

α,β -Unsaturated and Saturated Derivatives of Be, Mg, and Ca: Are They Carbon or Metal Acids in the Gas Phase?

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Abstract: The gas-phase acidity of R–XH (R = H, CH₃, CH₂CH₃, CH=CH₂, C≡CH; X = Be, Mg, Ca) alkaline-earth-metal derivatives has been investigated through the use of high-level CCSD(T) calculations by using a 6-311+G(3df,2p) basis set. BeH₂ is a stronger acid than BH₃ and CH₄ for two concomitant reasons: 1) the dissociation energy of the Be–H bond is smaller than the dissociation energies of the B–H and C–H bonds, and 2) the electron affinity of BeH[•] is larger in absolute value than those of BH₂[•] and CH₃[•]. The acidity also increases on going from BeH₂ to MgH₂ due to these

two same factors. Quite importantly, despite the fact that the X–H bonds in the R–XH (X = Mg, Ca) derivatives exhibit the expected X^{δ+}–H^{δ-} polarity, they behave as metal acids in the gas phase and only Be derivatives behave as carbon acids in the gas phase. The ethylberyllium hydride exhibits an unexpected high acidity compared with the methyl derivative because deproto-

nation of the system is accompanied by a cyclization that stabilizes the anion. Similarly to that found for derivatives that contain heteroatoms from groups 14, 15, and 16, the unsaturated compounds are stronger acids than the saturated counterparts, with the only exception of the Ca–vinyl derivative. Most importantly, among ethyl, vinyl, and ethynyl derivatives containing a heteroatom of the main group of the Periodic Table, those containing Be, Mg, and Ca are among the strongest gas-phase acids.

Keywords: ab initio calculations • acidity • alkaline earth metals • density functional calculations • gas-phase properties

Introduction

Gas-phase ion chemistry can, in some ways, be considered to be a new chemistry because the “intrinsic” basicity of a given chemical compound is often masked by solvation. One of the obvious consequences of the absence of solvation interactions is that it contributes to a better understanding of the origin of substituent effects^[1–20] on the reactivity of many compounds; it was also possible to “design” com-

pounds with a given reactivity pattern by using an adequate selection of substituents or molecular motifs because the substituent effects would not be altered by solvent effects. This has been wisely exploited in the design of superacids and superbases.^[21–29] Another obvious consequence is that gas-phase reactivity trends are very often different from the trends observed in solution, in which these trends are very often dominated by the specific solvation of the reactants or the products, or both. In our group, we have devoted some effort to establishing and analyzing the acidity trends of heterocompounds. The main conclusions of these studies were that α,β -unsaturated amines, phosphines,^[30] arsines,^[31] stibines,^[32] silanes, germanes, stannanes,^[33] thiols, selenols, and telluroles^[32] exhibit enhanced acidity compared with the corresponding saturated derivatives. In addition, for derivatives that contain heteroatoms from groups 14–16, this acidity enhancement depends mainly on the nature of the unsaturated moiety and on the heteroatom, which is mirrored in the existence of good linear correlations between the gas-phase acidities of homologous compounds of these three groups.^[32] However, primary saturated and α,β -unsaturated boranes, alanes, and galanes, in which the heteroatoms belong to a group to the left of carbon, were predicted to have quite pe-

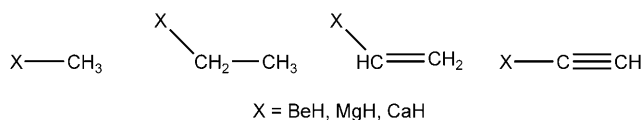
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cular behavior as acids in the gas phase.^[34] The first unexpected result is that methyl substitution increases the acidity of BH₃ by about 200 kJ mol⁻¹. Also unexpectedly, the saturated and α,β -unsaturated boranes are much stronger acids than the corresponding hydrocarbons, despite being carbon acids in the gas phase. Alanes also behave as carbon acids in the gas phase, but for Ga-containing compounds the deprotonation of the GaH₂ group is the most favorable process. This showed, for the first time, that acidity enhancement for primary heterocompounds is not only dictated by the nature of the substituent and the position of the heteroatom in the Periodic Table, but also by the bonding rearrangements triggered by the deprotonation of the neutral acid.^[34]

What changes can be expected when moving to the left in the Periodic Table? It is known,^[35] for instance, that BeH₂ and MgH₂ are stronger acids than methane, even though both metals are obviously less electronegative than carbon. However, it is not so obvious whether the corresponding alkyl, vinyl, or ethynyl derivatives will behave as carbon or metal acids. As expected, in saturated and α,β -unsaturated derivatives that contain substituents from groups 14, 15, and 16, deprotonation preferentially takes place at the heteroatom.^[30-33] The situation can be significantly different, however, if the heteroatom is Be, Mg, or Ca, the XH bonds of which present a X^{δ+}-H^{δ-} polarity. Herein, we aim to address these questions by investigating the acidities of the three hydrides BeH₂, MgH₂, and CaH₂, and also of the derivatives shown in Scheme 1, through the use of high-level density functional theory (DFT) and ab initio calculations.



Scheme 1.

Computational Details

The geometries of the neutral and deprotonated species included in this study were optimized at the B3LYP/6-311+G(d,p) level of theory. The use of this hybrid functional, which includes Becke's three-parameter nonlocal hybrid exchange potential^[36] with the nonlocal correlation functional of Lee, Yang, and Parr,^[37] together with flexible enough basis sets, has been proved to provide reliable geometries and vibrational frequencies. To obtain accurate calculated acidities, we have carried out single-point calculations on the B3LYP/6-311+G(d,p) optimized geometries by using a larger basis set expansion, namely 6-311+G(3df,2p), together with the CCSD(T) method, which includes single and double excitations and perturbative triples. Because this theoretical model can become prohibitively expensive when dealing with larger systems, we also carried out single-point calculations at the B3LYP/6-311+G(3df,2p) level, so that a comparison between CCSD(T) and B3LYP results can be used as a suitable assessment of the reliability of the latter. Unfortunately, this assessment cannot be carried out by comparing the calculated values with experimental values, which to the best of our knowledge are completely lacking. Only for some special cases, which will be discussed later on, were these CCSD(T) calculations also carried out on CCSD/6-311+G(d,p) optimized geometries. All these calculations have been performed by using the Gaussian 03 suite of programs.^[38]

Harmonic vibrational frequencies were obtained at the B3LYP/6-311+G(d,p) level to assess that the structures found correspond to local minima of the potential energy surface and to evaluate the zero point energy (ZPE) and other thermal corrections.

To offer a rationale on the acidity trends within a family of compounds, an analysis of the bonding of each neutral system and of the bonding perturbations triggered by its deprotonation process is unavoidable. This analysis will be carried out by means of atoms-in-molecules (AIM) theory,^[39] which is based on a topological survey of the electron density, and by means of the natural bond orbital (NBO) approach,^[40] which permits us to analyze the bonding in terms of localized hybrids and lone-pairs obtained as local block eigenvectors of the one-particle density matrix, and to measure the weight of different mesomeric forms through natural resonance theory (NRT). The Wiberg bond orders (BO) were also evaluated in the framework of this approach.

Results and Discussion

The gas-phase acidities of the compounds under investigation, defined as the enthalpy ($\Delta_{\text{acid}}H^0$) or the free energy ($\Delta_{\text{acid}}G^0$) of the reaction in Equation (1), are summarized in Table 1.



The total energies, thermal corrections, and entropy values are given in Table S1 of the Supporting Information.

Hydrides: Let us consider the hydrides first. The first important finding, already reported in the literature,^[35] is that the hydrides of the alkaline-earth elements are stronger acids than the hydrides of more electronegative elements, such as B and C. Our CCSD(T) results are slightly different than those reported previously in the literature, which were obtained at the G3(MP2) level, and predict BeH₂, MgH₂, and CaH₂ to be slightly less acidic.^[35] Thus, we decided to calculate the gas-phase acidity of these compounds at the G3 level. Our results are again slightly higher than those reported at the G3(MP2) level and in nice agreement with those obtained at the CCSD(T) level. It is also worth noting that for the three compounds, the B3LYP values are larger than the CCSD(T) and G3 values. We will come back to this point later.

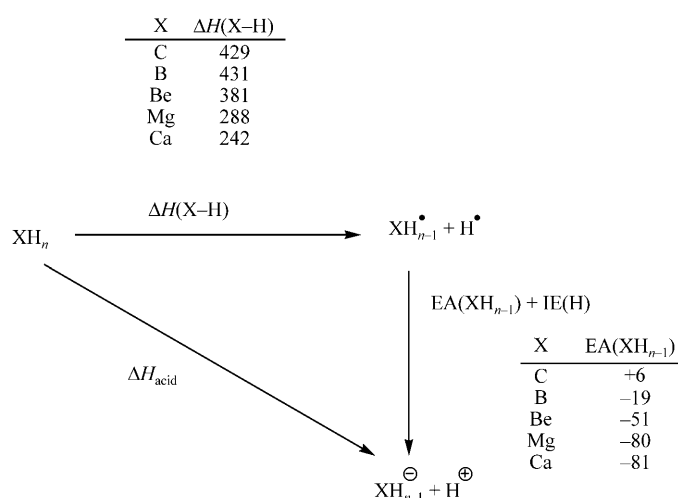
To offer a rationale for the origin of the enhanced acidity of BeH₂, MgH₂, and CaH₂ with respect to both BH₃ and CH₄, it is useful to consider the deprotonation reaction as a two-step process. The corresponding thermodynamic cycle (see Scheme 2) has been often used in the literature to analyze similar trends.^[41-45] In some senses this decomposition is similar to that of the triadic formula proposed by Maksić et al. to analyze intrinsic basicities and acidities.^[46,47]

From Scheme 2, it is obvious that only two thermodynamic magnitudes can be responsible for the differences in the intrinsic acidities, the energy associated with the homolytic cleavage of the X-H bond ($\Delta H(\text{X-H})$), and the electron affinity (EA) of the XH_{n-1}· fragment (EA(XH_{n-1})). It is apparent that the slightly higher acidity of BH₃ compared with CH₄ is exclusively due to the slightly higher EA of the BH₂· radical with respect to CH₃·. However, the origin of the en-

Table 1. Calculated gas-phase acidities, enthalpies ($\Delta_{\text{acid}}H$ [kJ mol⁻¹]), and Gibbs' free energies ($\Delta_{\text{acid}}G$ [kJ mol⁻¹]).^[a]

Compound	CCSD(T)/6-311 + (3df,2p)//B3LYP/6-311 + G(d,p)		B3LYP/6-311 + G(3df,2p)//B3LYP/6-311 + G(d,p)	
	$\Delta_{\text{acid}}H$	$\Delta_{\text{acid}}G$	$\Delta_{\text{acid}}H$	$\Delta_{\text{acid}}G$
BeH ₂	1642.2 (1642.9) ^[b]	1610.6 (1611.3) ^[b]	1660.2	1628.7
MgH ₂	1519.4 (1517.1) ^[b]	1488.5 (1486.5) ^[b]	1526.1	1495.2
CaH ₂	1477.8	1445.4	1490.5	1458.0
CH ₃ BeH	1620.6 (1619.3) ^[c]	1586.4	1618.6	1583.9
CH ₃ CH ₂ BeH	1577.0	1547.3	1576.6	1546.9
H ₂ C=CHBeH	1547.1	1518.1	1548.9	1519.9
HC≡CBeH	1542.3	1510.0	1541.5	1509.2
CH ₃ MgH	1512.3 (1516.5) ^[d]	1481.5	1521.2	1490.4
CH ₃ CH ₂ MgH	1508.5	1477.8	1518.3	1487.6
H ₂ C=CHMgH	1501.2	1470.2	1510.6	1479.6
HC≡CMgH	1488.1	1456.4	1496.0	1464.2
CH ₃ CaH	1454.5 (1458.4) ^[d]	1437.1	1472.6	1455.2
CH ₃ CH ₂ CaH	1450.7	1426.2	1471.8	1447.3
H ₂ C=CHCaH	1464.5	1436.4	1484.0	1455.9
HC≡CCaH	1450.0	1425.8	1468.6	1444.3

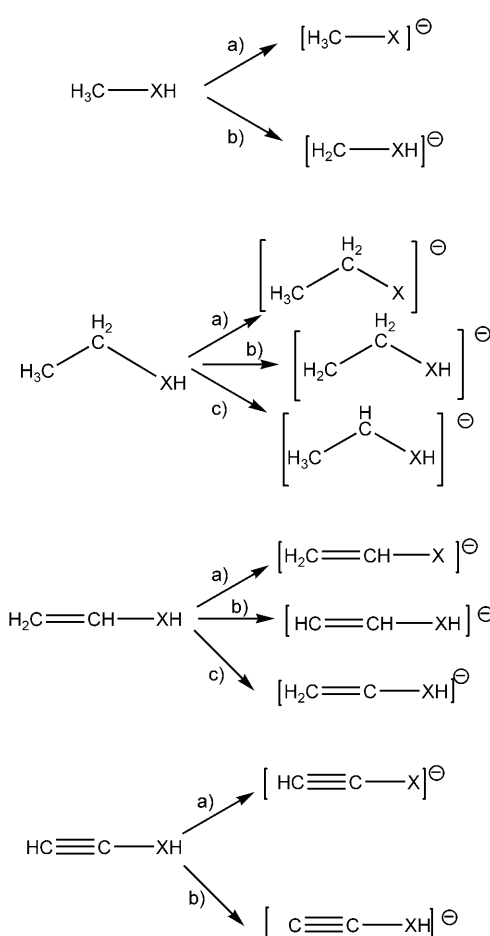
[a] Calculated at 298.2 K. [b] G3 calculated values. [c] Values calculated at the CCSD(T)/6-311 + (3df,2p)//CCSD(T)/6-311 + G(d,p) level. [d] Values calculated at the CCSD(T)/6-311 + (3df,2p)//CCSD(T)/6-311 + G(d,p) level.



Scheme 2. Thermodynamic cycle comparing the gas-phase acidities of CH₄, BH₃, BeH₂, MgH₂, and CaH₂. All values, calculated at the CCSD(T)/6-311 + G(3df,2p) level, are in kJ mol⁻¹.

hanced acidity of BeH₂ with respect to the hydrides that follow it in the Periodic Table, BH₃ and CH₄, is two-fold. On the one hand, the dissociation energy of the Be–H bond is smaller than the dissociation energies of the B–H and C–H bonds, and on the other hand, the EA of BeH₂ is larger in absolute value than those of BH₂[•] and CH₃[•]. The increase in acidity on going from BeH₂ to MgH₂ is again due to these two factors because, as shown in Scheme 2, the dissociation energy of the Mg–H bond is smaller than that of the Be–H bond, but at the same time, the EA of MgH is larger in absolute value than that of BeH. CaH₂ is predicted to be a slightly stronger acid than MgH₂, but in this case the acidity enhancement is almost exclusively due to the fact that the Ca–H bonds are weaker than the Mg–H ones.

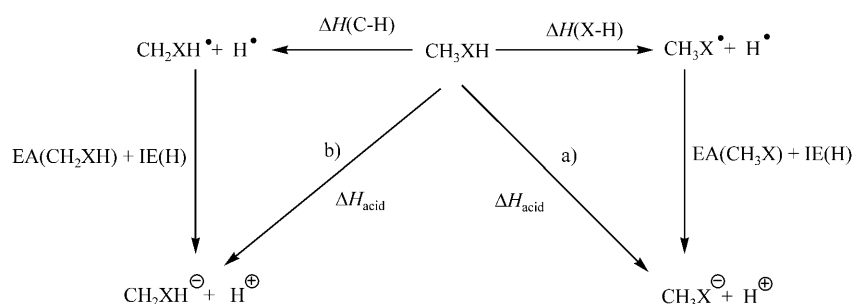
Alkyl, vinyl, and ethynyl derivatives: For alkyl, vinyl, and ethynyl derivatives, all possible deprotonation processes (shown in Scheme 3) have been investigated.



Scheme 3. Possible deprotonation routes for methyl-, ethyl-, vinyl-, and ethynyl-XH derivatives (X=Be, Mg, Ca).

The first unexpected result is that Be compounds behave differently to Mg and Ca derivatives. As shown by the values reported in Table S1 in the Supporting Information, for compounds that contain Mg and Ca, process a) is by far the most favorable one, that is, the most acidic site of the

system is the metal. Conversely, for Be derivatives the most favorable process is b), in which the proton is lost from the terminal carbon atom. To understand the origin of these dissimilarities, let us analyze in more detail the particular case of the methyl derivatives as a suitable and simple case. As mentioned above, the deprotonation process is essentially dictated by two kinds of thermodynamic magnitudes: bond dissociation energies and EAs. Indeed, as illustrated in Scheme 4, process a) involves the dissociation of an X–H bond and the EA of a $\text{CH}_3\text{X}^\bullet$ radical, whereas process b) depends on the dissociation of a C–H bond and the EA of a $\text{CH}_2\text{XH}^\bullet$ radical. The values for both processes for Be and Mg compounds are summarized in Table 2.



Scheme 4. Thermodynamic cycles for deprotonation processes a) and b).

Table 2. CCSD(T)/6-311+(3df,2p)//B3LYP/6-311+G(d,p) calculated values for the thermodynamic magnitudes involved in the two possible deprotonation processes of CH_3BeH and CH_3MgH , as shown in Scheme 4. All values are in kJ mol^{-1} .

X	$\Delta H(\text{X-H})$	$\Delta H(\text{C-H})$	$\text{EA}(\text{CH}_3\text{X}^\bullet)$	$\text{EA}(\text{CH}_2\text{XH}^\bullet)$	$\Delta_{\text{acid}}H^{[\text{a}]}$	$\Delta_{\text{acid}}H^{[\text{b}]}$
Be	384	394	-57	-100	1651	1618
Mg	281	398	-85	-57	1521	1666

[a] Values for deprotonation route a). [b] Values for deprotonation route b).

For the Be compound, the loss of the proton attached to the metal is favored by a bond dissociation enthalpy that is 10 kJ mol^{-1} smaller than the CH bond dissociation enthalpy, whereas the loss of the proton attached to the carbon is favored by the larger EA of the $\text{CH}_2\text{BeH}^\bullet$ radical (-100 kJ mol^{-1}) compared with $\text{CH}_3\text{Be}^\bullet$ radical (-57 kJ mol^{-1}). As a consequence, the second process (b) is favored over the first one (a) by 33 kJ mol^{-1} , and accordingly CH_3BeH behaves as a carbon acid. The situation is completely different as far as the Mg derivative is concerned. In this case, both magnitudes favor the process in which the proton is lost from the metal. On the one hand, the Mg–H bond dissociation enthalpy is 117 kJ mol^{-1} smaller than the C–H one, and the EA of the $\text{CH}_3\text{Mg}^\bullet$ radical is 28 kJ mol^{-1} more exothermic than that of $\text{CH}_2\text{MgH}^\bullet$ radical. Accordingly, CH_3MgH behaves as a metal acid, with the acidity of the carbon atom being 145 kJ mol^{-1} smaller.

To verify that these results were not an artifact of the method used, the structures of the different neutral and deprotonated species were reoptimized at the CCSD/6-311+G(d,p) level of theory. For the particular case of the Be de-

rivative, this geometry optimization was carried out by also including perturbative triple excitations. As shown in Table 1, the changes found in the calculated acidities are always very small, but more importantly, CH_3BeH also behaves as a carbon acid at the CCSD(T) level, whereas the Mg and Ca derivative still behave as metal acids.

The fact that Be derivatives behave as carbon acids rather than as Be acids explains the significant acidity enhancement on going from the methyl to the ethyl derivative. As indicated above, the most favorable deprotonation process corresponds to the loss of a proton from the methyl group. This triggers a cyclization of the system which contributes to significantly stabilize the anion (See Figure 1). A similar

acidity enhancement is not observed for either Mg- or Ca-containing compounds. In this case, the anion obtained by the deprotonation of the XH (X = Mg, Ca) group retains a structure similar to the neutral compound (See Figure 1), and the ethyl derivative is only slightly more acidic than the methyl one, which merely reflects the slightly larger stabilization of the anion by the ethyl group.

In general, the unsaturated compounds are stronger acids than the saturated ones, which is similar to that observed for similar systems that contain heteroatoms from groups 14, 15, and 16.^[30–33,48] Nevertheless, these acidity enhancements are rather small in all cases. This is so because the X–H (X = Mg,

Ca) bond dissociation enthalpies do not change significantly from the saturated to the unsaturated derivatives, as illustrated by the near-constancy of the electron density at the corresponding bond critical point (see Figure 2). This im-

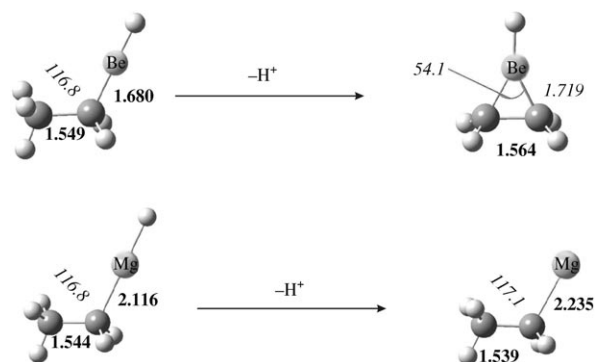


Figure 1. Geometrical changes undergone by ethylberyllium and ethylmagnesium hydrides after the most favorable deprotonation process. Bond angles [°] are given in italics and bond lengths [Å] are in bold.

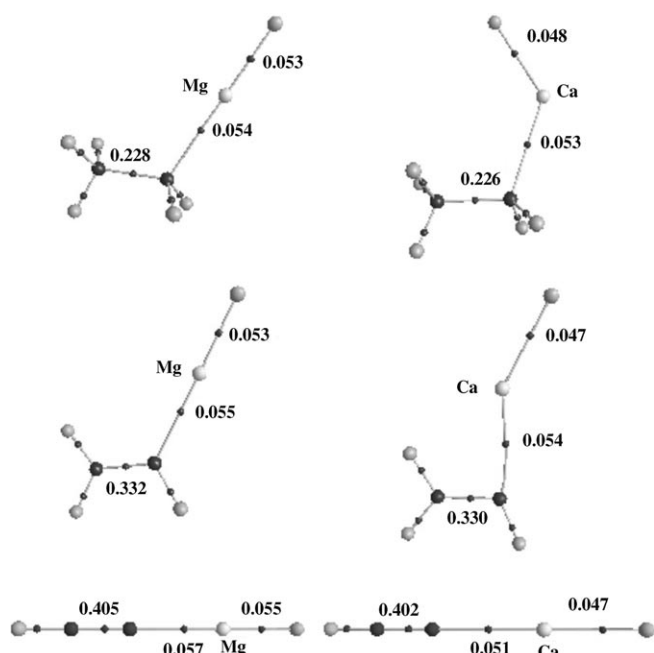


Figure 2. Molecular graphs for the ethyl, vinyl, and ethynyl derivatives of Mg and Ca. The electron densities at the bond critical points are in a.u.

plies that the acidity enhancement is only due to the slight increase in the EA of the R–X radical, which necessarily increases in the order ethyl < vinyl < ethynyl.

It is worth noting that the vinylcalcium hydride is an exception because it is predicted to be less acidic than the ethyl derivative. This is very likely due to an extra stabilization of the neutral compound through a nonbonding interaction between the C–Ca bond and the C–H bond *cis* to the Ca–H group, which would be responsible for the rather small (90.1°) C–C–Ca angle in this molecule. As a matter of fact, an analysis of the bonding in this compound shows that the C–Ca bond has a rather small contribution from the orbitals on Ca, with a very small (0.04) Wiberg bond order. In other words, this derivative could be viewed as the result of the interaction of a Ca–H cation with a $\text{CH}=\text{CH}_2$ anion. This is indeed ratified by a NRT analysis that indicates that this mesomeric form contributes as much as 35% to the stability of the system. The main consequence of this bonding pattern is that the C attached to the Ca atom becomes a very good electron donor. Indeed, a second-order perturbation NBO analysis shows the existence of a charge donation from the σ_{CCa} bonding orbital to the σ_{CH}^* antibonding orbital, which is mirrored in a lengthen-

ing of this bond (0.025 \AA) compared with the bond *trans* to the Ca–H group. To verify that this result does not arise from a limitation of our theoretical model, the geometry of this particular compound was also reoptimized at the CCSD/6-311+G(d,p) level by using the B3LYP method associated with a very extended cc-pWCTZ basis set, which is a theoretical model that performs particularly well for Ca-containing compounds.^[49] The changes observed both in the geometries and in the calculated acidities were negligibly small.

Perhaps the most unexpected finding in our study is that ethyl, vinyl, and ethynyl derivatives that contain alkaline-earth metals are among the most acidic compounds that contain a heteroatom from the main groups of the Periodic Table.

In Table 3, we compare our calculated values for this series of compounds with the experimental acidities for their analogues that contain heteroatoms from groups 13, 14, 15, and 16, if available. If the experimental values are not available, we report theoretical estimates obtained by using high-level ab initio calculations.

It is apparent that the derivatives of Be, Mg, and Ca are predicted to be systematically stronger acids than their analogues from groups 13 and 14. More importantly, with only the exception of the ethynyl derivatives, they are also stronger acids than the derivatives of group 15. Also surprisingly, the ethylberyllium hydride is predicted to be slightly more acidic than ethanol, whereas ethylmagnesium and ethylcalcium hydrides are only slightly less acidic than the corresponding S and Se derivatives.

CCSD(T) versus B3LYP: As indicated above, a comparison between the CCSD(T) and B3LYP calculated values can be useful as an assessment of the reliability of the DFT model. The values in Table 1 indicate that there is a rather good agreement between both sets of values for those compounds that behave as carbon acids (alkyl, vinyl, and ethynyl Be derivatives). Interestingly, when the proton is lost from the

Table 3. Gas-phase acidities ($\Delta_{\text{acid}}G^\ominus$ [kJ mol^{-1}]) for the ethyl ($\text{CH}_3\text{CH}_2\text{X}$), vinyl ($\text{CH}_2=\text{CHX}$), and ethynyl ($\text{CH}\equiv\text{CX}$) derivatives.^[a]

Group	X = BeH, MgH, CaH	X = BH ₂ , AlH ₂ , GaH ₂	X = CH ₃ , SiH ₃ , GeH ₃	X = NH ₂ , PH ₂ , AsH ₂	X = OH, SH, SeH
CH₃CH₂X					
1	1547	1484 ^[b]	1726 ^[c]	1640 ^[c]	1555 ^[f]
2	1478	1498 ^[b]	1540 ^[d]	1530 ^[e]	1460 ^[f]
3	1426	1509 ^[b]	1500 ^[d]	1501 ^[e]	1416 ^[f]
CH₂=CHX					
1	1518	1493 ^[b]	160 ^[c]	1546 ^[e]	1460 ^[g]
2	1470	1501 ^[b]	1530 ^[d]	1492 ^[e]	1432 ^[f]
3	1436	1502 ^[b]	1467 ^[d]	1443 ^[e]	1406 ^[f]
CH≡CX					
1	1510	1524 ^[b]	1559 ^[d]	1477 ^[e]	1380 ^[g]
2	1456	1535 ^[b]	1507 ^[d]	1460 ^[e]	1360 ^[g]
3	1425	1515 ^[b]	1435 ^[d]	1433 ^[e]	1340 ^[g]

[a] 1, 2, 3 stand for the first, second and third element in each group, i.e., Be, Mg, Ca in group 12, etc. [b] CCSD(T) calculated values taken from ref. [34]; [c] Experimental values taken from ref. [50]; [d] Experimental values taken from ref. [33]; [e] Experimental values taken from ref. [30]; [f] Experimental values taken from ref. [32]; [g] G2 calculated values taken from ref. [32].

metal, the B3LYP acidities always underestimate the CCSD(T) ones, which indicates that the DFT approach underestimates the stability of the anions if these are produced by the deprotonation of the X–H (X=Be, Mg, Ca) group. Nevertheless, both methods give the same trends as illustrated by the excellent linear correlations between the CCSD(T) calculated enthalpies and Gibbs' free energies and the B3LYP values (See Figure 3).

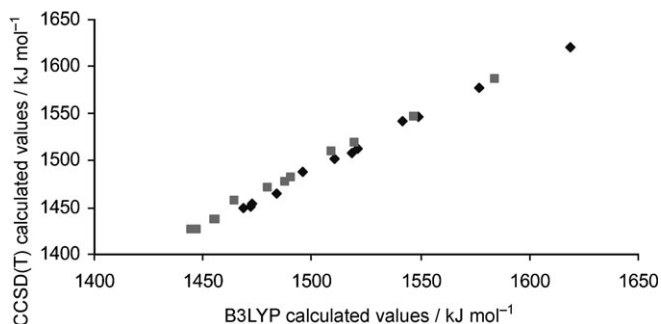


Figure 3. Linear correlations between CCSD(T)- and B3LYP-calculated gas-phase acidities ($\Delta_{\text{acid}}H^\circ$) and Gibbs' free energies ($\Delta_{\text{acid}}G^\circ$) for Be, Mg, and Ca derivatives. \blacklozenge : ΔH_{acid} , \blacksquare : ΔG_{acid} .

Thus, we can conclude that the B3LYP method can be used with confidence to reproduce acidity trends for these kinds of compounds, although in general the predicted acidities are too low (by about 10 kJ mol^{-1} on average, although for Ca-containing compounds the average deviation is almost twice this value) compared with those obtained if a CCSD(T) approach is employed.

Conclusion

From our theoretical survey on the intrinsic acidities of Be, Mg, and Ca derivatives, we can conclude that the hydrides of alkaline-earth metals, BeH_2 , MgH_2 , and CaH_2 , are stronger acids than BH_3 and CH_4 . BeH_2 is a stronger acid than BH_3 and CH_4 for two concomitant reasons: 1) the dissociation energy of the Be–H bond is smaller than the dissociation energies of the B–H and C–H bonds, and 2) the EA of BeH^\cdot is larger, in absolute value than those of BH_2^\cdot and CH_3^\cdot . Due to these same two factors, the acidity increases on going from BeH_2 to MgH_2 because the dissociation energy of the Mg–H bond is smaller than that of the Be–H bond, but at the same time the EA of MgH^\cdot is larger in absolute value than that of BeH^\cdot . The further acidity enhancement on going from MgH_2 to CaH_2 essentially reflects the fact that Ca–H bonds are weaker than Mg–H bonds.

For methyl, ethyl, vinyl, and ethynyl Mg and Ca derivatives, the most acidic site of the system is the metal. This is an unexpected result if one takes into account that the X–H (X=Mg, Ca) bonds in the neutral systems systematically exhibit the expected $\text{X}^{\delta+}\text{--H}^{\delta-}$ polarity. Conversely, the Be derivatives behave as carbon acids in the gas phase. The analy-

sis performed for the methyl derivatives shows that when the heteroatom is Be, the bond dissociation enthalpy of Be–H would favor the proton loss from the BeH group. However, the EA of the radical formed after the dissociation would favor the proton loss from the methyl group, and this latter effect is dominant. In contrast with Mg derivatives, both effects favor the proton loss from the MgH group.

The ethylberyllium hydride exhibits an unexpected high acidity with respect to the methyl derivative because the deprotonation of the system is accompanied by a cyclization which stabilizes the anion.

Similarly to that found for derivatives that contain heteroatoms from groups 14, 15, and 16, the unsaturated compounds are stronger acids than their saturated counterparts, with the only exception being vinylcalcium hydride, which is predicted to be a weaker acid than the ethyl derivative due to an extra stabilization of the neutral form.

Most importantly, among ethyl, vinyl, and ethynyl derivatives that contain a heteroatom from the main groups of the Periodic Table, those that contain Be, Mg, and Ca are among the strongest gas-phase acids. In fact, the ethylberyllium hydride, for instance, is predicted to be slightly more acidic than ethanol but much more than ethylamine, propane, or ethylborane.

An excellent linear correlation exists between CCSD(T)- and B3LYP-calculated acidities if a 6-311+G(3df,2p) basis set expansion is used. However, the absolute acidities obtained if the DFT approach is used are systematically smaller than those predicted at the CCSD(T) level.

Acknowledgements

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