is a stable species, $CH_3CH^{]\bullet}$ has been shown not to occupy a minimum on

the ionized ethene potential energy surface [1]. Poon and Mayer calculated G3 heats of formation and bond strengths for several closed- and open-shell boron-containing neutral species [2]. They found that the $\Delta_f H^\circ_{298}$ decreases by 72–74 kJ mol^{-1} with successive methyl substitution on BH_2CH_3 and a similar 62–66 kJ mol^{-1} decrease is observed for $CH_2BH_2^{]\bullet}$. Methyl substitution increases the B—C bond length and decreases its bond strength in both the open- and closed-shell species [2]. The formation of $CH_2BH_2^{]\bullet}$ and $CH_3BH^{]\bullet}$ has been observed by IR spectroscopy and investigated theoretically in the reaction of boron atoms with methane [3–6]. Reaction products $CH_3BH^{]\bullet}$, $CH_2BH_2^{]\bullet}$, $H_2C=BH$, $HC=BH^{]\bullet}$ and $HB=C=BH$ were determined by isotopic substitution and comparisons from ab initio calculations. The major reaction product is $CH_3BH^{]\bullet}$, which can rearrange to $CH_2BH_2^{]\bullet}$ or lose a hydrogen atom to form $CH_2BH + H^\bullet$.

The analogous cations $CH_2BH_2^{]+}$ and $CH_3BH^{]+}$ are isoelectronic with the doubly charged $CH_2CH_2^{]2+}$ and

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$CH_3CH^{]2+}$ ions. Pople et al. [7] investigated the $CH_4B^{]+}$ ions at the MP4SDTQ/6-31G*//HF/3-21G level of theory. It was found that $CH_2BH_2^{]+}$ lies 127 kJ mol^{-1} higher in energy than $CH_3BH^{]+}$ and that the transition state for their interconversion lies only 32 kJ mol^{-1} above $CH_2BH_2^{]+}$. The transition state for the interconversion was found to be a bridged structure having C_S symmetry, while $CH_2BH_2^{]+}$ and $CH_3BH^{]+}$ have C_{2V} and C_{3V} symmetry, respectively. There have been no attempts to make either of these ions in the laboratory. Similarly, the anionic isomers $CH_2BH_2^{]-}$ and $CH_3BH^{]-}$, which are isoelectronic with CH_2CH_2 and CH_3CH, have not been experimentally investigated.

The goal of this study was to explore the potential energy surface for the cations, radicals and anions in order to predict the observability of these species by experiment. To do this, an assessment was carried out to find a reliable level of theory at which to calculate geometries, vibrational frequencies and energies. Tandem mass spectrometry experiments were then performed to test the theoretical predictions.

2. Computational procedures

Standard ab initio molecular orbital calculations [8] were carried out using the Gaussian 98 [9] suite of programs. Geometries were optimized (and vibrational frequencies calculated) with several electron correlation treatments (HF, ROHF, B3-PW91, B3-LYP, MP2, ROMP2, CCSD, QCISD, CCSD(T) and QCISD(T)) using a variety of basis sets (using a frozen core). Single point energies on selected optimized geometries were obtained at the G3 level of theory [10]. Scaling factors for the zero-point energy (ZPE) values were those recommended by Scott and Radom [11]. If a basis set was not in the previously mentioned paper, the scale factor for the closest match was used. Heats of formation at 0 K were calculated by the atomization method [12], using the experimental heats of formation of the constituent atoms [10].

$CH_3BH^{]+}$ and $CH_2BH_2^{]\bullet}$ are calculated to have C_{3V} and C_{2V} symmetry, respectively, at most levels of theory employed in this study. However, it proved impossible to optimize these high symmetry species at CCSD, QCISD(T) and CCSD(T) (and QCISD for $CH_2BH_2^{]\bullet}$) using Gaussian 98 or 03, the symmetry always lowering, sometimes to C_1. At the precision of the geometric parameters quoted in the tables in this paper $CH_3BH^{]+}$ and $CH_2BH_2^{]\bullet}$ appear to be C_{3V} and C_{2V}, but we have retained the lower symmetry designation according to the output of the calculations. Fang and Peyerimhoff quote a C_{2V} symmetry for $CH_2BH_2^{]\bullet}$ at the QCISD level of theory using Gaussian 94 [6]. A test of $CH_2BH_2^{]\bullet}$ using the MOLPRO and ACES II suite of programs confirmed a C_{2V} symmetry [13]. For the purposes of investigating the observability of these species in the gas phase, the exact nature of their symmetry is irrelevant as there are no energy consequences from the above symmetry changes.

3. Experimental procedures

Tandem mass spectrometry experiments were carried out on a modified VG ZAB mass spectrometer consisting of a magnetic sector followed by two electrostatic analyzers (BEE geometry) [14]. Mass analyzed ion-kinetic energy (MIKE) and collision-induced dissociation mass spectra were obtained in the second and third field-free regions of the instrument by the normal procedures [15]. Helium target gas was employed in CID experiments with a collision cell pressure sufficient to reduce the precursor ion flux by 20%. Neutralization–reionization mass spectra [16] employed O_2 in both the neutralization and reionization collision cells and a deflector voltage of +500 V. Charge reversal mass spectra [17] also employed O_2 target gas.

4. Results and discussion

4.1. Determination of an appropriate level of theory at which to optimize the geometries of CH_4B ions and radicals

Optimized values for selected geometric parameters for the cation, anion and radical isomers of CH_4B are listed in Tables 1–6 according to structure definitions in Fig. 1. All HF results can be found in Supporting information Tables S1–S6.

4.1.1. $CH_3BH^{]-}$
Table 1 shows that all levels of theory give C_1 symmetry since the three carbon hydrogen bonds are not equivalent. The lone pair of electrons is located on boron, so this anion is stabilized by their interaction with the vacant pseudo-$\pi*$ orbital on the methyl group. The B3-LYP, B3-PW91, and MP2 levels of theory all yield similar geometric parameters when using the 6-31+G(d) basis set. Interestingly the 6-311+G(d) basis set has the effect of slightly lengthening the C—B and B—H bonds relative to the 6-31+G(d) basis set at the MP2 level of theory, but shortening them when using the B3-LYP level of theory. The addition of polarization (6-311+G(2df, p)) to the basis set at both these levels of theory has the affect of shortening the bond lengths. The QCISD and CCSD levels of theory give very similar results to each other. The geometries are not greatly affected by the addition of the triples excitation with either of these levels of theory. B3-LYP is the best at reproducing both the CCSD(T) and QCISD(T) results.

4.1.2. $CH_3BH^{]\bullet}$
Similar to the anion, all levels of theory give C_1 symmetry for the neutral $CH_3BH^{]\bullet}$ species (Table 2). This species differs from the anion in that it has a single electron on B rather than a lone pair, and is stabilized only by the single electron interaction with the pseudo-π^* orbital on the methyl group resulting in less antibonding character (and thus shorter) C—B, C—H and B—H bonds. The QCISD and CCSD results are very similar to each other and are not affected a great deal by the addition of triples excita-