J. Am. Chem. Soc. **2001,** *123,* 6353−6359

Acidity Trends in α,*β*-Unsaturated Alkanes, Silanes, Germanes, and Stannanes

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Received November 27, 2000

Abstract: The gas-phase acidity of ethyl-, vinyl-, ethynyl-, and phenyl-substituted silanes, germanes, and stannanes has been measured by means of FT-ICR techniques. The effect of unsaturation on the intrinsic acidity of these compounds and the corresponding hydrocarbons was analyzed through the use of G2 ab initio and DFT calculations. In this way, it was possible to get a general picture of the acidity trends within group 14. As expected, the acid strength increases down the group, although the acidity differences between germanium and tin derivatives are already rather small. As has been found before for amines, phosphines, and arsines, the carbon, silicon, germanium, and tin α,*β*-unsaturated compounds are stronger acids than their saturated analogues. The acidifying effect of unsaturation is much larger for carbon than for Si-, Ge-, and Sn-containing compounds. The allyl anion is better stabilized by resonance than its Si, Ge, and Sn analogues, $[CH_2{}^{-\delta} \mathrel{=\!=} CH^{+\delta'} \mathrel{=\!=} CH_2{}^{-\delta}]^-$ vs $[CH_2{}^{-\delta^{II}} = CH^{-\delta^{III}} - XH_2{}^{-\delta^{IV}}]^-$ ($X = Si, Ge, Sn$). The enhanced acid strength of unsaturated compounds is essentially due to a greater stabilization of the anion with respect to the neutral, because the electronegativity of the α,*β*-unsaturated carbon group increases with its degree of unsaturation. The phenyl derivatives are systematically weaker acids than the corresponding ethynyl derivatives by 15−20 kJ mol^{-1}. Experimentally, toluene acidity is very close to that of propyne, because the deprotonation of propyne takes place preferentially at the $\equiv$CH group rather than at the $-CH_3$ group.

Introduction

Some α,*β*-unsaturated compounds, as ethynylamine, exhibit a quite peculiar reactivity in the gas phase.[1] Ethynylamine, which can be considered as a prototype of ynamine function, has a stronger acidity[2] but a relatively weaker gas-phase basicity than analogous saturated amines. Recently, we showed,[3,4] through a systematic analysis of the gas-phase acidity and basicity trends in α,*β*-unsaturated amines, phosphines, and arsines that, in general, α,*β*-unsaturated compounds are much stronger acids than the corresponding saturated analogues. This allowed us to conclude[3] that when an heteroatom bearing an electron lone pair is attached to an unsaturated moiety, the interaction between both functions has dramatic effects on the reactivity of the system.

We have also found[3] that, in general, first-row-containing bases follow quite a different reactivity pattern as compared to those exhibited by second- or third-row-containing bases of the same group. For instance, while vinyl- and ethynylamine behave as carbon bases in the gas phase, the corresponding phosphines and arsines protonate preferentially at the heteroatom.

Very little is known, however, of the reactivity trends of unsaturated compounds containing heteroatoms of other groups of the periodic table. This is the case for silicon-, germanium-, and tin-containing compounds, for several reasons. On one hand, many of these derivatives, particularly the tin derivatives, are of very low stability. Furthermore, all of them are pyrophoric and special techniques for their synthesis are required. The complex isotopic distribution of Ge and Sn adds a further complexity to the mass spectrometric studies of ion/molecule reactions. On the other hand, their theoretical treatment is relatively expensive or not-adequate basis sets have been described in the literature, as it is the case for tin. In fact, to the best of our knowledge, only the experimental gas-phase acidities for GeH_4 and $Me-GeH_3$, have been reported in the literature[5] so far. More recently, Morgon and Riveros[6] published density functional theory (DFT) calculated gas-phase acidities for these and other simple Ge-containing species.

The aim of the present work is the experimental determination, by means of Fourier transform ion cyclotron resonance (FT-ICR) techniques, of the gas-phase acidity of α,*β*-unsaturated silanes, germanes, and stannanes, defined as the Gibbs free energy for the reaction

$$AH(g) \rightarrow A^-(g) + H^+(g)$$

These values will be compared with those for the corresponding carbon derivatives, mostly from the literature, to analyze,

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(1) Ellemberger, M. R.; Dixon, D. A.; Farneth, W. E. *J. Am. Chem. Soc.* **1981**, *103*, 5377.

(2) Smith, B. J.; Radom, L. *J. Am. Chem. Soc.* **1992**, *114*, 36.

(3) Guillemin, J.-C.; Decouzon, M.; Maria, P.-C.; Gal, J.-F.; Mó, O.; Yáñez, M. *J. Phys. Chem. A* **1997**, *101*, 9525.

(4) Mó, O.; Yáñez, M.; Decouzon, M.; Gal, J.-F.; Maria, P.-C.; Guillemin, J.-C. *J. Am. Chem. Soc.* **1999**, *121*, 4653.

(5) Decouzon, M.; Gal, J.-F.; Gayraud, J.; Maria, P.-C. *J. Am. Soc. Mass Spectrom.* **1993**, *4*, 54.

(6) Morgon, N. H.; Riveros, J. M. *J. Phys. Chem. A* **1998**, *102*, 10399.

10.1021/ja004079j CCC: $20.00 © 2001 American Chemical Society
Published on Web 06/07/2001

by means of high-level ab initio and DFT techniques, the acidity trends down group 14 of the periodic system.

Our study was directed at the vinyl- and ethynylsilanes, -germanes, and -stannanes, as well as ethyl derivatives for comparison. For the sake of completeness, we have included in our work the corresponding phenyl derivatives, to see what the effect is of an unsaturated aromatic substituent on the intrinsic reactivity of these systems as compared with vinyl and ethynyl groups. Methyl derivatives were also included when experimental data were available.

Experimental Section

Safety Considerations. Silane, germane, and stannane derivatives are pyrophoric and/or potentially toxic compounds. All reactions and handling should be carried out in a well-ventilated hood.

Chemicals. Starting materials ($EtSiCl_3$, $CH_2{=}CH{-}SiCl_3$, $EtGeCl_3$, $PhSnCl_3$) and reference compounds ($CH_3{-}C{\equiv}C{-}CH_3$, SiH_4, $CH_3{-}SiH_3$, $PhSiH_3$, *t*-BuONO, MeOH, NH_3) used for the present study were commercially available and were used without further purification. $PhGeH_3$ was prepared by Dr. J. Escudié (Université Paul Sabatier, Toulouse).

SnH_4,[7] $H_2C{=}CH{-}GeH_3$,[8] $HC{\equiv}C{-}GeH_3$,[9] $H_2C{=}CH{-}SnH_3$,[10] $HC{\equiv}C{-}SnH_3$,[11] and $PhSnH_3$[12] were prepared as reported in the literature.

$EtSiH_3$,[5] $H_2C{=}CH{-}SiH_3$,[13] $EtGeH_3$,[14] and $EtSnH_3$[15] were prepared following an approach similar to the one used for the synthesis of ethenylgermane,[8] starting from the corresponding trichloroderivative. $HC{\equiv}C{-}SiH_3$ was prepared in a three-step reaction starting from vinyltrichlorosilane. After the addition of dibromine on vinyltrichlorosilane, the reaction with quinoline gave the ethynyltrichlorosilane,[16,17] which was reduced in $HC{\equiv}C{-}SiH_3$ by LAH in tetraglyme (yield 76%). This new approach presents the advantage of giving a very pure compound, free of a low-boiling solvent. The reported preparations normally use THF as solvent, which is very difficult to separate completely from the product.[18] All the ethyl, vinyl, and ethynyl hydrides were purified in a vacuum line by trap-to-trap distillation. The high-boiling impurities were condensed in a trap cooled at −90 °C, and the product was selectively condensed in a second trap cooled at −120 °C for removing the most volatile impurities (mainly XH_4 with X = Si, Ge, Sn). In the case of phenylstannane, the two traps were cooled at 0 and −40 °C, respectively.

FT-ICR Measurements and Results. Proton-transfer equilibrium measurements were conducted on an electromagnet FT-ICR mass spectrometer built at the University of Nice-Sophia Antipolis, using the methodology described previously.[4,19−21]

The proton-transfer reactions were monitored for 5−10 s, leading in general to an equilibrium constant determination.

$$AH + Ref^- \overset{K}{\rightleftharpoons} RefH + A^- \qquad (1)$$

$$\Delta G^\circ_{acid} = -RT \ln K \qquad (2)$$

The intensities of deprotonated species were summed over all the isotope peaks. In general, the relative intensities were accurately reflected in the spectra. When the intensity of the smallest isotope peaks were close to, or under, the noise, the total intensity of the deprotonated species was evaluated by multiplying the intensity of the largest peak by an appropriate factor calculated from the isotopic composition of the given element.

When equilibrium conditions could not be reached (impurities, secondary reactions), acidities were estimated by bracketing experiments. Ref^- and A^- ions were isolated in turn, and the reformation of the other ion in reaction 1 was monitored for 2−10 s. Equilibrium constants were obtained at an ICR cell temperature of 338 K. Literature ΔG°_{acid}[22] of reference compounds refer to the standard temperature of 298.15 K. As explained previously,[3,4,23,24] temperature corrections are minor as compared to other experimental uncertainties, and the reported absolute ΔG°_{acid} do not include such temperature corrections. The maximum bias introduced by the lack of temperature correction was estimated to be ± 2 kJ mol^{-1}, but this error was not included in the reported uncertainties. Further details on the experiments carried out are provided in Supporting Information.

Experimental ΔG°_{acid} for all C, Si, Ge, and Sn derivatives studied are collected in Table 1. Most of the data for hydrocarbons in Table 1 were taken from the NIST compilation,[22] except for $CH_3{-}C{\equiv}C{-}CH_3$, for which no ΔG°_{acid} was available, and $HC{\equiv}C{-}CH_3$ and $PhCH_3$, for which revised values were proposed.

Computational Details

The gas-phase acidities of the compounds under investigation were calculated using two different theoretical schemes, namely, the G2 theory[25] and B3LYP/6-311+G(3df,2p)//B3LYP/6-31G(d) density functional theory calculations. The G2 theory has been shown to reproduce gas-phase acidities within ±4 kJ mol^{-1}, the so-called *chemical accuracy*. Recently, extensions of this theory to molecules containing third-row elements, as well as an assessment of it for the computation of enthalpies of formation, have been published.[26,27] The reader is addressed to ref 25 for a complete description of this method.

For the larger systems, as the phenyl derivatives, for which the G2 formalism can become prohibitively expensive, we have used the G2-(MP2) alternative method. The corresponding entropy changes are evaluated at the HF/6-31G* level.

The B3LYP approach, when used with an extended basis set of a quality identical to the largest basis set expansion used in G2 theory, also provides proton affinities and acidities in very good agreement with the experimental values.[4]

However, neither of these two theoretical schemes can be applied to tin because no standard 6-31G or 6-311G basis has been reported so far for this atom. Hence, one aim of the present work was to develop G2-type basis sets for Sn. Glukhovtsev et al.[28] have shown, for the particular case of bromine- and iodine-containing compounds, that the G2 [ECP] theory, based on the use of effective core potentials (ECPs), yields results comparable in accuracy to those obtained in all-electron

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(7) Finholt, A. E.; Bond, A. C., Jr.; Wilzbach, K. E.; Schlesinger, H. I. *J. Am. Chem. Soc.* **1947**, *69*, 2692.

(8) Guillemin, J.-C.; Lassalle, L.; Janati, T. *Planet. Space Sci.* **1995**, *43*, 75.

(9) Lovejoy, R. W.; Baker, D. R. *J. Chem. Phys.* **1967**, *46*, 658. Chrostowska, A.; Métail, V.; Pfister-Guillouzo, G.; Guillemin, J.-C. *J. Organomet. Chem.* **1998**, *570*, 175.

(10) Janati, T.; Guillemin, J.-C.; Soufiaoui, M. *J. Organomet. Chem.* **1995**, *486*, 57.

(11) Lassalle, L.; Janati, T.; Guillemin, J.-C. *J. Chem. Soc. Chem. Commun* **1995**, 699.

(12) Neumann, W. P.; Niermann, H. *Justus Liebigs Ann. Chem.* **1962**, *653*, 164.

(13) Tannenbaum, S.; Kaye, S.; Lewenz, G. F. *J. Am. Chem. Soc.* **1953**, *75*, 3753.

(14) Teal, G. K.; Kraus, C. A. *J. Am. Chem. Soc.* **1950**, *72*, 4706.

(15) Dillard, C. R.; Holmes McNeill, E.; Simmons; D. E.; Yeldell, J. B. *J. Am. Chem. Soc.* **1958**, *80*, 3607.

(16) Chan, T. H.; Mychajlowskij, W.; Ong, B. S.; Harpp, D. N. *J. Org. Chem.* **1978**, *43*, 1526.

(17) Matsumoto, H.; Kato, T.; Matsubara, I.; Hoshino, Y.; Nagai, Y. *Chem. Lett.* **1979**, 1287.

(18) Ebsworth, E. A.; Frankiss, S. G. *J. Chem. Soc. (London)* **1963**, 661.

(19) Berthelot, M.; Decouzon, M.; Gal, J.-F.; Laurence, C.; Le Questel, J.-Y.; Maria, P.-C.; Tortajada, J. *J. Org. Chem.* **1991**, *56*, 4490.

(20) Maria, P.-C.; Leito, I.; Gal, J.-F.; Exner, O.; Decouzon, M. *Bull. Soc. Chim. Fr.* **1995**, *132*, 394.

(21) Decouzon, M.; Gal, J.-F.; Herreros, M.; Maria, P.-C.; Murrell, J.; Todd, J. F. J. *Rapid Commun. Mass Spectrom.* **1996**, *10*, 242.

(22) NIST Standard Reference Database 69, March 1998 Release: *NIST Chemistry WebBook* (data compiled by J. E. Bartmess).

(23) Decouzon, M.; Gal, J.-F.; Guillemin, J.-C.; Maria, P.-C. *Int. J. Mass Spectrom. Ion Processes* **1998**, *179*, 27.

(24) Decouzon, M.; Gal, J.-F.; Gayraud, J.; Maria, P.-C.; Vaglio, G. A.; Volpe, P. *J. Am. Soc. Mass Spectrom.* **1993**, *4*, 54.

(25) Curtiss, L. A.; Raghavachari, K.; Trucks, G. W.; Pople, J. A. *J. Chem. Phys.* **1991**, *94*, 7221.

(26) Curtiss, L. A.; McGrath, M. P.; Blaudeau, J.-P.; Davis, N. E.; Binning, R. C. Jr.; Radom, L. *J. Chem. Phys.* **1995**, *103*, 6104.

(27) Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Pople, J. A. *J. Chem. Phys.* **1997**, *106*, 1063.

(28) Glukhovtsev, M. N.; Pross, A.; McGrath, M. P.; Radom., L. *J. Chem. Phys.* **1995**, *103*, 1878.

Table 1. Gas-Phase Acidities (kJ/mol at 298.15 K) of Saturated and Unsaturated C, Si, Ge, and Sn Derivatives

compound	ΔGacid° (calc)[a] B3LYP/6-311+G(3df,2p)	ΔGacid° (calc)[a] G2	ΔGacid° (exp)[d]
C Compounds			
$\mathrm{CH_4}$	1718	1715	(1709.6 ± 3.8; 1715 ± 15)[e]
$\mathrm{CH_3{-}CH_3}$	1716	1724	(1721 ± 8.8)[e]
$\mathrm{CH_3CH_2{-}C}H_3$	1713	1712	(1721 ± 8.8)[e]
$\mathrm{CH_2{-}CH{-}C}H_3$	1592	1596	(1600 ± 6.7; 1607 ± 8.4; 1605 ± 2.1)[e]
$\mathrm{C}H\mathrm{{\equiv}C{-}CH_3}$	1564	1570	1559 ± 8.4 (1562 ± 8.4)[e]
$\mathrm{CH{\equiv}C{-}C}H_3$	1572	1575	
$\mathrm{CH_3{-}C{\equiv}C{-}CH_3}$	1584	1593	1597 ± 8.4
$\mathrm{Ph{-}C}H_3$	1563	1568[b]	1557 ± 8.4 (1579 ± 29; 1564 ± 8.4)[e]
Si Compounds			
$\mathrm{SiH_4}$	1526	1529	1530 ± 8.4[f]
$\mathrm{CH_3{-}Si}H_3$	1555	1556	1544 ± 8.4[f]
$\mathrm{CH_3CH_2{-}Si}H_3$	1553	1550	1540 ± 8.4[f]
$\mathrm{CH_2{=}CH{-}Si}H_3$	1525	1526	1530 ± 8.4[f]
$\mathrm{CH{\equiv}C{-}Si}H_3$	1498	1496	1507 ± 8.4
$\mathrm{Ph\text{-}Si}H_3$	1515	1515[b]	1515 ± 8.4[f]
Ge Compounds			
$\mathrm{GeH_4}$	1478	1483	1467 ± 5[g] (1467.9 ±5.1)[h]
$\mathrm{CH_3{-}Ge}H_3$	1498	1506	1502 ± 8.4 (1503.2)[h]
$\mathrm{CH_3CH_2{-}Ge}H_3$	1494	1499	1500 ± 11
$\mathrm{CH_2{=}CH{-}Ge}H_3$	1474	1481	1467 ± 5[g]
$\mathrm{CH{\equiv}C{-}Ge}H_3$	1441	1450	1435 ± 5[g]
$\mathrm{Ph{-}Ge}H_3$	1458	1459[b]	1448 ± 5[g]
Sn Compounds			
$\mathrm{SnH_4}$	1434	1431[c]	1432 ± 8.4
$\mathrm{CH_3CH_2{-}Sn}H_3$	1445	1438[c]	1433 ± 8.4
$\mathrm{CH_2{=}CH{-}Sn}H_3$	1430	1426[c]	1431 ± 8.4
$\mathrm{CH{\equiv}C{-}Sn}H_3$	1400	1394[c]	1386 ± 12
$\mathrm{Ph{-}Sn}H_3$	1422	1410[b,c]	1400 ± 16

[a] The tabulated $\Delta G^\circ_{\mathrm{acid}}$ (calc) correspond to the acidic hydrogen written in italic. [b] Values obtained at the G2(MP2) level of theory. [c] Values obtained using the Stuttgart ECP. [d] This work unless indicated (footnotes *e* and *h*). [e] Reference 22. [f] Relative acidities in Table 3 anchored to the Bartmess acidity scale.[22] Absolute $\Delta G^\circ_{\mathrm{acid}}$ (*t*-BuOH) = 1540 ± 8.4 kJ/mol[22]; the indicated uncertainty of 8.4 kJ/mol corresponds to the uncertainty of the anchoring acidity. The Free−Wilson treatment leads to a maximum standard deviation of 2.8 kJ/mol on relative acidities. [g] Relative acidities in Table 4 of the Supporting Information anchored to the absolute $\Delta G^\circ_{\mathrm{acid}}$ ($\mathrm{H_2S}$);[24] uncertainties were obtained from the uncertainty on $\Delta G^\circ_{\mathrm{acid}}$ ($\mathrm{H_2S}$) estimated to ±1.3 kJ/mol[24] (treated as a standard deviation) and the maximum standard deviation on our relative acidities (2 kJ/mol), leading to a standard deviation of 2.4 kJ/mol, which was enlarged by a factor of 2. [h] Reference 24.

calculations. Therefore, we have decided to use a similar formalism for Sn-containing systems.

Construction of the Valence Basis Sets for Sn To Be Used with ECP. Different effective core potentials have been proposed in the literature for Sn. In our study, we have considered three of them: the relativistic potential of Hay and Wadt,[29] the Stuttgart relativistic large-core ECP,[30] and the SKBJ of Stevens et al.[31] These three ECP approaches differ in the basis set used to describe the valence electrons for third- and fourth-row atoms. The SKBJ method uses a (5s,5p)/[2s,2p] basis set, which implies a [4,1] contraction scheme; the Stuttgart ECP employs a (4s,4p)/[2s,2p] basis set with a [3,1] contraction scheme; the Hay and Wadt ECP employs a smaller (3s,3p)/[2s,2p] basis with a [2,1] contraction scheme. On the other hand, the SKBJ approach adopts a typical shell structure ($\alpha_s = \alpha_p$) while this approximation is not used in the Hay and Wadt method. This last ECP is also known as LANL2, and this will be the nomenclature adopted hereafter.

Taking into account that, in the standard G2 formalism, the geometry optimizations are performed using a 6-31G(d) basis set, while the electron correlation contributions are based on the use of 6-311G(d,p) basis, the basis set developed for Sn to be used in conjunction with 6-31G or 6-311G basis for the remaining atoms will be also referred to as 6-31G or 6-311G basis sets, for the sake of simplicity.

The polarization d function to be included in geometry optimizations as well as the supplementary diffuse sp components and the d, f polarization functions required in G2 calculations were optimized following the same procedure described in ref 32 to obtain similar basis for antimony. For this purpose, we have used $\mathrm{SnH_4}$ and $\mathrm{SnH_3^-}$ on their LANL2DZ optimized geometries.

All the calculations have been carried out by using the Gaussian-98 series of programs.[33] The bonding characteristics of the different species have been investigated by using the atoms in molecules (AIM) theory of Bader.[34] For this purpose, we have located the bond critical points and calculated the Laplacian of the charge density, $\nabla^2\rho(\mathbf{r})$. The AIM analysis was performed using the AIMPAC series of programs.[35]

Reliability of the Basis Sets Obtained for Sn. To check the reliability of the three different ECP extended basis developed in the previous section for Sn-containing compounds, we have chosen some suitable small model compounds such as methylstannane, for which there is experimental information on its infrared spectrum, and tetramethylstannane, whose experimental heat of formation is known. We have also evaluated the ionization energy of tin. In all cases, the agreement between calculations and experiment was rather good. The harmonic vibrational frequencies of methylstannane, in particular those involving the Sn atom, are quite well reproduced when the three ECPs are used in B3LYP/6-31G(d) calculations. The ionization energy of tin, obtained at the B3LYP/6-311+G(3df,2p) level using the three ECP approaches considered in this work, differs by 0.128 eV, on average, from the experimental value, which is of the same order as the difference between the spin−orbit corrections for Sn and $\mathrm{Sn^+}$ (0.182 eV).[36] The heat of formation of tetramethylstannane estimated from the enthalpy of its atomization reaction $[\mathrm{(CH_3)_4Sn \rightarrow Sn + 4C + 12H}]$ at the B3LYP/6-311+G(3df,2p) level is in reasonably good agreement with the experimental values,[22] taking into account the large dispersion of the latter. The experimental heats of formation of C, Sn, and H were taken from ref 37.

Since our final goal was to determine gas-phase acidities, we have also used for this test the experimental acidities of $\mathrm{SnH_4}$, $\mathrm{H_3C{-}CH_2{-}SnH_3}$, $\mathrm{H_2C{=}CH{-}SnH_3}$, and $\mathrm{Ph{-}SnH_3}$, measured in this work. As

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(29) (a) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 270. (b) . Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 284, (c) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299.

(30) Kuechle, W.; Dolg, M.; Stoll, H.; Preuss, H. *Mol. Phys.* **1991**, *74*, 1245.

(31) Stevens, W. J.; Krauss, M.; Basch, H.; Jasien, P. G. *Can. J. Chem.* **1992**, *70*, 612.

(32) González, A. I.; Mó, O.; Yáñez, M. *J. Chem. Phys.* **2000**, *112*, 2258.

(33) Gaussian 98, Revision A.7. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, Jr. J. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Peterson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T. A.; Al-Laham, M. A.; Peng, C. Y.; Nanayaklara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. J.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A.; Gaussian, Inc., Pittsburgh, PA, 1998.

(34) Bader, R. F. W. *Atoms in Molecules. A Quantum Theory*; Oxford University Press: Oxford, U.K., 1990.

(35) The AIMPAC programs package has been provided by J. Cheeseman and R. F. W. Bader.

(36) For the neutral atom, the spin−orbit correction can be estimated using the equation, $E_{\mathrm{S-O}} = 5/9(E_2 - E_0) + 3/9(E_1 - E_0)$, where E_0, E_1, and E_2 are the experimental values of the corresponding J states taken from Moore, C. E., *Atomic Energy Levels;* NSRDS−NBS, **1971**, *35*, and the numerical factors 5/9 and 3/9 take into account their degeneracy. Similarly for $\mathrm{Sn^+}$, the spin−orbit correction can be obtained as: $E_{\mathrm{S-O}} = 4/6(E_{3/2} - E_{1/2})$.

(37) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *17* (Suppl. No. 1).

Table 2. G2(ECP) Total Energies (*E* in hartrees) of Some Model Compounds Containing Sn and Their Corresponding Anions[a]

ECP used	compound	E[b]	ΔG^{o}_{acid}	abs devn from expt	**a**v devn
SKBJ	SnH_4	−5.741 819	1435	3	8
	SnH_3^-	−5.185 473			
	$H_3C\text{-}CH_2{-}SnH_3$	−84.194 052	1440	7	
	$H_3C\text{-}CH_2{-}SnH_3$	−83.634 758			
	$H_3C{-}CH_2{-}SnH_3$	−82.982 990	1428	3	
	$H_2C{=}CH{-}SnH_2^-$	−82.428 308			
	$HC{\equiv}C{-}SnH_3$	−81.973 613	1400	14	
	$HC{\equiv}C{-}SnH_2^-$	−81.421 238			
	$PhSnH_3$	−236.818 915[c]	1414[c]	14[c]	
	$PhSnH_2^-$	−236.268 578[c]			
LANL2DZ	SnH_4	−5.703 603	1433	1	10
	SnH_3^-	−5.148 217			
	$H_3C{-}CH_2{-}SnH_3$	−84.158 436	1443	10	
	$H_3C{-}CH_2{-}SnH_2^-$	−83.599 004			
	$H_2C{=}CH{-}SnH_3$	−82.947 508	1431	5	
	$H_2C{=}CH{-}SnH_2^-$	−82.392 673			
	$HC{\equiv}C{-}SnH_3$	−81.732 567	1400	14	
	$HC{\equiv}C{-}SnH_2^-$	−81.189 439			
	$PhSnH_3$	−236.312 221[c]	1418[c]	18[c]	
	$PhSnH_2^-$	−235.763 488[c]			
Stuttgart	SnH_4	−5.741 819	1431	1	6
	SnH_3^-	−5.185 473			
	$H_3C{-}CH_2{-}SnH_3$	−84.194 052	1438	5	
	$H_3C{-}CH_2{-}SnH_3$	−83.634 758			
	$H_3C{-}CH_2{-}SnH_3$	−82.982 990	1426	5	
	$H_2C{=}CH{-}SnH_2^-$	−82.428 308			
	$HC{\equiv}C{-}SnH_3$	−81.732 993	1394	8	
	$HC{\equiv}C{-}SnH_2^-$	−81.192 063			
	$PhSnH_3$	−236.313 571[c]	1410[c]	10[c]	
	$PhSnH_2^-$	−235.759426[c]			

[a] The calculated gas-phase acidities (ΔG^{o}_{acid} in kJ mol^{-1}) were compared with the available experimental values. The deviations (in kJ mol^{-1}) are included in the last column. [b] These values include the corresponding zero-point energy correction. [c] Values obtained at the G2MP2 level.

illustrated in Table 2 the agreement between calculated and experimental values is fairly good, independent of the ECP used, although the Stuttgart is the one that leads to the smallest average deviation.

Results and Discussion

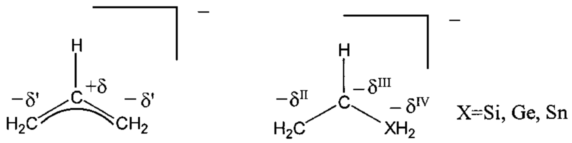
Structures. Although a detailed analysis of the structures of the systems under investigation is not the main objective of this work, some general trends deserve to be discussed. As was found[4] before for similar unsaturated compounds containing nitrogen, phosphorus, and arsenic, the C−X bond length decreases in the order ethyl > vinyl > ethynyl (See Table 3). This shortening is associated with an increase in the charge density at the C−X bond critical point (See Table 3), which reflects the polarization caused by a group of increasing electronegativity. In fact, on going from the ethyl derivative to the vinyl derivative, we are changing a $CH_3{-}CH_2$ group with a more electronegative one ($CH_2{=}CH$). This means that the carbon atom directly bonded to the heteroatom of the XH_3 group is more electron deficient in the unsaturated compound and polarizes the XH_3 group in such a way that the charge density within the C−X bonding region increases. This effect is particularly strong in the case of the carbon derivatives, and much smaller in Si-, Ge-, or Sn-containing compounds. Accordingly, the C−X stretching frequency is blue-shifted on going from the ethyl to the vinyl and the ethynyl derivatives. Consistently, this shifting is particularly large for the series of carbon compounds and much smaller for Si, Ge, and Sn derivatives. It should be noted that this behavior is in contrast with that found[4] for the series of amines, phosphines, and arsines, where the shortening of the C−X bond increases down the group.

Deprotonation of Si, Ge, and Sn derivatives leads to a systematic lengthening of both the C−X and the C−C bonds (See Table 3). This finding is also at variance with respect to what was found for α,*β*-unsaturated amines, phosphines, and arsines, where the deprotonation process is accompanied by a shortening of the C−X bond.

Carbon derivatives constitute a particular case, because deprotonation at the methyl group favors a delocalization which should result in a lengthening of the unsaturated bond and a shortening of the saturated one. This is obvious in the case of propene, $H_2C{=}CH{-}CH_3$, which upon deprotonation yields a $[H_2C{-}CH{-}CH_2]^-$ anion with two identical C−C linkages with a partial double bond character. Similarly, the C≡C triple bond of propyne becomes almost a double bond, upon deprotonation at the methyl group, while the C−C single bond acquires a significant double bond character. It must be noted, however, that for this particular compound the $[C{\equiv}C{-}CH_3]^-$ anion is predicted to be slightly (∼5 kJ mol^{-1}) more stable than the $[HC{\equiv}C{-}CH_2]^-$ one. Therefore, propyne is the only system among those included in this study for which deprotonation does not occur preferentially at the XH_3 group.

The aforementioned delocalization is much less favorable for Si, Ge, and Sn derivatives, because the double bonds between first-row and second-, third-, or fourth-row atoms are of low stability, due to the low efficiency of the π-overlap between p orbitals of very different size. On the other hand, because of the electropositive character of Si, Ge, and Sn, the charge distribution in the anions is completely different from that found in carbon compounds. For instance, in the $[H_2C{-}CH{-}CH_2]^-$ anion, most of the negative charge is located at the terminal CH_2 groups, while the central carbon atom bears a positive charge (See Chart 1). In contrast, in the corresponding Si, Ge, or Sn derivatives, the central carbon atom is more electronegative than the heteroatom of the XH_2 group. As a consequence, this central carbon atom bears a negative charge (see Chart 1). In other words, in Si-, Ge-, and Sn-containing anions, the negative charge is more delocalized and the three groups (CH_2, CH, XH_2) support a partial negative charge. This must be necessarily reflected in a lengthening of both, the C−C and the C−X bonds, in agreement with the results mentioned above.

Chart 1



We have also found sizable differences between toluene and its Si, Ge, and Sn analogues as far as the effects of the deprotonation process on the electronic structure of the system are concerned. In fact, an analysis of the charge distribution of $Ph{-}CH_2^-$ anion shows effects similar to those discussed above for vinyl derivatives. Consequently, the negative charge accumulates preferentially at ortho and para positions of the aromatic ring, while the charge density at bond critical points of the $C1{-}CH_n$ ($n = 3, 2$), C2−C3, and C5−C6 increases. Accordingly, these bonds significantly shorten (See Figure 1). Concomitantly, the charge density at the C1−C2, C1−C6, C3−C4, and C4−C5 bond critical points decreases and the corresponding bonds become longer. For $Ph{-}SiH_3$, $Ph{-}GeH_3$, and $Ph{-}SnH_3$, the π-overlap and the conjugation of the substituent with the aromatic moiety are much less significant and only a polarization of the system takes place. Accordingly, on going from the neutral to the anion, all bonds become slightly

Table 3. C−X (X = C, Si, Ge, Sn) and C−C Bond Distances (in Å) and Charge Densities (ρ, au) at the Corresponding Bond Critical Points for Ethyl, Vinyl, and Ethynyl Derivatives, Obtained at the B3LYP/6-31G* Level

	X = C				X = Si				X = Ge				X = Sn			
	R−XH3		[R−XH2]−		R−XH3		[R−XH2]−		R−XH3		[R−XH2]−		R−XH3		[R−XH2]−	
derivative	r_{CX}	ρ	r_{CX}	ρ	r_{CX}	ρ	r_{CX}	ρ	r_{CX}	ρ	r_{CX}	ρ	r_{CX}	ρ	r_{CX}	ρ
								C−X Bond								
ethyl	1.532	0.243	1.543	0.238	1.894	0.116	1.996	0.093	1.957	0.124	2.057	0.101	2.163	0.033	2.267	0.028
vinyl	1.502	0.256	1.395	0.302	1.871	0.117	1.927	0.101	1.930	0.127	2.005	0.106	2.130	0.034	2.224	0.031
ethynyl	1.460	0.267	1.351	0.378	1.827	0.118	1.908	0.096	1.887	0.128	1.966	0.106	2.080	0.036	2.197	0.035
								C−C Bond								
ethyl	1.532	0.243	1.521	0.241	1.539	0.266	1.535	0.238	1.535	0.239	1.530	0.240	1.569	0.238	1.569	0.240
vinyl	1.333	0.345	1.395	0.302	1.335	0.339	1.353	0.329	1.335	0.342	1.342	0.336	1.341	0.341	1.341	0.338
ethynyl	1.207	0.399	1.285	0.357	1.214	0.402	1.229	0.390	1.211	0.403	1.226	0.392	1.224	0.399	1.224	0.394

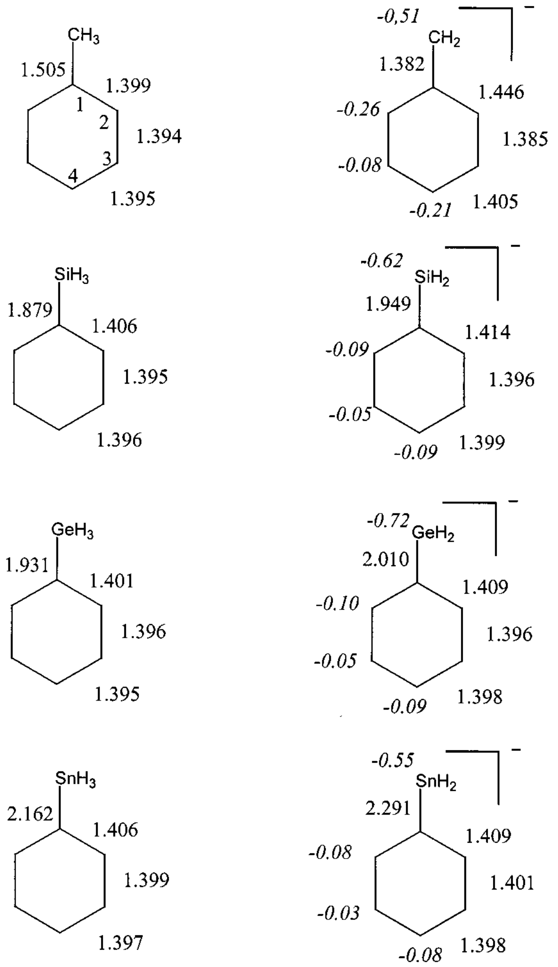


Figure 1. Variation of the bond lengths (in Å) of Ph−XH3 (X = C, Si, Ge, Sn) derivatives upon deprotonation. Numbers in italic correspond to the Mulliken net charges including the charge of the corresponding hydrogen atoms. It should be noted that in the case of Si, Ge and Sn derivatives most of the negative charge of the -XH2 group is located at the hydrogen atoms.

destabilized, as reflected in lower values of the charge density at the bond critical points and in larger bond lengths (see Figure 1).

Acidity Trends. The calculated and measured gas-phase acidities of the different compounds under investigation are compared in Table 1. The first conspicuous feature is that most of the $\Delta G°_{\text{acid}}$ calculated values agree with the experimental ones within the experimental error. On the other hand, in general, the estimates obtained using the G2 formalism are very close to those obtained when using the B3LYP approach, the average deviation being 3.8 kJ mol^{-1}. This implies that the B3LYP/6-311+G(3df,2p)//B3LYP/6-31G(d) approach, which is significantly more economical than the G2 formalism, is quite reliable to reproduce gas-phase acidities and therefore is a good alternative to high-level ab initio techniques, in particular when dealing with large systems for which the G2-type methods can be unaffordable.

It should also be emphasized that the deprotonation of the XH_3 group is the most favorable process, with the only exception of propyne, where the proton is lost from the ≡CH group. Although all the other possible deprotonations have been considered, only the most stable anion was taken into account to obtain the values summarized in Table 1. Since the deprotonation of propyne leads preferentially to a $[C{\equiv}C{-}CH_3]^-$ anion, we have considered it of interest to include in our survey the $CH_3{-}C{\equiv}C{-}CH_3$ derivative to have an estimate of the acidity of a CH_3 group attached to a C≡C triple bond.

As was already found for other α,β-unsaturated compounds,[4] the acid strength increases as the degree of the unsaturation of the system increases. Hence, in general, the ethynyl derivatives are more acidic than the vinyl derivatives and these are more acidic than the ethyl derivatives.

To gain some insight into the origin of these acidity trends and into the differences observed between C-, Si-, Ge-, and Sn-containing compounds, we have used the following isodesmic reactions:

$$H_2C{=}CH_2 + H_3C{-}CH_2{-}XH_3 \rightarrow H_3C{-}CH_3 + H_2C{=}CH{-}XH_3 \quad (3)$$

$$H_2C{=}CH_2 + H_3C{-}CH_2{-}XH_2^- \rightarrow H_3C{-}CH_3 + H_2C{=}CH{-}XH_2^- \quad (4)$$

$$HC{\equiv}CH + H_2C{=}CH{-}XH_3 \rightarrow H_2C{=}CH_2 + HC{\equiv}C{-}XH_3 \quad (5)$$

$$HC{\equiv}CH + H_2C{=}CH{-}XH_2^- \rightarrow H_2C{=}CH_2 + HC{\equiv}C{-}XH_2^- \quad (6)$$

which allow us to estimate the relative effect of the XH_3 group on the stability of the C=C and the C≡C bonds for neutral and deprotonated species, taking as a common reference the ethane and the ethylene molecules, respectively.

The results obtained, at the G2 level, are shown in the energy diagrams of Figures 2 and 3. It can be observed that, in general, the increase in acid strength on going from the saturated ethyl derivative to the unsaturated vinyl compound is due to a greater stabilization of the anion (see Figure 2). This can be easily explained if one takes into account that a $H_2C{=}CH$ group is more electronegative than a $H_3C{-}CH_2$ group.

The stabilization of the anion, in relative terms, is quantitatively less significant as we go down the group, because as the

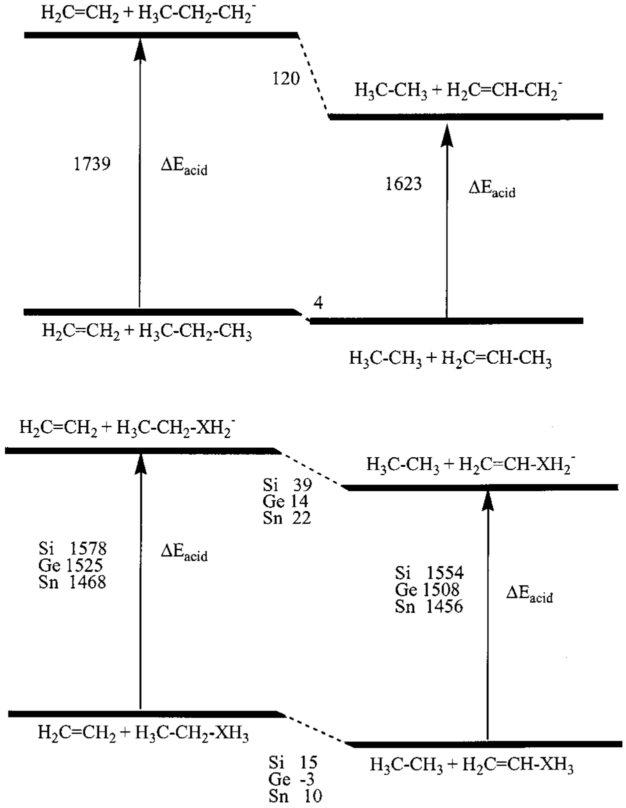


Figure 2. G2 calculated relative energies of species involved in the deprotonation processes of $CH_3{-}CH_2{-}XH_3$ vs $CH_2{=}CH{-}XH_3$ (X = C, Si, Ge, Sn) derivatives. All values in kilojoules per mole.

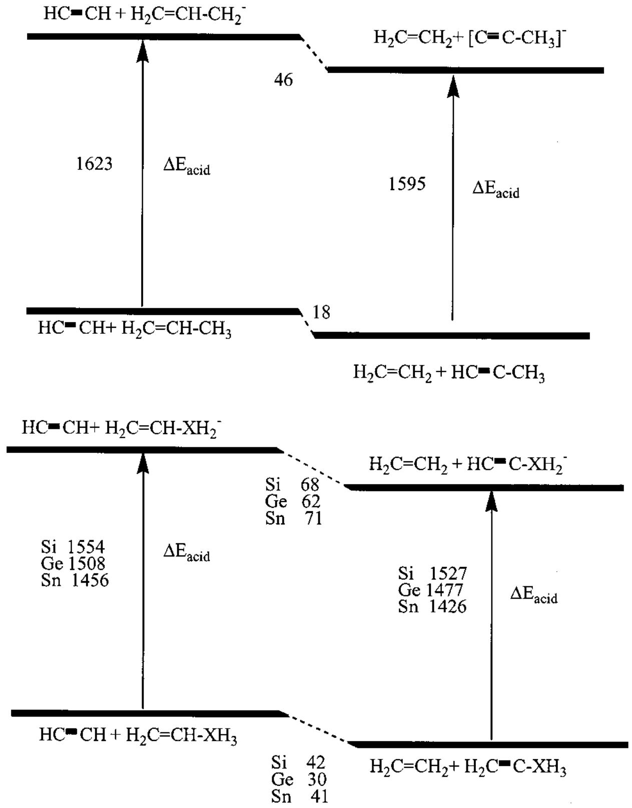


Figure 3. G2 calculated relative energies of species involved in the deprotonation processes of $CH_2{=}CH{-}XH_3$ vs $CH{\equiv}C{-}XH_3$ (X = C, Si, Ge, Sn) derivatives. All values in kilojoules per mole.

number of electrons of the heteroatom increases, the energetic effect of adding an extra electron must be smaller in relative terms. This explains that, while propene is found to be an acid ~120 kJ mol^{-1} stronger than propane, for the corresponding Sn derivatives, the gap is 10 times smaller. On the other hand, as we mentioned before, the allyl anion $[CH_2{=}{=}CH{=}{=}CH_2]^-$, is stabilized by charge delocalization, while this effect is less important for the Si, Ge, and Sn analogues.

Similar effects explain the acidity strengthening on going from the vinyl to the ethynyl derivatives (See Figure 3). As before, this is due to the fact that a $HC{\equiv}C$ group is more electronegative than a $H_2C{=}CH$ one. However, the acidity gap between propene and propyne is almost 5 times smaller than that found between propene and propane. Quite surprisingly, this dramatic difference is not observed for Si-, Ge-, or Sn-containing systems. This likely reflects that for second-, third-, and fourth-row atoms the influence of the substituent is much less significant than for first-row atoms, due to the poor overlap between the orbitals of first-row and second-, third-, or fourth-row atoms. In summary, unlike in the carbon systems, for Si-, Ge-, and Sn-containing compounds, the switch from vinyl to ethynyl as the substituent causes the greatest increase in the stability of both the neutral and the deprotonated species.

The phenyl derivatives are weaker acids than the ethynyl derivatives, although the gap increases on going from C to Sn. In fact, propyne and toluene exhibit almost identical acidity, while $Ph{-}SiH_3$, $Ph{-}GeH_3$, and $Ph{-}SnH_3$ are estimated to be weaker acids by at least 15 kJ mol^{-1} than the corresponding ethynyl derivatives. To gain some understanding of the origin of these differences, we have used the following isodesmic reactions:

$$HC{\equiv}C{-}XH_3 + Ph\text{-}H \rightarrow HC{\equiv}CH + Ph{-}XH_3 \qquad (7)$$

$$HC{\equiv}C{-}XH_2^{\,-} + Ph{-}H \rightarrow HC{\equiv}CH + Ph{-}XH_2^{\,-} \qquad (8)$$

which permit us to compare the effect of the XH_3 or XH_2^- on the stability of the phenyl or the ethynyl groups, as a function of the nature of the heteroatom. The results obtained at the G2-(MP2) level (See Figure 4) show that in general both the neutral and the anion are slightly destabilized by the aromatic moiety. For the carbon derivatives, however, this destabilization is practically equal for toluene and for its anion, and as a consequence, the acidity of toluene is about equal to that of propyne. For Si, Ge, and Sn aromatic derivatives, on the contrary, the destabilization of the anion is systematically greater (~15 kJ mol^{-1}) than the destabilization of the neutral, and therefore the phenyl derivative is a weaker acid than the corresponding ethynyl compound.

These findings are consistent with the electronic structure differences between deprotonated toluene and its Si, Ge, and Sn analogues, which have been discussed above.

Conclusions

The gas-phase acidity of vinyl-, ethynyl-, and phenylsilicon, -germanium, -and tin derivatives were measured by means of FT-ICR techniques and are in a good agreement with the theoretical estimates obtained through the use of either G2-type ab initio methods or B3LYP density functional theory calculations.

As expected, the acid strength increases down the group, although the acidity differences between Ge and Sn derivatives are already rather small. The acidifying effect of unsaturation is much larger for C- than for Si-, Ge-, and Sn-containing compounds because the allyl anion is better stabilized by resonance than its Si, Ge, and Sn analogues.

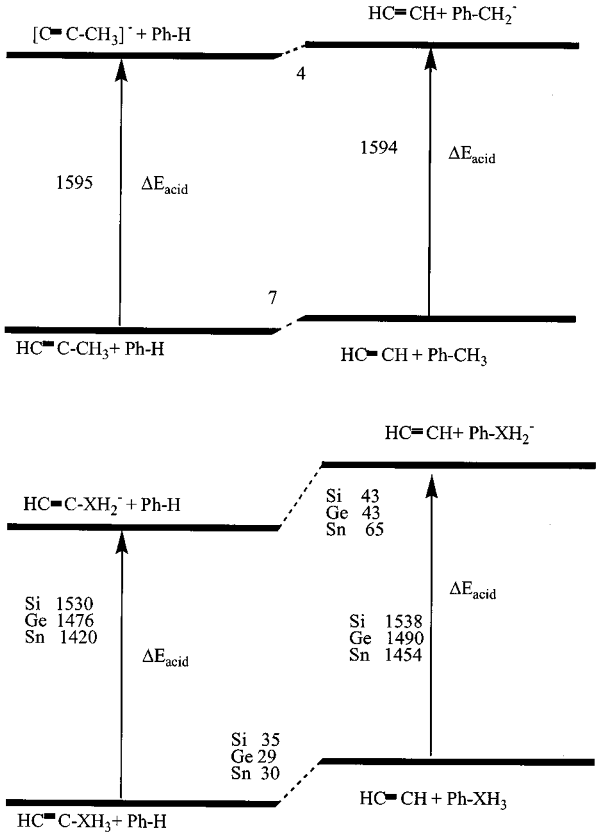


Figure 4. G2 calculated relative energies of species involved in the deprotonation processes of $CH{\equiv}C{-}XH_3$ vs $Ph{-}XH_3$ (X = C, Si, Ge, Sn) derivatives. For phenyl derivatives, the energies were evaluated at the G2(MP2) level. All values in kilojoules per mole.

As has been found before[3] for amines, phosphines, and arsines, the C, Si, Ge, and Sn α,β-unsaturated compounds are stronger acids than their saturated analogues. The enhanced acid strength of unsaturated compounds is due to a greater stabilization of the anion with respect to the neutral, because the electronegativity of the α,β-unsaturated carbon group increases with its degree of unsaturation.

The phenyl derivatives are systematically weaker acids by 15−20 kJ mol^{-1} than the corresponding ethynyl derivatives. Experimentally, toluene acidity is very close to that of propyne, because the deprotonation of propyne takes place at the ≡CH group rather than at the $-CH_3$ group.

Acknowledgment. This work has been partially supported by the DGES Project PB96-0067 and by the Picasso Project HF1999-0015. J.-C.G. thanks the PNP (INSU-CNRS) for financial support. We are grateful to Dr. Jean Escudié (Université Paul Sabatier, Toulouse) for a sample of phenylgermane. Bruker-France is gratefully acknowledged for help in improving the data system of the FT-ICR spectrometer at the University of Nice-Sophia Antipolis. A generous allocation of computational time at the CCC of the UAM is also acknowledged. We thank one of the reviewers for pointing out the interference of the HNO$^-$ ion from methyl nitrite, in measuring acidities relative to methanol.

Supporting Information Available: Details on the experiments carried out. Experimental relative ion gauge sensitivities. Experimental data concerning equilibrium and bracketing measurements. Values of the different exponents for Sn extended basis sets to be used with different ECPs. Harmonic vibrational frequencies of methylstannane. Ionization energy of tin. Estimated heat of formation of $(CH_3)_4Sn$. This material is available free of charge via the Internet at http:/pubs.acs.org.

JA004079J