Acidity Trends in α,β-Unsaturated Sulfur, Selenium, and Tellurium Derivatives: Comparison with C-, Si-, Ge-, Sn-, N-, P-, As-, and Sb-Containing Analogues

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Abstract: The gas-phase acidity of $CH_3{-}CH_2XH$ (X = S, Se, Te), $CH_2{=}CHXH$ (X = S, Se, Te) and PhXH (X = S, Se) compounds was measured by means of Fourier transform ion cyclotron resonance mass spectrometry. To analyze the role that unsaturation plays on the intrinsic acidity of these systems, a parallel theoretical study, in the framework of the G2 and the G2-(MP2) theories, was carried out for all ethyl, ethenyl (vinyl), ethynyl, and phenyl O-, S-, Se-, and Te-containing derivatives. Unsaturated compounds are stronger acids than their saturated analogues, because of the strong π-electron donor ability of the heteroatoms that contributes to a large stabilization of the unsaturated anions. Ethynyl derivatives are stronger acids than vinyl compounds, while phenyl derivatives have an intrinsic acidity intermediate between that of the corresponding vinyl and ethynyl analogues. The $CH_2{=}CHXH$ vinyl compounds (enol-like) behave systematically as slightly stronger acids than their $CH_3{-}C(H)X$ (keto-like) tautomers. Vinyl derivatives are stronger acids than ethyl compounds, because the anion stabilization attributable to unsaturation is greater than that undergone in the neutral compounds. Conversely, the enhanced acidity of the ethynyl derivatives with respect to the vinyl compounds is due to two concomitant effects, the stabilization of the anion and the destabilization of the neutral compound. The acidities of ethyl, vinyl, and ethynyl derivatives containing heteroatoms of Groups 14, 15, and 16 of the periodic table are closely related, and reflect the differences in electronegativity of the $CH_3CH_2{-}$, $CH_2{=}CH{-}$, and $CH{\equiv}C{-}$ groups.

Keywords: ab initio calculations • acidity • alkynes • chalcogens • mass spectrometry

Introduction

In 1989 Radom et al.[1] demonstrated by theoretical calculations the dramatic increase of acidity of ethynol relative to the corresponding saturated derivative, ethanol, in the gas phase. Since the publication of this article, we have demonstrated on experimental (Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometry) and theoretical grounds that such an increase of acidity also occurs for amines, phosphines, arsines,[2,3] silanes, germanes, and stannanes.[4] However, based on these results we cannot conclude that this increase of acidity does exist for any primary α,β-unsaturated derivatives of any element of the columns 2–16 of the periodic table. Such a generalization is not easy, because the scarcity of sufficiently stable primary vinyl and ethynyl heterocompounds limits the experimental part of this study. Even for arsenic or tin, it is only quite recently that the corresponding derivatives have been synthesized.[5–8] On the other hand, the high reactivity of other heterocom-

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pounds under FT-ICR conditions, such as the primary α,β-unsaturated antimony[9] or mercury derivatives,[10] did not allow us to measure their gas-phase acidity.

Alcohols and thiols are widely used as reagents in organic synthesis. For the following elements (selenium and tellurium),[11] it is well known that selenols are very important intermediates in many living systems,[12] whereas the studies devoted to the kinetically unstable tellurols are much more limited. For the heaviest elements of Group 16, the effect of unsaturation on intrinsic acidity, when compared to the saturated analogue, has never been established by experiments. The recent preparation by some of us at Rennes of ethene-selenol and ethenetellurol[13] prompted us to develop this general study.

In this paper we report a study of the gas-phase acidities of $CH_2{=}CHXH$ ($X = S$, Se, Te) and PhXH ($X = S$, Se) compounds. Ethynyl derivatives were not included in the experimental survey, because all attempts to synthesize them failed. Nevertheless, in the parallel theoretical study carried out, we have included all vinyl, ethynyl, and phenyl derivatives. For the sake of a more complete comparison we have added to these series of compounds that of the corresponding saturated ethyl derivatives, $CH_3{-}CH_2XH$ ($X = S$, Se, Te), as well as the corresponding oxygen-containing systems, whose experimental gas-phase acidities, when available, were taken from the literature.

Through the text, when comparing acidities, we have systematically used the terminology "stronger/weaker acidity", instead of "higher/smaller acidity" to avoid confusion between strength and numerical values, as stronger acidities correspond to smaller $\Delta_{acid}G$ or $\Delta_{acid}H$ and vice versa.

Results and Discussion

Structural considerations: Some structural aspects of the compounds under study deserve some attention. As it was found for similar unsaturated compounds containing C, Si, Ge, Sn, N, P, and As,[3,4] the calculated C–X bond length decreases in the order ethyl > vinyl > ethynyl (See Table 1). Also interesting and similarly to what was found before for α,β-unsaturated amines, phosphines, and arsines,[3] but at variance with what was found for hydrocarbons, silanes, germanes, and stannanes,[4] the decrease is larger for systems with second- and third-row heteroatoms (S and Se) than for those containing oxygen. Furthermore, this effect is observed both in the neutral compounds and in their deprotonated species. On going from the ethyl to the vinyl and ethynyl derivatives, the electronegativity of the group attached to the heteroatom increases, leading to a polarization of its charge density into the C–X bonding region. Consistently, the charge density at the C–X bond critical points (BCPs; See Table 1) increases and the bond shortens. Evidently, the polarizability of the heteroatom is larger in the anion and, therefore, the electron density accumulated into the C–X bonding region is also larger, explaining why in the unsaturated anions, with the only exception of the Te-derivatives, the C–X bond is shorter than in the corresponding neutral compound.

Let us focus now our attention on the structural effects of the deprotonation process of the unsaturated compounds. In all cases the C–C bond lengthens significantly, while the C–X bond, with the only exception of the Te derivatives, becomes shorter. It is also apparent from the bond lengths reported in Table 1 that these effects decrease down the group, with a maximum for the oxygen derivatives. The shortening of the C–X bond shows the tendency of this bond to become a double bond, as in a typical aldehyde function. On the other hand, an inspection of the natural bond orbital (NBO) second-order orbital interactions reveals that after deprotonation the heteroatom becomes an electron-rich center, and accordingly a good electron donor (See Table 2). As a matter of fact a quite strong interaction between the heteroatom lone-pairs and the π^*_{CC} antibonding orbital (σ^*_{CC} antibonding orbital in the case of the saturated compounds) is taking place. Evidently, the partial occupation of the π^*_{CC} (σ^*_{CC}) antibonding orbital results in the observed lengthening of the C–C bond. In addition, in line

Table 1. Bonding characteristics of CH_3CH_2XH, $CH_2{=}CHXH$, $CH{\equiv}CXH$ ($X = O$, S, Se, Te) compounds and their anions obtained by deprotonation at the XH group. Bond lengths[a] (R) are in Å and the charge densities[a] at the BCPs ($\rho(\mathbf{r})$) are in e au^{-3}.

CX Bond	O		S		Se		Te
	R	$\rho(\mathbf{r})$	R	$\rho(\mathbf{r})$	R	$\rho(\mathbf{r})$	R
neutral derivatives							
CH_3CH_2XH	1.427	0.260	1.819	0.186	1.963	0.149	2.251
$CH_2{=}CHXH$	1.374	0.279	1.759	0.204	1.907	0.160	2.194
$CH{\equiv}CXH$	1.324	0.315	1.698	0.212	1.820	0.171	2.149
phenyl	1.373	0.291	1.787	0.190	1.921	0.157	2.224
CC bond							
CH_3CH_2XH	1.516	0.266	1.520	0.258	1.521	0.257	1.528
$CH_2{-}CHXH$	1.333	0.353	1.337	0.350	1.336	0.351	1.346
$CH{\equiv}CXH$	1.215	0.372	1.220	0.388	1.220	0.389	1.232
phenyl	1.396	0.330	1.398	0.320	1.397	0.321	1.407
anions							
CX bond							
$CH_3CH_2X^-$	1.324	0.341	1.820	0.177	1.972	0.136	2.283
$CH_2{=}CHX^-$	1.275	0.367	1.735	0.198	1.880	0.154	2.208
$CH{\equiv}CX^-$	1.249	0.383	1.674	0.203	1.806	0.165	2.160
phenyl	1.273	0.370	1.736	0.193	1.880	0.158	2.236
CC bond							
$CH_3CH_2X^-$	1.558	0.243	1.528	0.255	1.524	0.256	1.526
$CH_2{=}CHX^-$	1.380	0.321	1.355	0.338	1.351	0.341	1.353
$CH{\equiv}CX^-$	1.246	0.350	1.238	0.372	1.234	0.378	1.242
phenyl	1.444	0.301	1.418	0.318	1.414	0.313	1.414

[a] Values obtained at the MP2/6–31G* level of theory.

Table 2. Second-order orbital interaction energies [kJ mol^{-1}] for RX$^-$ (X = O, S, Se, Te) anions.

X	R = CH_3CH_2– LP(X)→σ^*_{CC}	R = CH_2=CH– LP(X)→π^*_{CC}	R = CH≡C– LP(X)→π^*_{CC}	R = Ph LP(X)→π^*_{CC}
O	105	590	845	336
S	33	213	426	225
Se	23	159	326	198
Te	14	84	176	101

with our previous discussion, the interaction energy decreases down the group, because O$^-$ is a better electron donor than S$^-$, Se$^-$, and Te$^-$, due to its higher electronegativity. Also, the stronger electron-donation effect observed in $CH_3CH_2O^-$, indicates, as Smith et al. have already pointed out,[1] that the O$^-$ substituent is not only a good π-electron donor, but also a weak σ-electron donor. In that respect it is worth noting that for the three series of compounds, there is a very good linear correlation between the aforementioned orbital interaction energies and the lengthening of the C–C bonds (see Figure 1). The different slopes show that triple bonds are more difficult to stretch than double or single bonds. Similar good correlations (not shown in the figure) can be found between the C–C lengthening and the decrease of the charge density at the BCP. Consistently, a significant red shift of the C–C stretching frequency is found for all systems upon deprotonation (see Table 3). It is worth noting that our calculated stretching frequencies, when scaled by the empirical factor 0.893,[14] are in good agreement with available experimental data;[15–17] therefore, our estimates for the corresponding anions can be confidently assumed to be relatively accurate.

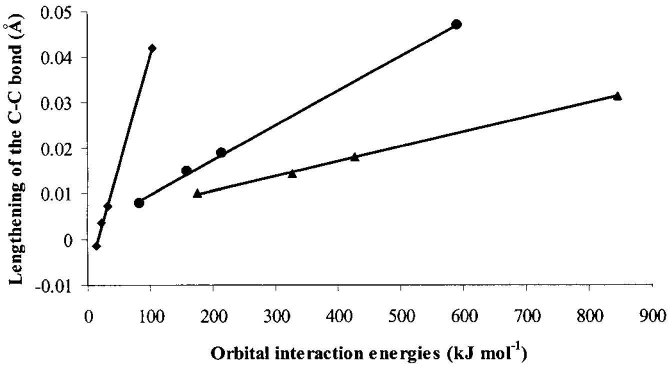


Figure 1. Linear correlations between the lengthening of the C–C bonds upon deprotonation of the XH group and the second-order interaction energies between the heteroatom lone pair and the σ^*_{CC} or π^*_{CC} antibonding orbital in the corresponding anion. These correlations obey the following equations (units of Å and kJ mol^{-1} for ΔR and E_{int} respectively): Ethyl derivatives (◆): $\Delta R = 4.76 \times 10^{-4} E_{int} - 0.0078$, $r^2 = 0.9997$; vinyl derivatives (●): $\Delta R = 7.62 \times 10^{-5} E_{int} + 0.0021$, $r^2 = 0.9989$; ethynyl derivatives (▲): $\Delta R = 3.22 \times 10^{-5} E_{int} + 0.0042$, $r^2 = 0.999$.

The NBO analysis also shows that for the anions a small charge donation takes place from the heteroatom lone-pair into an empty orbital of the substituted carbon atom. As before, this interaction decreases down the group and is reflected in the concomitant shortening of the C–X linkage. Consistently, the C–O stretching frequencies (see Table 3) appear normally blue-shifted. This is not the case for the C–S, C–Se, and C–Te stretching vibrations that shift only weakly. The reason for this is that although the deprotonation process leads to an increase of the corresponding force constant, there is also an increase in the reduced mass of the vibrational mode that nearly balances the first effect.

As far as the phenyl derivatives are concerned, the effects are similar in the sense that in the anion there is a π-donation from the lone pairs of the heteroatom towards the antibonding π-orbitals in which the *ipso*-carbon atom participates. Accordingly, these two C–C bonds become longer. Consequently, the two *ortho*-carbon atoms become electron deficient and polarize the π-cloud leading to an increase of the charge density into the other C–C bonds, which, accordingly, become slightly shorter.

Acidities: The calculated gas-phase acidities of the compounds under investigation are summarized in Table 4. The total energies of the neutral compounds and their anions are given in Table S1 of the Supporting Information. There is a good agreement between the calculated and experimental values,[18–24] considering the quite large errors due to the experimental difficulties encountered during acidity measurements on these rather unstable compounds. However, for the vinyl derivatives, the calculated acidities are systematically slightly stronger than the experimental ones. These differences might be due to the occurrence of isomerization processes along the deprotonation reaction. To investigate

Table 3. C–X and C–C stretching frequencies[a] [cm^{-1}] of R–XH (X = O, S, Se, Te) neutral compounds and their R–X$^-$ anions.

	O		S		Se		Te	
R	C–X	C–C	C–X	C–C	C–X	C–C	C–X	C–C
neutral compounds								
CH_3CH_2–	1217, (1061),[b] 1274	978, (883),[b] 1729	720, (663)[c]	1059, (963)[c]	606	1053	507	1083
CH_2=CH–	(1118),[d] 1169	(1663),[d] 2480	770	1835, 2365	642	1826	524	1650
CH≡C–	(1072)[d]	(2198)[d]	749	(2065)[d]	602	2358	452	2031
anions								
CH_3CH_2–	1335	890	726	1042	596	1034	488	1069
CH_2=CH–	1613[e]	1228	768	1758	618	1765	497	1612
CH≡C–	1338	2339	739	2265	577	2270	419	1947

[a] Values obtained at the HF/6–31G* level of theory. [b] Experimental values taken from reference [17]. [c] Experimental values taken from reference [16]. [d] Experimental values taken from reference [15]. [e] Strongly coupled with the C–C stretch.

Table 4. Calculated and experimental gas-phase acidities[a] [298 K, kJ mol^{-1}].

System	$\Delta_{acid}H°$(calcd)	$\Delta_{acid}G°$(calcd)	$\Delta_{acid}H°$(exptl)	$\Delta_{acid}G°$(exptl)
CH_3CH_2XH				
X=O	1587	1556	1583 ± 4.2[d] 1582 ± 8.4[e]	1555 ± 4.6[d] 1554 ± 8.8[e]
X=S	1490	1460	1486 ± 8.2[f]	1460 ± 8.4[f]
X=Se	1449	1420	–	1416 ± 8.4[g]
X=Te	1405	1377	–	1403 ± 12[g]
CH_2=C(H)XH				
X=O	1490	1460	1490[f]	
X=S	1444	1414	–	1432 ± 16[g]
X=Se	1415	1386	–	1406 ± 29[g]
X=Te	1382	1355	–	1382 ± 11[g]
CH_3–C(H)X[b]				
X=O	1541	1511	1531 ± 9.2[f]	1502 ± 8.4[f]
X=S	1455	1425	1456 ± 14[h]	1427 ± 13[h]
X=Se	1424	1394	–	–
X=Te	1380	1350	–	–
CH≡CXH				
X=O	1391	1380	–	–
X=S	1384	1360	–	–
X=Se	1364	1340	–	–
X=Te	1347	1329	–	–
PhXH[c]				
X=O	1457	1426	1466 ± 2.5[i] 1461 ± 8.8[j]	1432 ± 8.4[j]
X=S	1425	1397	1424 ± 8.8[k]	1395 ± 8.4[g] 1397 ± 8.4[k]
X=Se	1398	1369	–	1386 ± 10[g]
X=Te	1373	1344	–	–

[a] Unless otherwise stated calculated acidities were obtained at the G2 level. [b] To yield the most stable anion CH_2=C(H)X$^-$. [c] Values obtained at the G2(MP2) level of theory. [d] Reference [18]. [e] Reference [19]. [f] Reference [20]. [g] This work. [h] Reference [21]. [i] Reference [22]. [j] Reference [23]. [k] Reference [24].

that possibility we have examined also the gas-phase acidity of the corresponding $CH_3C(H)X$ tautomers. As illustrated in the diagrams of Figure 2, in all cases, with the exception of the tellurium derivative, the keto tautomer is estimated to be slightly more stable than the corresponding enol form. Conversely, the most stable anion corresponds systematically to that in which the proton is lost from the XH group of the vinyl derivative, while the CH_3–CX^- isomer lies much higher in energy. This means that both CH_2=C(H)XH and CH_3–C(H)X compounds yield, upon deprotonation, a common anion (CH_2=C(H)X$^-$). Since the CH_3–C(H)X isomer is more stable than the vinyl one, with the only exception of the tellurium derivative, for which both isomers are very close in energy, the CH_3–C(H)X form is systematically a weaker acid than the CH_2=C(H)XH isomer. Quite interestingly, for the sulfur and selenium derivatives the estimated acidity for the CH_3–C(H)X isomer is quite close to the experimental one measured for the vinyl derivative, CH_2=C(H)XH, so we decided to investigate whether the CH_2=C(H)XH→CH_3–C(H)X isomerization can be easily produced in the gas phase. For this purpose we have evaluated the activation barrier associated with the corresponding 1,3 H transfer at the G2 level of theory. The estimated barriers for both S (317 kJ mol^{-1}) and Se (331 kJ mol^{-1}) derivatives are very large, and, therefore, in the absence of some extra-catalytic effects, we have to conclude that the CH_2=C(H)XH→CH_3–C(H)X isomerization would not take place under normal ICR experimental conditions.

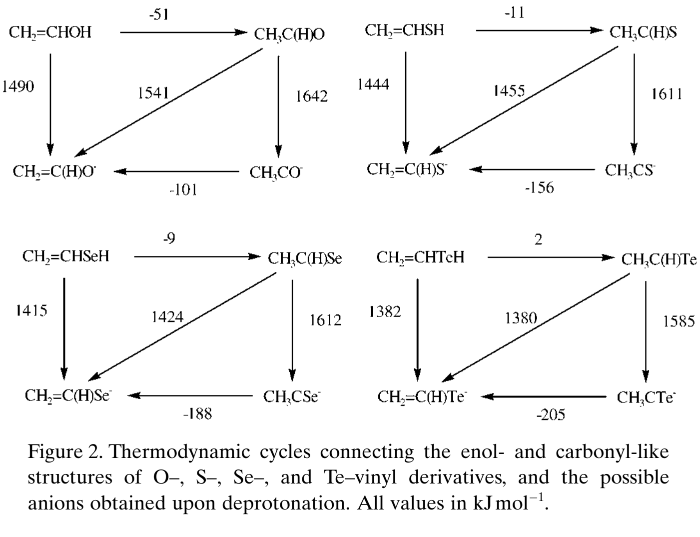


Figure 2. Thermodynamic cycles connecting the enol- and carbonyl-like structures of O–, S–, Se–, and Te–vinyl derivatives, and the possible anions obtained upon deprotonation. All values in kJ mol^{-1}.

Acidity trends: As was already found for other α,β-unsaturated compounds,[3,4] the acidity of the system increases with its degree of unsaturation, so vinyl derivatives are more acidic than ethyl derivatives, and ethynyl derivatives more acidic than the vinyl ones. In this respect, it is interesting to note that phenyl derivatives have an intrinsic acidity intermediate between that of vinyl and ethynyl compounds. The acidity enhancement on going from saturated to unsaturated systems may have a double origin, either the neutral compound becomes less stable, or the anion becomes more stable, or both. The relative weight of these two effects may be easily analyzed by using appropriate isodesmic reactions, as shown graphically in Figure 3. The first conspicuous feature in this figure is that the anions are increasingly stabilized as the unsaturation of the system increases. This is a clear reflection of the π-electron donor ability of the different heteroatoms that we discussed above, which is enhanced upon deprotonation. Hence, on going from the ethyl to the vinyl derivatives (see Figure 3a), one observes a stabilization of both the neutral compound and the anion; however, since this effect is much larger in the latter, the net effect is an acidity strengthening.

The situation is different on going from the vinyl to the ethynyl derivatives (see Figure 3b). As was already pointed out by Radom et al.[1] for the particular case of vinyl alcohol and ethynol, the neutral compounds are clearly destabilized because of the unfavorable σ interaction of the OH group with the triple bond. Therefore, the enhanced acidity of ethynol with respect to vinyl alcohol is due to two concomitant factors, the stabilization of the anion and the destabili-

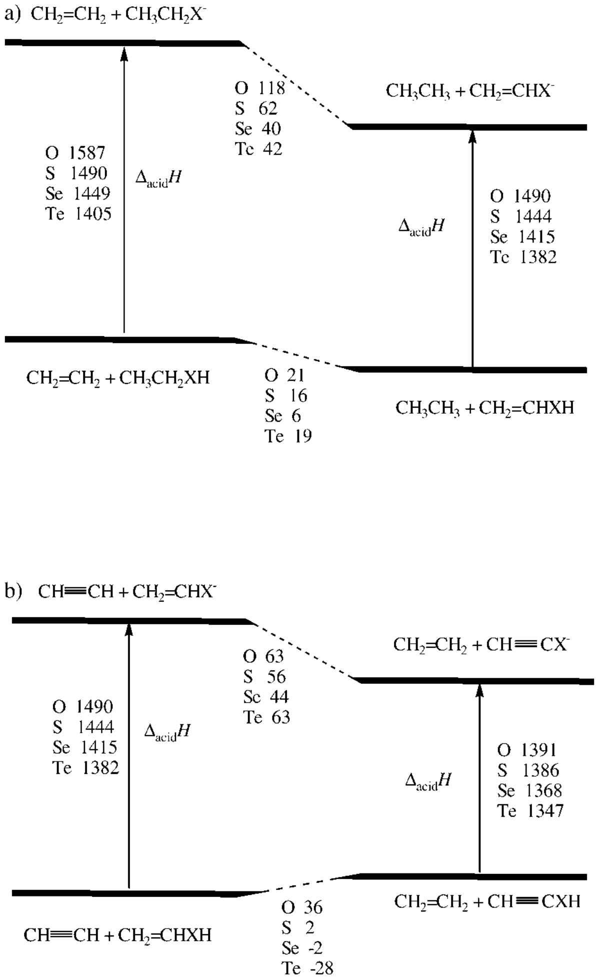


Figure 3. G2 calculated relative enthalpies of species involved in the deprotonation processes of a) CH_3CH_2XH versus $CH_2=CHXH$ and b) $CH_2=CHXH$ versus $HC\equiv CXH$ (X = O, S, Se, Te). All values in kJ mol^{-1}.

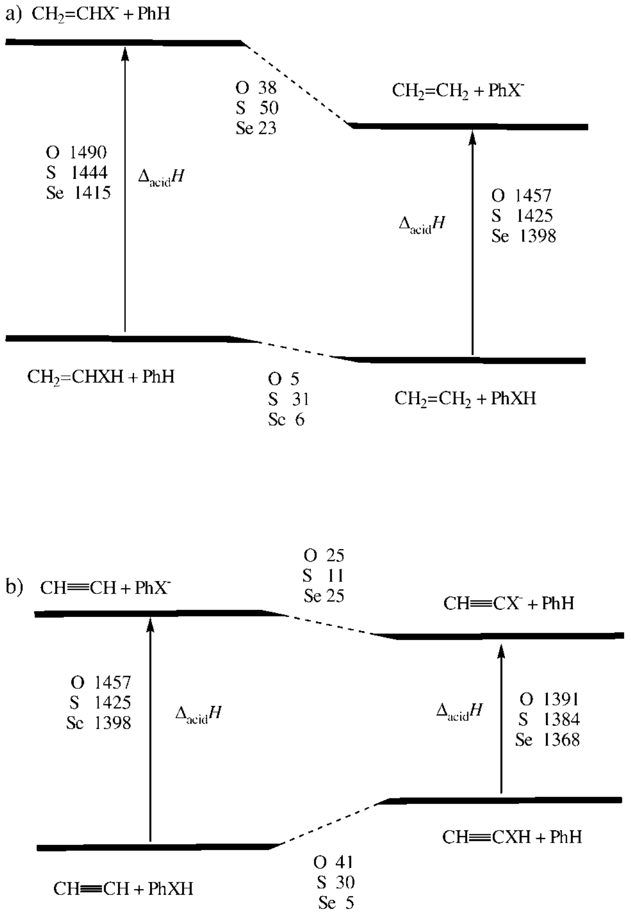


Figure 4. G2 calculated relative enthalpies of species involved in the deprotonation processes of a) $CH_2=CHXH$ versus PhXH and b) $HC\equiv CXH$ versus PhXH (X = O, S, Se, Te). All values in kJ mol^{-1}.

zation of the neutral compound by replacing a double bond with a triple bond.

The situation is qualitatively similar for the corresponding sulfur derivatives. However, since sulfur is less σ-electron-withdrawing than oxygen, the destabilization of $HC\equiv CSH$ with respect to $CH_2=CHSH$ is much smaller than that found for the corresponding O-containing compounds. Since tellurium is a fourth row atom, its electronegativity is smaller than that of a $HC\equiv C-$ group, and behaves as a σ-electron donor, thereby also stabilizing the neutral system.

Since in other ethynyl derivatives, such as propyne ($HC\equiv C\text{-}CH_3$), the proton is lost from the $\equiv CH$ group,[4] we have investigated this possibility for ethynol and the S-, Se-, and Te-containing analogues. However, our results showed that the $^-C\equiv C{-}XH$ (X = O, S, Se, Te) anion was systematically less stable (204, 166, 177, and 191 kJ mol^{-1}, respectively) than the $HC\equiv CX^-$ (X = O, S, Se, Te) anion. Hence, although these compounds were not experimentally examined, it is expected that they will all behave as XH acids and not as $\equiv CH$ acids.

Let us analyze now, why the phenyl derivatives have an intrinsic acidity intermediate between the acidities of the corresponding vinyl and ethynyl compounds, taking advantage again of appropriate isodesmic reactions as illustrated in Figure 4. It seems evident that the acidity enhancement on going from vinyl to phenyl derivatives is associated with a larger stabilization of the anion by the phenyl group; this stabilization energy being larger than that experienced by the corresponding neutral compound (see Figure 4a). However, the increase in acidity on going from the phenyl derivatives to the corresponding ethynyl ones is the result of the stabilization of the anion and of simultaneous destabilization of the neutral compound due to the unfavorable interaction of the XH groups with the triple bond already mentioned (see Figure 4b). It can be also observed that these effects decrease down the group.

Comparison with C-, Si-, Ge-, Sn-, N-, P-, As-, and Sb-containing analogues: Since the acidities of most of these compounds were determined only recently, we thought it of interest to compare the intrinsic acidities of the α,β-unsaturated compounds of Groups 14, 15, and 16 of the periodic table. For the first two groups we have used the intrinsic acidities reported in the literature[3,4] calculated at the same level used in the present paper. For the particular case of Group 15, only the acidities of the amines, phosphines, and arsines have been calculated before, so for the sake of completeness we have evaluated those of the corresponding ethyl, vinyl, and ethynyl stibines by using a similar approach to that employed for Te-containing compounds and the extended G2-type basis set reported by González et al.[25]

As expected compounds of Group 15 and 16 are stronger acids than compounds of Group 14, showing that more electronegative heteroatoms confer a greater acidity to the system. It is worth noting that there is an extremely good linear correlation between the calculated acidities of the three series of compounds (see Figure 5), which shows the existence of proportionality among the acidity increase down the group for the three series. A similar correlation has been reported between the experimental gas-phase acidities of the hydrides series HX and YH_2, with X and Y being elements of Groups 17 and 16, respectively.[26]

For ethyl derivatives, the slope of the correlations between the calculated acidities of compounds of Groups 15 and 16 versus acidities of compounds of Group 14 is significantly smaller than unity. This shows that the acidity of compounds of Groups 14 increases faster down the group than that of compounds of Groups 15 and 16 (see Figure 5a), similarly to what is found for the corresponding hydrides (CH_4, SiH_4, GeH_4, NH_3, PH_3, AsH_3, H_2O, SH_2, SeH_2).[15] As shown in Figure 5a, both slopes are rather similar, which means that the acidity of compounds of Group 16 is only slightly less sensitive to changes in the acidic function than that of the analogues of Group 15. Actually, the correlation between both series of acidities fulfills Equation (1) in which the slope is quite close to unity.

$$\begin{gathered}\Delta_{\text{acid}}G(\text{Group 16}) = 0.9617\Delta_{\text{acid}}G(\text{Group 15}) - 14.776 \\ r^2 = 0.9927\end{gathered} \tag{1}$$

What is important, however, is that this is not the case when the unsaturated vinyl and ethynyl derivatives are considered (see Figures 5b, c). Again, for compounds of Group 14, the acidity is more sensitive to changes in the acidic function than that of Groups 15 and 16; however, now the slopes of the correlations are quite different, which means that for compounds of Group 15 the acidity changes down the group faster than for derivatives of Group 16. Actually, for vinyl and ethynyl derivatives the correlations obey Equations (2) and (3), with slopes much smaller than unity.

$$\begin{gathered}\Delta_{\text{acid}}G(\text{Group 16}) = 0.7826\Delta_{\text{acid}}G(\text{Group 15}) + 258.27 \\ r^2 = 0.9975\end{gathered} \tag{2}$$

$$\begin{gathered}\Delta_{\text{acid}}G(\text{Group 16}) = 0.6611\Delta_{\text{acid}}G(\text{Group 15}) + 402.38 \\ r^2 = 0.9987\end{gathered} \tag{3}$$

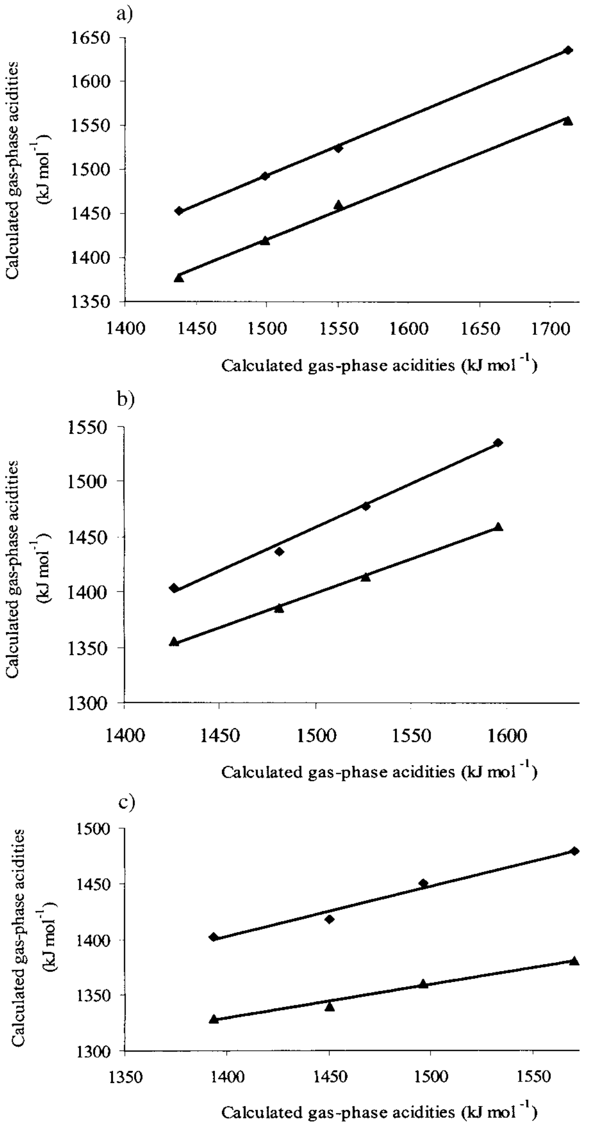


Figure 5. Linear correlations between the gas-phase acidities (kJ mol^{-1}) of: a) $CH_3CH_2{-}ZH_3$ (Z = C, Si, Ge, Sn) versus $CH_3CH_2{-}YH_2$ (Y = N, P, As, Sb) (◆) and $CH_3CH_2{-}XH$ (X = O, S, Se, Te) (▲), which obey the equations: $\Delta_{\text{acid}}G°(\text{Group 14}) = 0.6739\Delta_{\text{acid}}G°(\text{Group 15}) + 482.1$, $r^2 = 0.9994$; $\Delta_{\text{acid}}G°(\text{Group 14}) = 0.6495\Delta_{\text{acid}}G°(\text{Group 16}) + 446.72$, $r^2 = 0.9964$; b) $CH_2{=}CH{-}ZH_3$ (Z = C, Si, Ge, Sn) versus $CH_2{=}CH{-}YH_2$ (Y = N, P, As, Sb) (◆) and $CH_2{=}CH{-}XH$ (X = O, S, Se, Te) (▲), which obey the equations: $\Delta_{\text{acid}}G°(\text{Group 14}) = 0.7885\Delta_{\text{acid}}G°(\text{Group 15}) + 275.31$, $r^2 = 0.9937$; $\Delta_{\text{acid}}G°(\text{Group 14}) = 0.6193\Delta_{\text{acid}}G°(\text{Group 16}) + 470.26$, $r^2 = 0.9986$; c) $CH{\equiv}C{-}ZH_3$ (Z = C, Si, Ge, Sn) versus $CH{\equiv}C{-}YH_2$ (Y = N, P, As, Sb) (◆) and $CH{\equiv}C{-}XH$ (X = O, S, Se, Te) (▲), which obey the equations: $\Delta_{\text{acid}}G°(\text{Group 14}) = 0.4514\Delta_{\text{acid}}G°(\text{Group 15}) + 769.8$, $r^2 = 0.9750$; $\Delta_{\text{acid}}G°(\text{Group 14}) = 0.3000\Delta_{\text{acid}}G°(\text{Group 16}) + 908.96$, $r^2 = 0.9842$.

These findings can be explained in terms of the electronegativity gap between the group attached to the heteroatom and that of the heteroatom itself. The electronegativity of an ethyl group is rather small relative to that of the heteroatom, whether the heteroatom belongs to Group 15 or 16, so the acidity trends are not very different from those of the corresponding hydrides. The perturbation is, however, larger in the vinyl and ethynyl derivatives, because

$CH_2{=}CH{-}$ and $HC{\equiv}C{-}$ groups are more electronegative than a $CH_3CH_2{-}$ group, and the differences between compounds containing heteroatoms of Groups 15 and 16 become necessarily more evident. In fact, although an OH group is still clearly more electronegative than a $HC{\equiv}C{-}$ group, an SH group is not. Therefore the intrinsic acidity of the $-SH$ group will be enhanced by a $HC{\equiv}C{-}$ group, to a greater extent than that of the $-OH$ group, and therefore the acidity gap must become smaller.

Conclusion

As it has been found before for amines, phosphines, and arsines, as well as for silanes, germanes, and stannanes, α,β-unsaturated compounds containing O, S, Se, and Te as heteroatoms are stronger acids than their saturated analogues, because the strong π-electron donor ability of the heteroatoms contributes to a significant stabilization of the unsaturated anions.

This electron donation, which populates the σ^*_{CC} or π^*_{CC} antibonding orbitals, results in a systematic lengthening of the C–C bond upon deprotonation; this is also reflected in a sizable red shifting of the C–C stretching frequency. Simultaneously, a shortening of the C–X bond is also observed.

Ethynyl derivatives are stronger acids than vinyl compounds, while phenyl derivatives have an intrinsic acidity intermediate between that of the corresponding vinyl and ethynyl analogues. The $CH_2{=}CHXH$ vinyl compounds behave systematically as slightly stronger acids than their $CH_3{-}C(H)X$ isomers. Vinyl derivatives are stronger acids than ethyl compounds, because the stabilization undergone by the anion on going from the saturated to the unsaturated system is greater than that undergone by the neutral compound. The enhanced acidity of the ethynyl derivatives with respect to the vinyl compounds is due to two concomitant effects, the stabilization of the anion and the destabilization of the neutral compound.

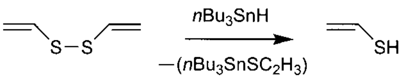
Similar arguments explain why phenyl derivatives are stronger acids than the corresponding vinyl analogues, but weaker acids than the ethynyl ones.

The acidities of ethyl, vinyl, and ethynyl derivatives containing heteroatoms of Groups 14, 15, and 16 of the periodic table are closely related. The linear correlations found between the acidities of the different series of compounds show that, as expected, the derivatives of Groups 14 and 16 are the less and the most acidic, respectively. Quite importantly, however, the acidity differences change significantly from ethyl to vinyl and to ethynyl derivatives, reflecting the different electronegativity of $CH_3CH_2{-}$, $CH_2{=}CH{-}$, and $CH{\equiv}C{-}$ groups.

Experimental Section

Materials: Tetraethyleneglycol dimethyl ether, selenium, tellurium, ethanethiol, thiophenol, phenyl selenol, and diphenyldiselenide were purchased from ACROS and used without further purification, except phenyl selenol which was purified by distillation in vacuo. Divinyldisulfide,[27] diethyl-[28] and divinyldiselenide,[29] and diethyl-[30] and divinylditelluride[31] were prepared as previously reported.

General procedure for the preparation of low-boiling thiol,[32] selenols,[13,33] and tellurols[13,33] [Eqs. (4)–(6)]:


(4)

$$\mathrm{R{-}Se{-}Se{-}R} \xrightarrow[-(n\mathrm{Bu_3SnSeR})]{n\mathrm{Bu_3SnH}} \mathrm{R{-}SeH} \qquad \mathrm{R{=}Et,\ CH_2{=}CH} \tag{5}$$

$$\mathrm{R{-}Te{-}Te{-}R} \xrightarrow[-(n\mathrm{Bu_3SnSeR})]{n\mathrm{Bu_3SnH}} \mathrm{R{-}TeH} \qquad \mathrm{R{=}Et,\ CH_2{=}CH} \tag{6}$$

Caution: Selenols and tellurols are potentially highly toxic. All reactions and handling should be carried out in a well-ventilated hood.

Ethenethiol, selenols, and tellurols were prepared starting from the corresponding disulfide, diselenide, or ditelluride by the approach reported for etheneselenol[13,29] and using the apparatus described in reference [29]. A two-necked 50 mL flask containing the precursor (2 mmol in 10 mL of tetraglyme) was fitted on a vacuum line equipped with two traps, and the solution was degassed. Tributyltin hydride (0.95 g, 3 mmol) was then added very slowly (20 min) at room temperature with a syringe through the septum. During and after the addition, thiol, selenol, or tellurol was distilled off in vacuo (10^{-1} mbar) from the reaction mixture. A cold trap (−60 °C) selectively removed the less volatile products and the expected product was condensed in a second trap cooled at −120 °C and equipped with two stopcocks. At the end of the reaction, the stopcocks were closed and the trap, immersed in a liquid nitrogen bath, was connected to the mass spectrometer inlet.

FT-ICR experiments: Gas-phase acidity measurements were performed by bracketing or proton-transfer equilibrium-constant determination. The general methodology is very similar to that used in previous work[3,4] on similar compounds of Groups 14 and 15 and is briefly described. Proton-transfer equilibrium measurements were conducted on an electromagnet Fourier-transform ion cyclotron resonance (FT-ICR) mass spectrometer. For equilibrium constant determinations, variable pressure ratios between the unknown acid AH under study and the reference compound RefH were used, with total pressures (read on a Bayard–Alpert ion gauge) in the range 2×10^{-5} to 8×10^{-5} Pa. Relative (to N_2) sensitivities S_r of the Bayard–Alpert gauge were estimated by using the Bartmess and Georgiadis equation [Eq. (7)].[34]

$$S_r = 0.36\alpha + 0.30 \tag{7}$$

The molecular polarizability α was taken as α(ahc), calculated by using the atomic hybrid components (τ_A(ahc)) approach of Miller.[35] From a previous determination of $S_r(TeH_2)$,[26] τ_A(ahc) of tellurium was estimated to be 8.92 $Å^{3/2}$. A τ_A(ahc) value for selenium of 6.39 $Å^{3/2}$ was interpolated from a linear relationship between $[\tau_A(\mathrm{ahc})]^2/N$ (N being the number of electrons in the atom) and the atomic ionization cross section of Otvos and Stevenson[36] for H, O, S, and Te.

Negative ions were generated by proton abstraction from the neutral reactant by $t\mathrm{BuO}^-$, which was obtained through dissociative electron capture at 0.1 eV (nominal) of tBuONO, introduced in the spectrometer at a partial pressure of about 10^{-5} Pa. For two compounds (CH_3CH_2SeH and PhSH), we were able to determine equilibrium constants K and $\Delta\Delta_{\mathrm{acid}}G^0$ by monitoring the proton exchange for about 10 s [Eqs. (8) and (9)].

$$\mathrm{AH} + \mathrm{Ref}^- \xrightarrow{K} \mathrm{RefH} + \mathrm{A}^- \tag{8}$$

$$\Delta\Delta_{\mathrm{acid}}G^0 = -RT\ln K \tag{9}$$

Equilibrium constants were obtained at an ICR cell temperature of 338 K. Literature values of gas-phase acidities $\Delta_{acid}G°$ of RefH[15] refer to the standard temperature of 298.15 K. The reported absolute $\Delta_{acid}G$ are not corrected for the 338 to 298.15 K temperature change, as such corrections were assumed to be minor with respect to other experimental uncertainties. Uncertainties on relative acidities $\Delta\Delta_{acid}G$ are of this order, but the uncertainties on the absolute acidities are dominated by the uncertainty on the reference scale, which has been estimated[15] to be about 2 $kcal\,mol^{-1}$ or 8.4 $kJ\,mol^{-1}$, and therefore applied to our $\Delta_{acid}G$ given in Table 5. When β-dicarbonyl compounds are used as references, additional uncertainties may arise from variations in their effective acidity due to tautomeric displacement induced by changes in experimental conditions. For various reasons (impurities, secondary reactions, unstable compounds), in most cases equilibrium conditions could not be reached, and acidities were estimated from bracketing experiments. Ref^- or A^- ions were isolated in turn, and the reformation of the other ion was monitored for 2–10 s, leading to the qualitative acidity order. When $CH_2{=}CHTeH$ was bracketed, we found that for three references the reformation of competing ions was in both directions: the acidity order was not clearly established and it was concluded that RefH and AH were close in acidity, probably within ±5–10 $kJ\,mol^{-1}$. In the case of vinyl tellurol, EtTeH was always present as an impurity. It was used as a bracketing standard, as well as HCl, because Cl^- was present due to chlorinated impurities. Uncertainties on bracketed acidities correspond to two times the standard deviation (on the mean value) estimated from the range between the two closest standards. For vinyl tellurol, the mean acidity value given was calculated from the acidities of the three standards giving proton exchange in both directions. PhTeH could not be measured because of its low vapor pressure. All experimental data concerning equilibrium and bracketing measurements are reported in Table 5.

Table 5. Experimental gas-phase acidities [$kJ\,mol^{-1}$, 298.15 K].

AH	RefH	$\Delta_{acid}G°$ (RefH)[a]	$\Delta\Delta_{acid}G°$[b]	$\Delta_{acid}G°$ (AH)
CH_3CH_2SeH	CF_3COMe	1431	-10.65 ± 0.94	
	$MeCOCH_2COMe$	1409	3.33 ± 0.54	1416 ± 8.4[c]
CH_3CH_2TeH	$MeCOCH_2COMe$	1409	<0	
	PhSH	1397	>0	1403 ± 12[d]
	$3\text{-}CF_3C_6H_4OH$	1391	>0	
$CH_2{=}CHSH$	$PhCH_2CN$	1440	<0	
	EtCOOH	1424	>0	1432 ± 16[d]
$CH_2{=}CHSeH$	*n*PrCOOH	1420	<0	
	$3\text{-}CF_3C_6H_4OH$	1391	>0	1406 ± 29[d]
$CH_2{=}CHTeH$	CH_3CH_2TeH	1403	$\leqslant 0$	
	$3\text{-}CF_3C_6H_4OH$	1391	≈ 0	
	$4\text{-}CF_3C_6H_4OH$	1381	≈ 0	
	HCl	1374	≈ 0	1382 ± 11[d]
	CF_3COCH_2COMe	1347	$\geqslant 0$	
PhSH	$PhCOCH_2COMe$	1393	0.25 ± 0.06	
	$3\text{-}CF_3C_6H_4OH$	1391	6.43 ± 0.20	1395 ± 8.4[c]
PhSeH	$3\text{-}CF_3C_6H_4OH$	1391	<0	
	$4\text{-}CF_3C_6H_4OH$	1381	>0	1386 ± 10[d]

[a] Reference [15]. [b] Gibbs energies for the reaction $AH + Ref^- \rightarrow A^- + RefH$ (at 338 K, see Experimental Section). [c] The indicated uncertainty corresponds to the uncertainty on the reference acidity scale. [d] The indicated uncertainty corresponds to twice the estimated standard deviation, see text.

Computational methods: The gas-phase acidities of the compounds under investigation were calculated by using the G2 theory,[37] as implemented in the Gaussian 98 series of programs.[38] The G2 theory is a composite procedure based on the 6–311G(d,p) basis set and several basis extensions, in which electron correlation effects are treated at the MP4 and QCISD(T) levels of theory. The final energies were effectively at the QCISD(T)/6–311+G(3df,2p) level, assuming that basis set effects on the correlation energies were additive. A small empirical correction (HLC) to accommodate remaining deficiencies was finally added as well as the corresponding zero-point energy (ZPE) correction, estimated at the HF/6–31G* level. The corresponding entropy changes were also evaluated at the HF/6–31G* level. The reader is addressed to reference [37] for a complete description of this method. G2 theory has been shown to reproduce gas-phase acidities within ±4 $kJ\,mol^{-1}$, the so-called chemical accuracy. A similar accuracy was found when extensions of this theory to molecules containing third-row elements were applied. In addition, an assessment of this method for the computation of enthalpies of formation has been published.[39,40] For the larger systems, for example, the phenyl derivatives, for which the G2 formalism can become prohibitively expensive, we used the cheaper G2(MP2) method.[41] In previous work, we have found that this simplified version of the G2 theory yielded reliable acidity values.

For Te-containing compounds, we used the SKBJ relativistic potential of Stevens et al.,[42] which accounts for the most important relativistic effects in conjunction with the basis set proposed by Sanz et al.[43] For geometry optimizations and harmonic frequency calculations the aforementioned effective core potential was used together with the [4,1]+d basis for Te,[43] whereas for the first-, second-, and third-row atoms, a 6–31G(d) basis set was adopted. Hereafter, for the sake of simplicity we will refer to this basis set as 6–31G(d). The corresponding final energies were evaluated by using the (6s,6p,3d,1f) G2-type basis set[43] for Te and a 6–311+G(3df,2p) basis set expansion for the remaining atoms of the system. Again for the sake of simplicity the (6s,6p,3d,1f) basis for Te will be named hereafter as a 6–311+G(3df,2p) basis. In this respect it is worth noting that Glukhovtsev et al.[44] 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 (ECP), yields results comparable in accuracy to those obtained in all-electron calculations.

The bonding characteristics of the different species were investigated by using the atoms in molecules (AIM) theory.[45] For this purpose, we located the bond critical points (BCPs) by means of the AIMPAC series of programs.[46] We also employed the natural bond orbital (NBO) method[47] to carry out a second-order perturbation analysis of the orbital interactions between the heteroatom and the rest of the molecule, in order to estimate the σ- and π-electron donor ability of the former, and its role in the stabilization of the anions produced upon deprotonation.

To check the reliability of the G2(ECP) approach adopted for the calculation of the intrinsic acidity of Te-containing compounds, we evaluated the gas-phase acidity of TeH_2, which, to the best of our knowledge, is the only experimental acidity of tellurium-containing systems available. Our G2(ECP) calculated value, $\Delta_{acid}H = 1369\ kJ\,mol^{-1}$, is in very good agreement with the experimental value reported by Freidhoff et al.[48] ($\Delta_{acid}H = 1370.3 \pm 3.3\ kJ\,mol^{-1}$) obtained from photoelectron spectroscopy data on TeH^-, but is somewhat smaller than the value measured by some of us in Nice[26] by means of proton transfer equilibrium techniques ($\Delta_{acid}H = 1385 \pm 8.8\ kJ\,mol^{-1}$).

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