DOI: 10.1002/chem.200701254

Strong Dissimilarities Between the Gas-Phase Acidities of Saturated and α,β-Unsaturated Boranes and the Corresponding Alanes and Gallanes

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Abstract: The effect that unsaturation has on the intrinsic acidity of boranes, alanes, and gallanes, was analyzed by B3LYP and CCSD(T)/6–311+G(3df,2p) calculations on methyl-, ethyl-, vinyl-, and ethynylboranes, -alanes and -gallanes, and on the corresponding hydrides XH_3. Quite unexpectedly, methylborane, which behaves as a carbon acid, is predicted to have an intrinsic acidity almost 200 kJ mol^{-1} stronger than BH_3, reflecting the large reinforcement of the C−B bond, which upon deprotonation becomes a double bond through the donation of the lone pair created on the carbon atom into the empty p orbital of the boron. Also unexpectedly, and for the same reason, the saturated and α,β-unsaturated boranes are much stronger acids than the corresponding hydrocarbons, in spite of being carbon acids as well. The Al derivatives also behave as carbon acids, but in this case the most favorable deprotonation process occurs at C_β, leading to the formation of rather stable three-membered rings, again through the donation of the C_β lone pair into the empty p orbital of Al. For Ga-containing compounds the deprotonation of the GaH_2 group is the most favorable process. Therefore only Ga derivatives behave similarly to the analogues of Groups 14, 15, and 16 of the periodic table, and the saturated derivatives exhibit a weaker acidity than the unsaturated ones. Within Group 13, boranes are stronger acids than alanes and gallanes. For ethyl and vinyl derivatives, alanes are stronger acids than gallanes. We have shown, for the first time, that acidity enhancement for primary heterocompounds is not only dictated by the position of the heteroatom in the periodic table and the nature of the substituent, but also by the bonding rearrangements triggered by the deprotonation of the neutral acid.

Keywords: ab initio calculations • acidity • alanes • boranes • gallanes • gas-phase reactions

Introduction

Since the discovery in 1989 of the dramatic increase of acidity of ethynol relative to the corresponding saturated derivative, ethanol, reported by Radom et al.[1] through the use of theoretical calculations, similar gas-phase acidity enhancements have been reported for a large set of *α*,*β*-unsaturated heterocompounds, on both experimental (Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometry) and theoretical grounds. The sets investigated included amines, phosphines,[2] arsines,[3] silanes, germanes, stannanes,[4] thiols, selenols, and tellurols.[5] Theoretical calculations also predicted unsaturated stibines to exhibit the same behavior.[5] It has also been demonstrated that the acidity of heterocompounds bearing the same substituent depends mainly on the nature of the unsaturated group and on the heteroatom. Accordingly, good linear correlations were found between the gas-phase acidities of homologous compounds of Groups 14, 15, and 16.[5] However, these results, which only concern the heteroatoms of Groups 14–16, are not sufficient to conclude safely that the aforementioned increase in acidity is a general rule for any α,β-unsaturated derivatives of a divalent (or more) heteroatom of the periodic table, because these sets only include heteroatoms of the carbon group or groups to the right of carbon. The aim of this paper is to extend the study of intrinsic acidities to derivatives in which the heteroatoms belong to Group 13 of the periodic table.

Among organoborane compounds, special attention was devoted to borirene $(CH)_2BH$,[6,7] which can be considered

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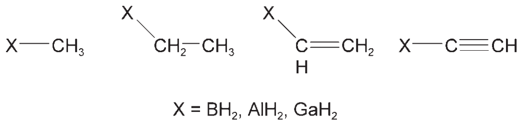
the smallest aromatic molecule. This molecule was detected and identified, together with ethynylborane and borallene ($HBCCH_2$), by reactions of laser-ablated boron atoms with ethylene and ethane.[8] Other small organoborane species, such as CH_3BH, HCBH, H_2CBH, H_2CBH_2, and HBCBH, were also generated by pulsed-laser evaporated boron atom reactions with methane.[9] Systematic theoretical investigations on BC_2H_2, BC_2H_4, and BC_2H_5 species, including vinylborane, have been also reported by different groups.[10–15] However, the information on anionic species is very scarce. The properties of $[H_2BC{=}CH_2]^-$ and the rearrangements of $[BH_2C{\equiv}C]^-$ have been described in two different theoretical papers.[16,17] Particular attention was also paid to AlC_2H_2 and AlC_2H_4 complexes,[10,11,18–24] but the information on similar Ga derivatives is much more scarce[25,26] and, to the best of our knowledge, almost completely absent for the corresponding anions.[17]

Boranes, alanes, and gallanes are usually considered as hydrides in the condensed phase, but the development of gas-phase ion chemistry in the last three decades of the twentieth century has led to a significant change in our view of chemical reactivity. The absence of solute–solvent and counterion interactions revealed the existence of reactivity trends very different from those usually accepted and obtained in condensed media. Thus, similarly to what was found for the hydrides of Groups 14, 15, and 16, the acidities of which follow the trends:[27] $CH_4 < SiH_4 < GeH_4$; $NH_3 < PH_3 < AsH_3$; $H_2O < SH_2 < SeH_2$, in a recent paper,[28] it was found by means of high-level theoretical calculations, that AlH_3 and GaH_3 were more acidic in the gas phase than BH_3 or the corresponding alkane (CH_4). Surprisingly, however, the experimental gas-phase acidity of borane (BH_3) is slightly stronger than that of methane,[27] even though B is to the left of C in the periodic table. In the light of these results, one would expect that for alkylboranes, alkylalanes, or alkylgallanes the most acidic hydrogen atoms should be those linked to the heteroatom. However, as shown in this paper, this is only the case when dealing with Ga derivatives.

Not surprisingly, in saturated and α,β-unsaturated derivatives containing substituent groups from columns 14, 15, and 16 in the periodic table, deprotonation takes place preferentially at the heteroatom, which is better prepared to accommodate an excessive electron density. However, the situation may be different when dealing with compounds from Group 13, which have an ns^2np^1 configuration, and behave as electron-deficient systems. As for compounds from Groups 14, 15, and 16, the proton can be lost from the heteroatom, but if the deprotonation takes place at one of the carbon atoms, the lone pair so created can be donated into the empty p orbital of the heteroatom, X, forming a new C−X bond or reinforcing an already existing C−X bond. Therefore, in organic compounds containing Group 13 heteroatoms, a critical competition between how effectively this new dative bond stabilizes the anion, and the natural tendency of the systems to lose the proton from the heteroatom,[28] comes into play. We show, through a theoretical study of the gas-phase acidity of methyl-, ethyl-, vinyl-, and ethynylboranes, -alanes, and -gallanes (Scheme 1), that in fact there is no straightforward answer to the question of which of the two effects dominates, since the behavior of the system upon deprotonation depends on the nature of the heteroatom (X = B, Al, Ga).



Scheme 1.

Computational Methods

The theoretical treatment of the various systems under study was performed by using the Gaussian-03 suite of programs.[29] In the first step, we optimized the geometries of all the different conformers of both neutral and anionic species, considering deprotonation from any possible position to yield all possible isomers. These calculations were performed at the B3LYP/6-31+G(d,p) level, which usually yields accurate geometries, while being not too computationally demanding. To obtain reliable energies, single-point calculations at higher levels were carried out, in a second step, for the most stable structures. These high-level calculations were performed by using two different approaches: the already mentioned B3LYP hybrid functional, and the coupled cluster CCSD(T) method that includes single and double excitations and perturbative triples. Both methods were used in association with two different basis set expansions: 6–311+G(3df,2p), and aug-cc-pVTZ.

Harmonic vibrational frequencies were obtained at the B3LYP/6-31+G(d,p) level in order to confirm that the structures found corresponded to local minima of the potential-energy surface and to evaluate the zero-point energy (ZPE) and other thermal corrections.

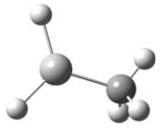
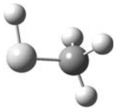
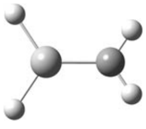
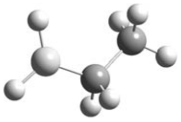
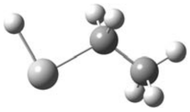
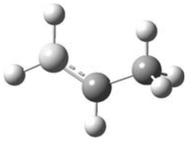
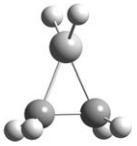
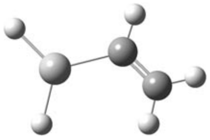
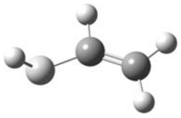
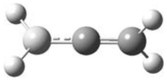
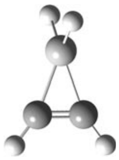
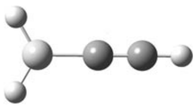
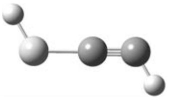
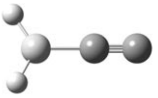
To gain some insight into the electronic structure and into the bonding of the systems under investigation we also used the Atoms-In-Molecules (AIM) theory[30] to analyze the topology of the electron density. For this purpose we evaluated the electron density at the different bond critical points (bcp) which would help us to understand the changes occurring on going from the neutral to the anionic compounds.

Results and Discussion

Structural effects of deprotonation and relative stability: In Table 1 we have summarized the relative stability of the different anions that can be formed by deprotonation of saturated and α,β-unsaturated derivatives containing B, Al, and Ga as heteroatoms. In this table, only the most stable conformer in each case is reported. The structures of all the conformers investigated are schematized in the Supporting Information. The first conspicuous fact is that the most stable anion dramatically depends on the nature of the heteroatom, and is different for B, Al, and Ga.

As far as the methyl derivatives are concerned, the carbon deprotonation is strongly favored compared to deprotonation at the heteroatom in the case of the boron derivative, while for Al both processes involve essentially the same amount of energy. Conversely, for the Ga derivative, deprotonation of the GaH_2 group is clearly favored.

Table 1. B3LYP/6–31+G(d,p) relative stabilities in terms of ΔG [kJ mol^{-1}], for the most stable conformers obtained by deprotonation at the heteroatom, at C_α or at C_β, of $R{-}XH_2$ (X = B, Al, Ga) derivatives.

	Deprotonation site	Structure	ΔG		
			X = B	X = Al	X = Ga
R = methyl	neutral				
	X		236	0	0
	C_α		0	2	20
R = ethyl	neutral				
	X		224	27	0
	C_α		0	33	18
	C_β		13	0	13
R = vinyl	neutral				
	X		192	12	0
	C_α		0	27	23
	C_β		136	0	50
R = ethynyl	neutral				
	X		139	3	0
	C_β		0	0	28

For the ethyl and vinyl boron derivatives, deprotonation occurs preferentially at C_α, while for the corresponding Al derivatives, C_β deprotonation is clearly favored, leading to the cyclization of the anion. Fascinatingly, gallium compounds exhibit completely different behavior from the two previous elements of its group, since in this case deprotonation from the heteroatom gives rise to the most stable anion.

These dissimilarities also appear as far as the deprotonation of the ethynyl derivatives is concerned. As shown in Table 1, deprotonation at C_β is strongly favored for the boron derivative, but only weakly for the Al-containing compound, whereas the gallium derivative loses the proton from the GaH_2 group.

These strong dissimilarities may be explained in terms of the electron-density redistribution undergone by the system upon deprotonation. Let us consider the boron compounds in the first place. C_α deprotonation is strongly favored by the formation of a double bond between B and C_α, through a donation of the carbon lone pair created in the deprotonation process into the empty p orbital of B. Consistently, for the methyl, ethyl, and vinyl derivatives there is a remarkable shortening of the C−B bond and a concomitant increase of the electron density of the corresponding bond critical point (bcp) on going from the neutral species to the corresponding anion (see Table 2). The aforementioned dative bond from C_α towards the boron atom enhances the electronegativity of the former, which, according to the bond activation–reinforcement (BAR) rule,[31] results in a slight shortening of the C−C bond in both ethyl and vinyl derivatives (see Table 2).

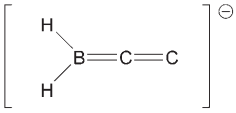
For the ethynyl derivative, C_β deprotonation is much more favorable than B deprotonation (note that C_α deprotonation is not possible in this case), leading to an anion with a significant contribution from the allene-type structure shown in Scheme 2, as suggested previously in the literature.[16] Accordingly, the C−C bond lengthens, and its bcp electron density decreases, while the C−B bond shortens and the electron density at the bcp increases (see Table 2).

When deprotonation occurs at C_β, a three-membered ring structure is formed. As mentioned previously, boron is an electron-deficient system and therefore behaves as a very good electrophilic centre able to accommodate the lone pair

Table 2. Bond lengths [Å] and electron densities at the bond critical points [a.u., within parentheses] for the most stable anions, obtained by deprotonation of R−XH$_2$ (X = B, Al, Ga) derivatives.

R	Bond	Neutral	Anions (Deprotonation site)		
			X[a]	C_α	C_β
boron compounds					
CH_3	C−B	1.559 (0.193)	1.613 (0.167)	1.465 (0.209)	
CH_3−CH_2	C−B	1.560 (0.195)	1.607 (0.165)	1.461 (0.210)	1.621 (0.145)
	C−C	1.537 (0.236)	1.551 (0.231)	1.518 (0.243)	1.539 (0.223)
CH_2=CH	C−B	1.542 (0.195)	1.504 (0.193)	1.429 (0.209)	1.617 (0.138)
	C−C	1.350 (0.341)	1.376 (0.336)	1.329 (0.346)	1.323 (0.342)
CH≡C	C−B	1.505 (0.188)	1.413 (0.213)		1.473 (0.200)
	C−C	1.220 (0.402)	1.305 (0.360)		1.266 (0.392)
aluminum compounds					
CH_3	C−Al	1.966 (0.087)	2.082 (0.069)	1.853 (0.097)	
CH_3−CH_2	C−Al	1.974 (0.087)	2.085 (0.070)	1.857 (0.097)	2.002 (0.070)
	C−C	1.541 (0.231)	1.540 (0.234)	1.519 (0.246)	1.566 (0.216)
CH_2=CH	C−Al	1.951 (0.088)	2.068 (0.069)	1.834 (0.094)	1.959 (0.070)
	C−C	1.348 (0.339)	1.350 (0.337)	1.328 (0.349)	1.354 (0.330)
CH≡C	C−Al	1.913 (0.083)	2.045 (0.062)		1.852 (0.093)
	C−C	1.222 (0.402)	1.234 (0.393)		1.266 (0.394)
gallium compounds					
CH_3	C−Ga	1.957 (0.119)	2.074 (0.094)	1.846 (0.137)	
CH_3−CH_2	C−Ga	1.963 (0.119)	2.067 (0.085)	1.845 (0.137)	2.012 (0.094)
	C−C	1.535 (0.236)	1.531 (0.237)	1.511 (0.245)	1.552 (0.230)
CH_2=CH	C−Ga	1.934 (0.123)	2.029 (0.099)	1.829 (0.135)	1.991 (0.095)
	C−C	1.344 (0.343)	1.348 (0.336)	1.324 (0.350)	1.346 (0.337)
CH≡C	C−Ga	1.906 (0.115)	2.055 (0.083)		1.855 (0.127)
	C−C	1.218 (0.403)	1.232 (0.394)		1.262 (0.393)

[a] X = B, Al, or Ga.



Scheme 2.

created on the C_β carbon atom after deprotonation, which behaves accordingly as a good nucleophilic centre. The interaction between both centers leads to the cyclization of the molecule through the formation of a new C−B covalent bond (see Figure 1). However, this three-membered ring is less stable than its doubly-bonded counterpart produced upon C_α deprotonation. The situation is similar to that of propene and cyclopropane, the enthalpies of formation of which clearly show that the latter is less stable than the former, due to ring strain.[32–34]

If we move now to the aluminum series, a different situation arises. As indicated above, deprotonation takes place preferentially at the C_β position due to two concomitant effects. On the one hand, the tendency to form multiple bonds is smaller for second-row elements than for first-row elements, as has been discussed previously in the literature.[23,24] On the other hand, the stabilities of three-membered cycles containing Al are larger, in relative terms, than those containing B, because of a more efficient interaction of the radial p orbitals of Al with the C orbitals in the corresponding a_1 bonding molecular orbitals (MOs) (see Scheme 3). Both effects make C_β deprotonation for Al derivatives energetically more favorable than C_α deprotonation.

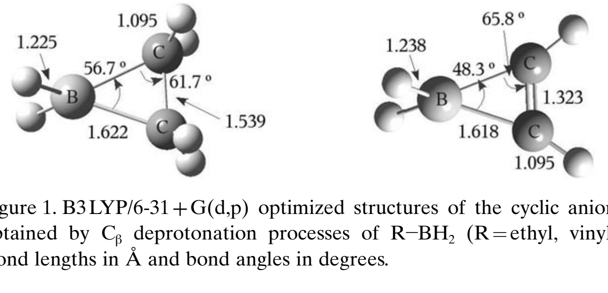
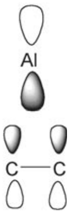


Figure 1. B3LYP/6-31+G(d,p) optimized structures of the cyclic anions obtained by C_β deprotonation processes of R−BH$_2$ (R = ethyl, vinyl). Bond lengths in Å and bond angles in degrees.

For gallium compounds one would expect behavior rather similar to that observed for aluminum, in the sense that cyclic structures produced by C_β deprotonation should be more stable than the structures with a formal C=Ga double bond obtained by C_α deprotonation. However, for this heteroatom, the deprotonation of GaH$_2$ is systematically the most favorable process, in spite of the fact that Ga-containing three-membered rings are not very different from Al-containing ones (see Figure 2). Since the apparent relatively smaller stability of these cyclic structures does not correspond to geometrical features, we must invoke other factors to explain why the deprotonation of the GaH$_2$ group becomes the most favorable process. This seems to indicate a non-negligible role of the electronegativity of the heteroatom, as we shall show in the subsequent sections.



Scheme 3.

Acidity trends: To investigate the influence of the intrinsic properties of the heteroatom on the acidity of these compounds it would be convenient to investigate the behavior of systems in which the connectivity of the heteroatom cannot change, either by changing a single bond to a double bond, or by forming a new bond. The best candidates for this purpose would be the corresponding hydrides, XH$_3$ (X = B, Al, Ga), which fulfill this condition. Furthermore, the systems we are dealing with can be regarded as derivatives of these hydrides. At the same time, we considered it advisable to compare the acidities of these three systems with that of methane, the simplest carbon hydride, since in

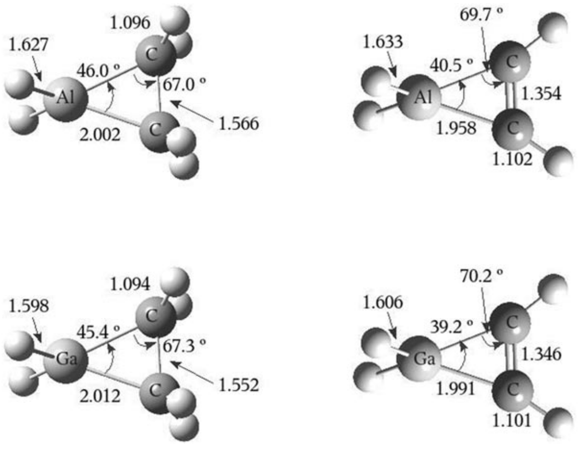


Figure 2. B3LYP/6-31+G(d,p) optimized structures of the cyclic anions obtained by C_{β} deprotonation processes of R−XH_2 (X=Al, Ga; R=ethyl, vinyl). Bond lengths in Å and bond angles in degrees.

the organic derivatives under investigation in this paper sometimes a competition between deprotonation at X or at carbon is predicted. Only the gas-phase acidity of CH_4 is experimentally known (see Table 3), but, as expected, previous high-level ab initio and DFT calculations, in agreement with our estimates, indicate[28] that BH_3 is significantly less acidic than both AlH_3 and GaH_3, while GaH_3 is a slightly stronger acid than AlH_3. However, taking into account that along the first row the hydride acidity increases with electronegativity ($CH_4 < NH_3 < H_2O < FH$) it would be reasonable to expect BH_3 to be less acidic than CH_4, which is not the case. In this respect, it is worth mentioning that acidity trends in a large series of hydrides have been analyzed in terms of the electron reorganization energy[28] defined as the energy required to create an A^-H^+ pair of ions, without having to pay the enthalpy price for separating them. However, although the correlation between the electron reorganization energy so defined and the electronegativity of A is very good for a large series of hydrides, those of CH_4, BH_3, and AlH_3 deviate significantly.[28]

Table 3. Theoretical and experimental acidity enthalpies (ΔH_{acid}) and free energies (ΔG_{acid}) of XH_3 (B, Al, Ga) and CH_4. Values in kJ mol^{-1}.

	CCSD(T)				Literature
	aug-cc-pVTZ		6-311+G(3df,2p)		
Molecule	ΔH_{acid}	ΔG_{acid}	ΔH_{acid}	ΔG_{acid}	ΔH_{acid}
CH_4	1743	1709	1748	1714	1744 ± 3[b]
BH_3[a]	1724	1689	1725	1690	1720[c]
AlH_3	1556	1522	1559	1525	1561.5[d] 1553.9[c]
GaH_3	1555	1524	1536	1505	1536.4[c]

[a] To estimate the acidity values we considered the triplet electronic state of BH_2^-, which lies lower in energy than the singlet state. [b] Experimental values taken from reference [27]. [c] G3(MP2) calculated values taken from reference [28]. [d] B3LYP/aug-cc-pVTZ calculated value taken from reference [35].

To understand these findings we evaluated the intrinsic acidities of these hydrides with a reasonably high accuracy, through CCSD(T)/aug-cc-pVTZ and CCSD(T)/6–311+G-(3df,2p) calculations. The values so obtained, independently of the basis set used, are in fairly good agreement with the experimental values or with previous theoretical estimates,[28,35] the only exception being the CCSD(T)/aug-cc-pVTZ value for GaH_3 which is too high with respect to the previous G3(MP2) reported value,[28] which in contrast is in very good agreement with our CCSD(T)/6–311+G(3df,2p) estimate. In what follows we always refer to the CCSD(T)/6–311+G(3df,2p) results in our discussion.

The apparent contradiction between the acidity trends and the electronegativity trends can be understood assuming that the deprotonation reaction can be considered as a two-step process defining the thermodynamic cycle shown in Figure 3, which has been widely used in the literature to answer similar questions.[36–40] The first step corresponds to the homolytic cleavage of the X−H bond, and the second one to the formation of the corresponding ion pair by an electron transfer from the hydrogen atom towards the XH_{n-1} fragment. This second step is characterized energetically by the ionization energy of hydrogen (IE(H)) and the electron affinity of the XH_{n-1} moiety (EA(XH_{n-1})).

$$\begin{tikzcd}
XH_n \arrow[r, "\Delta H(X\text{-}H)"] \arrow[dr, "\Delta H_{acid}"'] & XH^{\bullet}_{n-1} + H^{\bullet} \arrow[d, "EA(XH_{n-1}) + IE(H)"] \\
& XH^{\ominus}_{n-1} + H^{\oplus}
\end{tikzcd}$$

Figure 3. Thermodynamic cycle decomposing the deprotonation of XH_n species into a two-step process involving a homolytic cleavage of the X−H bond and an electron transfer from hydrogen to the remaining fragment.

Taking into account that IE(H) is a constant in the process, the acidities of the XH_n compounds depend exclusively on two factors: the strength of the X−H linkage, and the electron affinity of the radical produced by the X−H bond cleavage. The calculated values obtained for the homolytic dissociation of the X−H bonds as well as for the electron affinities of the XH_{n-1} systems are summarized in Table 4. It can be observed that, as expected, the acidity gaps between the four compounds under investigation are essentially equal to the differences between the ΔH(X−H) and EA-

Table 4. Acidity enthalpies (ΔH_{acid}), X−H bond dissociation enthalpies, and XH_{n-1} electron affinities (EA) calculated at the CCSD(T)/6–311+G(3df,2p) level. All values are in kJ mol^{-1}.

	ΔH(X−H)	EA(XH_{n-1})	ΔH(X−H) + EA(X)	ΔH_{acid}
CH_4	429	-6	435	1748
BH_3	431	19	413	1725
AlH_3	346	100	246	1559
GaH_3	327	103	224	1536

(XH_{n-1}) terms, demonstrating the consistency of our calculations.

More importantly, our results, in agreement with previous theoretical estimates,[41,42] indicate that in methane and borane the X–H bond dissociation energies are rather similar, and therefore the difference in their acidities essentially reflects the fact that the $BH_2^{\bullet}$ radical has a much higher electron affinity than the $CH_3^{\bullet}$ radical. When we move to the aluminum and gallium hydrides there is a great acidity enhancement due to two concomitant factors: a great increase of the electron affinity of the $AlH_2^{\bullet}$ and $GaH_2^{\bullet}$ radicals, which shows the ability of second- and third-row atoms to accommodate excessive electron density, and a decrease of the X–H bond dissociation energy. Hence, the main conclusion is that the acidities of the hydrides of the three first elements of Group 13 of the periodic table are stronger than that of methane, even though carbon is more electronegative than B, Al, and Ga.

From the acidity values in Table 4, it would be logical to expect that the RXH_2 organic derivatives of B, Al, and Ga should lose the proton from the XH_2 (X = B, Al, Ga) group rather than from the carbon. Nonetheless, this is not the case when X = B or Al, since, as we have shown above, B and Al derivatives behave as carbon acids because the electron-deficient nature of these heteroatoms favors the formation of double bonds or of new bonds between the heteroatom and the deprotonated carbon atom. Consequently, it is this factor, and only this, which is responsible for the carbon deprotonation for those compounds, whereas gallium analogues follow the natural trend dictated by the intrinsic electronegativity of the heteroatom and the strength of the X–H bonds.

One of the most important consequences of this is the large acidity enhancement on going from the boron hydride to its organic derivatives (see Table 5). However, even more important is the fact that, although the organic derivatives behave as carbon acids, their acidities are much stronger than those of the corresponding purely organic analogues. For instance, the acidity of methylborane is 1519 kJ mol^{-1}, whereas the acidity of ethane is much weaker, 1758 kJ mol^{-1}.[4] The same occurs if one compares vinylborane ($\Delta H_{acid} = 1524$ kJ mol^{-1}) and propene ($\Delta H_{acid} =$ 1623 kJ mol^{-1}[4]). This reflects the extent of the stabilization produced by the formation of the $C_{\alpha}{=}B$ double bond after deprotonation. There is at least one experimental indication that our conclusion is correct: trimethylboron is a much stronger acid ($\Delta H_{acid} = 1532 \pm 26$ kJ mol^{-1})[27] than any alkane.[43] As a matter of fact, the acidity of a methyl group in an alkane with a structure similar to trimethylboron [2,2-dimethyl-propane] is significantly weaker ($\Delta H_{acid} =$ 1711 kJ mol^{-1}) than that of Me_3B. Furthermore, the acidity predicted for trimethylboron using the theoretical scheme adopted in this work agrees with the experimental value within the error limits ($\Delta H_{acid} = 1552$ kJ mol^{-1}).

It is also interesting to note that the intrinsic acidities of Ga derivatives follow the trend dictated by the electronegativity of the organic moiety attached to the GaH_2 group, so the observed acidity trend is ethynyl > vinyl > ethyl > methyl. However, this trend is not observed for B and Al derivatives, which behave essentially as carbon acids. In fact, the vinyl derivatives are predicted to be slightly less acidic than the ethyl ones due to a slightly lower stability of the anion as a consequence of its allene-like structure, in the case of the B derivatives.

It is also worth noting the good agreement between B3LYP and CCSD(T) results. This indicates that the former method can be a reliable alternative for calculating acidities of systems of much larger size than those investigated here, and for which the CCSD(T) calculations can be prohibitively expensive.

As far as aluminum and gallium derivatives are concerned, it is observed that the variation in acidity from the hydrides to the organic derivatives is not as dramatic as for boron. This, again, shows the very different behavior of first-row elements compared to the remaining elements of the same group. On the one hand, AlH_3 and GaH_3 already have a much stronger acidity than BH_3, and on the other hand the stabilization of the system due to the formation of C=X double bonds is much lower for Al and Ga than for B.

These dissimilarities also have remarkable consequences as far as the acidity pattern within the group is concerned. With the exception of the hydride, boron derivatives are more acidic than the corresponding aluminum and gallium partners, reflecting the greater stability of the C=B double bonds. When Al and Ga derivatives are compared, one should expect the latter to be more acidic, since Ga is not only a third-row atom, but is also slightly more electronegative than Al. However, ethyl- and vinylalane are slightly more acidic than the Ga-containing analogues due to the enhanced stability of the Al cyclic anions.

Table 5. Acidity enthalpy (ΔH_{acid}) and acidity Gibb's free energy (ΔG_{acid}, within parentheses) for RXH_2 derivatives calculated using a 6–311+G(3df,2p) basis set. All values are in kJ mol^{-1}.

	CCSD(T) ΔH_{acid} (ΔG_{acid})			B3LYP ΔH_{acid} (ΔG_{acid})		
R	X = B	X = Al	X = Ga	X = B	X = Al	X = Ga
H	1725 (1690)	1559 (1525)	1536 (1505)	1725 (1690)	1563 (1529)	1530 (1499)
CH_3	1519 (1491)	1569 (1543)	1545 (1517)	1520 (1492)	1577 (1550)	1542 (1514)
CH_2CH_3	1511 (1484)	1524 (1498)	1540 (1509)	1513 (1483)	1530 (1505)	1539 (1508)
$CH{=}CH_2$	1524 (1493)	1529 (1501)	1534 (1502)	1518 (1488)	1539 (1511)	1534 (1502)
$C{\equiv}CH$	1524 (1492)	1535 (1501)	1515 (1481)	1520 (1490)	1532 (1499)	1519 (1483)

Conclusion

The high-level DFT and ab initio calculations presented here lead to the conclusion that, although carbon is more electronegative than boron, BH_3 is a slightly stronger acid than methane, reflecting the fact that the electron affinity of the $BH_2^{\bullet}$ radical is greater than that of the methyl radical. On going from BH_3 to AlH_3 and GaH_3 a large increase in acid strength occurs, because the X–H bonds becomes weaker and the electron affinities of the $AlH_2^{\bullet}$ and $GaH_2^{\bullet}$ radicals are much larger than that of BH_2.

Quite unexpectedly, however, for boron there is a dramatic increase of the acidity by methyl substitution, and methylborane is predicted to have an intrinsic acidity almost 200 $kJ\,mol^{-1}$ larger than BH_3, because it behaves as a carbon acid. Hence, this acidity enhancement reflects the large reinforcement of the C–B bond, which upon deprotonation becomes a double bond through the donation of the lone pair created on the carbon atom into the empty p orbital in boron. Also unexpectedly, and for the same reason, the saturated and α,β-unsaturated boranes are much stronger acids than the corresponding hydrocarbons, in spite of also being carbon acids.

Al derivatives also behave as carbon acids in the gas phase, although in this case the most favorable deprotonation process occurs at C_β, leading to the formation of rather stable three-membered rings, again through the donation of the C_β lone pair into the empty p orbital of Al. For Ga-containing compounds the deprotonation of the GaH_2 group is the most favorable process. Therefore only Ga derivatives behave similarly to the analogues of Groups 14, 15, and 16 of the periodic table, in the sense that deprotonation takes place at the heteroatom. The main consequence is that an acidity enhancement on going from the saturated to the unsaturated compounds, similar to that found for the analogues of Groups 14, 15 and 16, is observed only for Ga derivatives.

Within Group 13, boranes are stronger acids than alanes and gallanes, and for ethyl and vinyl derivatives alanes are stronger acids than gallanes, due to the cyclization of the anion formed upon deprotonation.

In spite of the unambiguous correlations observed for the derivatives with a heteroatom of Groups 14–16 of the periodic table,[5] the results presented here indicate, for the first time, that the increase of acidity for primary heterocompounds is not only dictated by the position of the heteroatom in a column of the periodic table and the nature of the substituent, because this property may strongly depend on bonding rearrangements triggered by the deprotonation of the neutral acid.

Acknowledgements

This work has been partially supported by the DGI Project No. CTQ2006-08558/BQU and by the Project MADRISOLAR of the Comunidad Autónoma de Madrid Ref.: S-0505/PPQ/0225. A generous allocation of computing time at the CCC of the UAM is also acknowledged. J.A.G. acknowledges a contract from the Comunidad Autónoma de Madrid. J.-C.G. thanks the CNES for financial support.

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Received: August 10, 2007