Ab Initio Study of XH_2^+ (X = B, Al, and Ga) Isomers[†]

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Ab initio calculations at the MP2/6-311++G(3df,2pd) and CCSD(T)/cc-pVTZ levels were carried out to calculate the structure and energetics of isomers of singlet XH_2^+ (X = B, Al and Ga). Energy comparison shows that although the linear $D_{\infty h}$ structure **1a** is the global minimum for BH_2^+, the global minima of AlH_2^+ and GaH_2^+ are not of $D_{\infty h}$ symmetry **2a** and **3a**, respectively, but of C_{2v} symmetry **2b** and **3b** with a 3c-2e bond. The $D_{\infty h}$ symmetric **2a** and **3a** are significantly less stable than **2b** and **3b**, respectively, by 13.1 and 21.5 kcal/mol. Relative hydride affinities of the cations **1a**, **2b**, and **3b** were also calculated.

Introduction

DePuy et al. recently investigated the gas-phase reactions of BH_2^+ with simple saturated hydrocarbons by experiment as well as theory.[2] In contrast to the reactive methyl cation, the exothermicity of the reactions with BH_2^+ was found to be moderate and the energy profiles of the reactions were found to be well defined.[2] The linear $D_{\infty h}$ symmetrical structure was calculated for the singlet BH_2^+ at the MP2(FU)/6-311G** level.[2,3] Linear $D_{\infty h}$ symmetrical structure was also calculated for the isoelectronic carbon analogue CH_2^{2+} at the HF/6-31G* level by Pople, Tidor, and Schleyer.[4]

Recently, density functional theory (DFT) study on the structure and energetics of SiH_2^{2+} dications we reported[5] that highly symmetric $D_{\infty h}$ structure as well as C_{2v} symmetric structure with a three-center two-electron (3c-2e) bond are minima on the potential energy surface. Interestingly, the $D_{\infty h}$ form was found to be significantly less stable than C_{2v} form by 14.7 kcal/mol (Scheme 1).[5]

We report now the ab initio theoretical investigation of the isomers of XH_2^+ (X = B, Al, and Ga) cation. Studies show that although the $D_{\infty h}$ symmetrical form is the global minimum for BH_2^+, the global minima of AlH_2^+ and GaH_2^+ are not of $D_{\infty h}$ symmetry but of C_{2v} symmetry with a 3c-2e bond.

Results and Discussion

The geometry optimizations were performed at the ab initio MP2/6-311++G(3df,2pd) level.[6] Vibrational frequencies at the MP2/6-311++G(3df,2pd)//MP2/6-311++G(3df,2pd) level were used to characterize stationary points as minima (number of imaginary frequency (NIMAG) = 0) or transition structure (NIMAG = 1) and to evaluate zero-point vibrational energies (ZPE) which were scaled by a factor of 0.93. For the MP2/6-311++G(3df,2pd) optimized structures further geometry optimizations were carried out with the coupled cluster method at the CCSD(T)/cc-pVTZ[7] level (for the boron and aluminum compounds). For boron and aluminum compounds final energies were calculated at the CCSD(T)/cc-pVTZ//CCSD(T)/cc-pVTZ + ZPE level and for the gallium compounds at the MP2/6-311++G(3df,2pd)//MP2/6-311++G(3df,2pd) + ZPE level. Calculated energies are given in Table 1. Calculations were carried out with the Gaussian 98 program.[8]

SCHEME 1

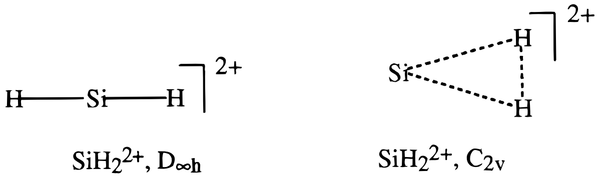

TABLE 1: Total Energies (−au) and ZPE[a] (kcal/mol)

	MP2/6-311++G(3df,2pd)	CCSD(T)/cc-pVTZ	rel. energy[b]
BH_2^+ **1a**	25.54728 (10.3)	25.56506	0.0
BH_2^+ **1b**	25.44263 (6.9)	25.47520	52.7
BH_2^+ **1c**	25.30547 (3.5)	25.38012	108.9
BH + H^+	25.20305 (3.2)	25.23062	106.4
AlH_2^+ **2a**	242.84576 (7.2)	242.86754	13.1
AlH_2^+ **2b**	242.86310 (6.7)	242.88760	0.0
AlH_2^+ **2c**	242.67228 (2.2)	242.74649	84.1
AlH + H^+	242.51945 (2.3)	242.54567	209.9
GaH_2^+ **3a**	1924.14044 (7.5)		[21.6][c]
GaH_2^+ **3b**	1924.17347 (6.7)		[0.0][c]
GaH_2^+ **3c**	1923.96763 (2.2)		[123.7][c]
GaH + H^+	1923.82032 (2.2)		[217.1][c]

[a] Zero-point vibrational energies (ZPE) at MP2/6-311++G(3df,2pd)//MP2/6-311++G(3df,2pd) scaled by a factor of 0.93 are given in parentheses. [b] Relative energy based on CCSD(T)/cc-pVTZ//CCSD(T)/cc-pVTZ+ ZPE. [c] Relative energies based on MP2/6-311++G(3df,2pd)//MP2/6-311++G(3df,2pd) + ZPE are given in square brackets.

BH_2^+. Linear $D_{\infty h}$ structure **1a** and triangular-shaped C_{2v} structure **1b** (Figure 1) were found to be minima on the potential energy surface (PES) of singlet BH_2^{2+} at the MP2/6-311++G(3df,2pd) level as indicated by frequency calculations at the same level. The structure **1a** is 65.7 kcal/mol more stable than **1b** at the MP2/6-311++G(3df,2pd) level (Table 1). The difference becomes 52.7 kcal/mol at our highest level, i.e., at the CCSD(T)/cc-pVTZ//CCSD(T)/cc-pVTZ + ZPE level.

Structure **1b** is characterized with a 3c-2e bond and can be considered as a complex between B^+ and a hydrogen molecule. The interaction between boron and hydrogens can also be

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[†] Dedicated to W. Goddard on the occasion of his 60th birthday.

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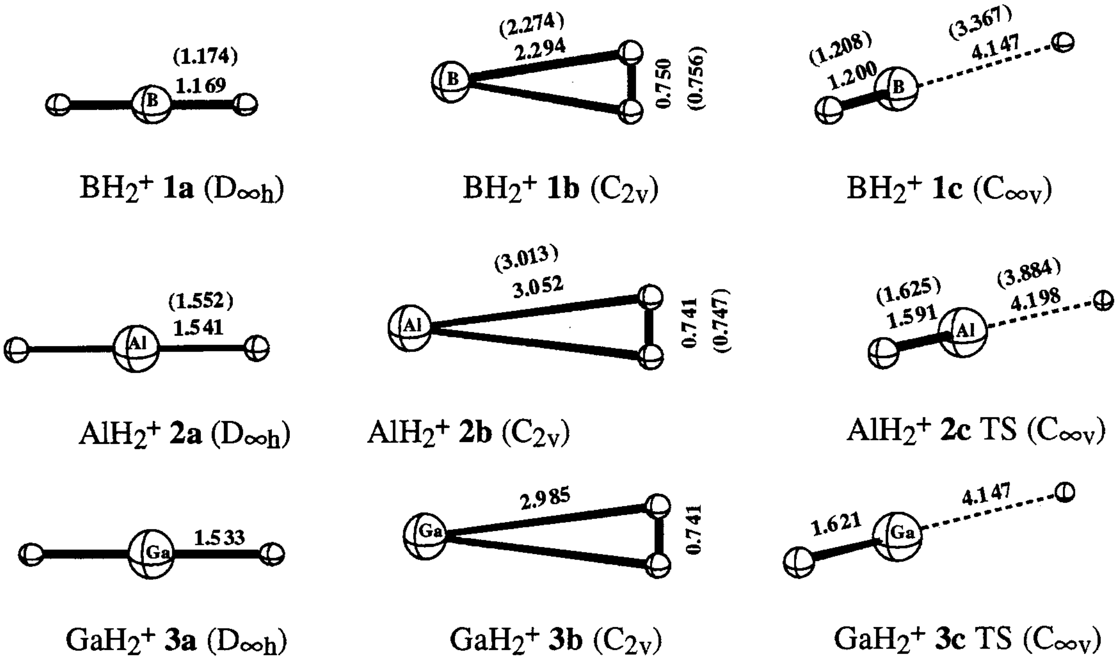

Figure 1. MP2/6-311++G(3df,2pd) optimized structures of **1**−**3**.

TABLE 2: ΔH_0 of Dehydrogenation (in kcal/mol)[a]

reaction	ΔH_0
BH_2^+ **1b** → $B^+ + H_2$	+3.1
AlH_2^+ **2b** → $Al^+ + H_2$	+0.8
GaH_2^+ **3b** → $Ga^+ + H_2$	[+1.0][b]

[a] Based on CCSD(T)/cc-pVTZ//CCSD(T)/cc-pVTZ+ ZPE. [b] Value based on MP2/6-311++G(3df,2pd)//MP2/6-311++G(3df,2pd) + ZPE is given in square brackets.

considered as a three-center four-electron (3c-4e) bond as there are four electrons involved including the boron lone pair. However, such bonding involving two hydrogen atoms and silicon is highly unlikely.[9] The 3c-2e B−H bond distance in **1b**, calculated at the CCSD(T)/cc-pVTZ level, is 2.274 Å. This is expectedly longer than that of two-center two-electron (2c-2e) B−H bond of **1a** (1.174 Å).

We have located transition structures **1c** (Figure 1), for the deprotonation process in **1a** which lies 108.9 kcal/mol higher in energy (Table 2). Thus, **1a** has a very high kinetic barrier for deprotonation and the deprotonation process is also highly endothermic by 106.4 kcal/mol. The transition state **1c** was also checked by IRC (intrinsic reaction coordinate) calculations at the MP2/6-311++G(3df,2pd) level.[8]

AlH_2^+. Similar to BH_2^+, $D_{\infty h}$ structure **2a** and C_{2v} structure **2b** were found to be minima on the PES of singlet AlH_2^+ (Figure 1). However, unlike BH_2^+, the structure **2a** is even 10.9 kcal/mol less stable than **2b** at the MP2/6-311++G(3df,2pd) level (Table 1). The difference becomes 13.1 kcal/mol at our highest level of theory, i.e., at the CCSD(T)/cc-pVTZ//QCISD (T)/6-311G** + ZPE level. Thus, the structure **2b** is the global minimum on the PES of singlet AlH_2^+. AlH_2^+ is isoelectronic with SiH_2^{2+}. Similar $D_{\infty h}$ structure of the singlet SiH_2^{2+} was also calculated for AlH_2^+ and was found to be significantly less stable than the C_{2v} form by 14.7 kcal/mol at the DFT B3LYP/6-311++G(3df,2pd)//B3LYP/6-311++G(3df,2pd) level.[5] Structure **2b** contains a 3c-2e bond and can be considered as a complex between Al^+ and a hydrogen molecule. Dissociation of **2b** into AlH and H^+ was calculated to be also highly endothermic by 210.2 kcal/mol (Table 1). Transition structure, **2c** (Figure 1), for the deprotonation process in **2a** was also located. Structure **2c** lies 71.0 kcal/mol higher in energy than structure **2a**. Thus, the deprotonation process in **2a** through transition state **2c** has a very high kinetic barrier.

GaH_2^+. Similar to BH_2^+ and AlH_2^+, $D_{\infty h}$ structure **3a** and C_{2v} structure **3b** (Figure 1) were found to be minima on the PES of GaH_2^+ at the MP2/6-311++G(3df,2pd) level. The structure **3b**, with a 3c-2e bond, is 21.6 kcal/mol more stable than **3a** (Table 1). Dissociation energies of **3b** are listed in Table 1. Transition states **3c** for deprotonation of **3a** was calculated, and the parameters are given in Figure 1.

Thus, in the higher analogues of XH_2^+ (X = B, Al, and Ga) the 3c-2e bonded C_{2v} structures are increasingly more favorable than the corresponding linear $D_{\infty h}$ structures. A similar trend was also found in the series XH_3^+ (X = B, Al, and Ga)[10] and XH_3^+ (X = C, Si, Ge, Sn, and Pb).[11] The bent structures can be considered as donor−acceptor complexes of H_2 and X^+ (X = B, Al, and Ga). The nature of the interaction between donor and acceptor of the complexes depends on the relative electron-transfer ability of the σ_{H-H} to the empty p orbital at X. Therefore, the stability of the bent structures depend on the size as well as electronegativity of the X. Localization of lone pair of electrons thus readily takes place at the heavier atoms (inert pair effect).[12]

The relative hydride affinities of the most stable isomers **1a** and **2b** (CCSD(T)/cc-pVTZ//CCSD(T)/cc-pVTZ + ZPE level) and **3b** (MP2/6-311++G(3df,2pd)//MP2/6-311++G(3df,2pd) + ZPE) were calculated using the isodesmic reaction (eq 1). For cations **1a**, the reaction is exothermic by 205.1 kcal/mol. On the other hand, for cations **2b** and **3b** the reactions are significantly less exothermic by 127.8 and 128.2 kcal/mol, respectively, compared to the reaction of **1a**. In comparison, for methyl cation CH_3^+ a similar reaction (eq 2) is much more exothermic by 240.9 kcal/mol (CCSD(T)/cc-pVTZ//CCSD(T)/cc-pVTZ + ZPE level). Such unexpected behavior can now be rationalized based on electronegative character of boron compared to carbon (Pauling electronegativity: B, 2.0; C, 2.5). These calculational results are in agreement with the reported experimental gas-phase reactions of BH_2^+ with simple hydrocarbons which showed that in contrast to the reactive methyl cation, the exothermicity of the reactions of BH_2^+ are moderate.[2]

$$\begin{array}{ccc} XH_2^+ + BH_4^- & \rightarrow & XH_3 + BH_3 \\ X = B, \mathbf{1a}; Al, \mathbf{2b}; Ga, \mathbf{3b} & & X = B, Al, Ga \end{array} \quad (1)$$

$$CH_3^+ + BH_4^- \rightarrow CH_4 + BH_3 \quad (2)$$

The relative stabilities of XH_2^+ (X = B, Al, and Ga) cations toward dissociation into X^+ and H_2 were also calculated and listed in Table 2. Our attempts to locate the transition states for these dissociations were not successful. The dissociation of boron complex is unfavored by 3.1 kcal/mol. On the other hand, dissociation of aluminum and gallium complexes are unfavored by only 0.8 and 1.0 kcal/mol, respectively.

Conclusions

The isomers of singlet XH_2^+ (X = B, Al, and Ga) cations were calculated by using the ab initio method at the MP2/6-311++G(3df,2pd) and CCSD(T)/cc-pVTZ levels. Studies show that although the linear $D_{\infty h}$ structure **1a** is the global minimum for BH_2^+, the global minima of AlH_2^+ and GaH_2^+ are not of $D_{\infty h}$ symmetry **2a** and **3a**, respectively, but of C_{2v} symmetry **2b** and **3b** with a 3c-2e bond. The $D_{\infty h}$ symmetric **2a** and **3a** are significantly less stable than **2b** and **3b** by 13.1 and 21.5 kcal/mol, respectively. However, the dissociation of **2b** and **3b** into $Al^+ + H_2$ and Ga^+ and H_2 are unfavored by only 0.8 and 1.0 kcal/mol, respectively. The relative hydride affinities of the cations **1a**, **2b**, and **3b** were also calculated.

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