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Vinyl- and ethynylsilanes, -germanes and -stannanes. A new case of dissociative proton attachment†

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ABSTRACT: The gas-phase protonation of $H_2C{=}C(H)XH_3$ and $HC{\equiv}CXH_3$ (X = Si, Ge, Sn) compounds was investigated through the use of high-level density functional theory methods. The structures of neutral and protonated species were optimized at the B3LYP/6–31G* level of theory, while the final energies were obtained by single-point B3LYP/6–311 + G(3df,2p) calculations. In the gas phase, vinyl- and ethynylsilanes, -germanes and -stannanes behave as carbon bases of moderate strength, with the only exception of vinylstannane, which is predicted to be about 20 kJ mol^{-1} more basic than ammonia. In all cases C_α protonation is the most favorable process. This protonation is followed by a C—X bond cleavage, so that the protonated form corresponds to a tightly bound complex between ethylene (or acetylene) and the corresponding XH_3^+ cation. This implies that dissociative proton attachments can be observed when the basic center is an atom of low electronegativity, provided that the other atoms bonded to it are much less electronegative than the basic center itself, and that the fragments formed as products of the dissociation are intrinsically stable. Copyright © 2002 John Wiley & Sons, Ltd.

KEYWORDS: proton affinity; dissociative proton attachment; vinyl- and ethynylsilanes, -germanes and -stannanes

INTRODUCTION

Ion–molecule gas-phase interactions are unavoidably accompanied by a more or less intense charge density reorganization of the neutral species. These effects reach their maximum expression when the attacking ion is a proton, which creates a strong coulombic field. The first effect is a significant polarization of the base and the final result is the formation a new covalent bond between the active site of the neutral species and the incoming proton. We have shown[1] that these charge redistributions result in an activation of the bond in which the basic center participates only when the active site is the most electronegative atom. In contrast, if protonation takes place on the less electronegative atom, the corresponding bond becomes reinforced. Consistently, when the basic site is the more electronegative atom the corresponding heterolytic bond dissociation energy decreases significantly.[2,3] In the limit of very electronegative basic centers, a spontaneous heterolytic cleavage can be expected, and a dissociative proton attachment should be observed. We have proved this, on both theoretical and experimental grounds, using fluoro- and chloroadamantane as suitable benchmark cases.[4] For both systems, gas-phase protonation, which takes place at the halogen atom, leads to a heterolytic cleavage of the C—F (or C—Cl) bond. Accordingly, the equilibrium structure predicted by means of *ab initio* calculations for the protonated species corresponds to an ion–dipole complex between adamantyl cation and a neutral molecule of hydrogen fluoride or hydrogen chloride, respectively. These theoretical predictions are in line with the experimental evidence, which shows unambiguously that after the protonation the ion detected has, in both cases, the mass of the adamantyl cation.

This experimental observation would be used in a posteriori study to generate, for the first time, a quantitative stability scale for the bridgehead and other bulky carbocations.[5] The advantage of generating these carbocations by dissociative proton attachment of their halogen derivatives or the corresponding alcohols is that after the process in which a hydrogen halide or á water molecule is lost, the carbocation remains with very little (if any) excess energy, so that it cannot undergo fragmentation or isomerization, as is often the case when using other techniques such as electron ionization.

A related question needs to be answered: is it possible

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to observe dissociative proton attachment processes when the basic center is not very electronegative? According to Alcami *et al.* rule,[1] the bond activation upon protonation depends on the relative electronegativity of the atoms of the bond rather than on their absolute electronegativities. This means that a dissociative proton attachment could be observed even when the basic center is not very electronegative, provided that the other atom of the bond is significantly less electronegative. A second condition to be fulfilled is for the two fragments generated in the heterolytic bond cleavage to be very stable.

The SiH_3, GeH_3 and SnH_3 substituted derivatives of ethylene and acetylene are good candidates for dissociative proton attachment. We have recently studied the gas-phase acidity of these systems,[6] but all the attempts to determine their basicity led to reactions others than simple proton exchange. In particular, the protonated molecules rapidly disappeared. The important point is that the existence of a C=C or a C≡C unsaturated moiety opens up the possibility that the basic center is a carbon atom. Hence, for C_α protonation, the basic center will be more electronegative than the other atom (Si, Ge, Sn) of the bond, and a dissociative proton attachment would, in principle, be possible. The aim of this paper is to show, through the use of high-level density functional theory calculations, that C_α protonation is thermodynamically favored over C_β protonation and that indeed it corresponds to a dissociative proton attachment process.

COMPUTATIONAL DETAILS

The theoretical treatment of the different species included in this work was carried out by using the B3LYP density functional theory (DFT) approach as implemented in the Gaussian 98 series of programs.[7] This method combines Becke's three-parameter non-local hybrid exchange potential[8] with the non-local correlation functional of Lee, Yang and Parr.[9] This formalism has been found to be very reliable as far as the description of ion–molecule complexes is concerned.[10–13] In general, geometries obtained using the aforementioned DFT method are in fairly good agreement with experimental values[14–19] and the harmonic vibrational frequencies are closer to experiment than those obtained by using other correlated methods such as MP2.

In our study, the geometries and harmonic vibrational frequencies of Si- and Ge-containing compounds were obtained at the B3LYP/6–31G* level. For the corresponding stannanes we used the basis set reported in Ref. 6, together with the Stuttgart relativistic large-core effective core potential (ECP),[20] which was used for the study of the gas-phase acidity of the same systems, with reasonably good results. It should be noted that this ECP takes implicitly into account the most important relativistic effects. The final energies of neutral and protonated silanes and germanes were obtained by single-point calculations carried out at the B3LYP/6–311 + G(3df,2p) level. For the case of the Sn derivatives, the extended basis developed in Ref. 6 was used. For the sake of simplicity, we will designate these calculations also as B3LYP/6–311 + G(3df,2p), even though the basis set used for Sn is quintuple-Z for the valence shell rather than triple-Z.

The atoms in molecules (AIM) theory of Bader[21] was used to investigate the possible bond activations undergone by the neutral species upon protonation. For this purpose we evaluated the charge density, ρ (**r**), and also the energy density, H(**r**),[22] at the bond critical points. This analysis was complemented with that carried out in terms of the lengthening or shortening of the bond lengths and in terms of the shifting of the corresponding stretching frequencies.

RESULTS AND DISCUSSION

The optimized geometries of the different bases investigated and those of their protonated species are schematized in Fig. 1. Their total energies are summarized in Table 1, together with the calculated proton affinities. The bonding characteristics are given in Table 2. Table 3 contains the harmonic stretching frequencies. It is worth noting that for the neutral compounds there is fairly good agreement between our calculated values and the experimental values obtained in different infrared studies.[23–26]

The first conspicuous fact is that for vinyl and ethynyl Si, Ge and Sn derivatives protonation at C_α is more favorable than protonation at C_β. It can be also observed that the energy gap between the C_α- and the C_β-protonated species does not change significantly with

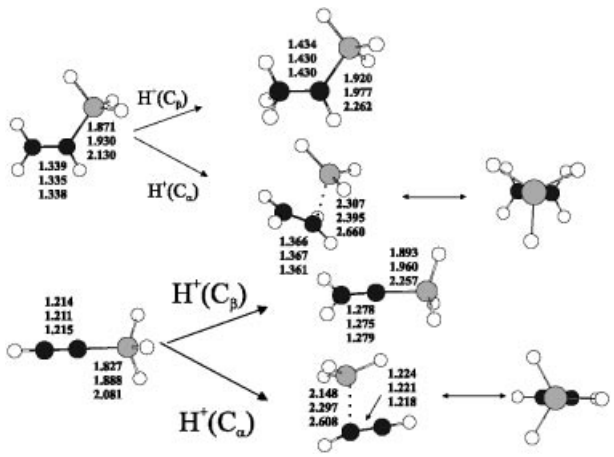

Figure 1. Optimized geometries for vinyl- and ethynylsilanes, -germanes and -stannanes and their corresponding C_α- and C_β-protonated forms. Bond lengths (Å) are given in the order Si, Ge and Sn derivatives. For the C_α-protonated species two different views of the system are given to show the C_s arrangement of the two building blocks

Table 1. Total energies (*E*, hartree), zero point energies (*ZPE*, hartree) and proton affinities (*PA*, kJ mol^{-1})

System	*E*	*ZPE*	*PA*
$H_2C{=}CH{-}SiH_3$	−369.34768	0.06726	
$[H_3C{-}CH{-}SiH_3]^+$	−369.62627	0.07568	716
$[H_2C{=}CH_2{\cdots}SiH_3]^+$	−369.65761	0.07901	789
$H_2C{=}CH{-}GeH_3$	−2156.83005	0.06502	
$[H_3C{-}CH{-}GeH_3]^+$	−2157.11248	0.07350	726
$[H_2C{=}CH_2{\cdots}GeH_3]^+$	−2157.15277	0.07679	823
$H_2C{=}CH{-}SnH_3$	−83.18635	0.06168	
$[H_3C{-}CH{-}SnH_3]^+$	−83.47466	0.07041	740
$[H_2C{=}CH_2{\cdots}SnH_3]^+$	−83.52913	0.07387	875
$HC{\equiv}C{-}SiH_3$	−368.10368	0.04362	
$[H_2C{=}C{-}SiH_3]^+$	−368.38193	0.05187	715
$[HC{\equiv}CH{\cdots}SiH_3]^+$	−368.39225	0.05347	738
$HC{\equiv}C{-}GeH_3$	−2155.58330	0.04247	
$[H_2C{=}C{-}GeH_3]^+$	−2155.86787	0.04979	728
$[HC{\equiv}CH{\cdots}GeH_3]^+$	−2155.88633	0.05118	779
$HC{\equiv}C{-}SnH_3$	−81.94454	0.03835	
$[H_2C{=}C{-}SnH_3]^+$	−82.23547	0.04644	749
$[HC{\equiv}CH{\cdots}SnH_3]^+$	−82.26453	0.04825	821

the nature of the heteroatom, although it is slightly larger for Ge than for Si derivatives. This gap is, however, sizably smaller for ethynyl than for vinyl compounds. As we shall discuss later, this is probably due to the fact that in the former case C_α protonation implies a certain distortion of the HCCH moiety which, in the protonated species, is not linear. The energetic cost of this distortion approaches energetically the C_α- and the C_β-protonated structures. Nevertheless, the energy gap between C_α- and C_β-protonated species is large enough for us to assume that the former should be the only ones observed in the gas phase.

As could be expected, protonation on C_β leads to a sizable lengthening of the C—C bond, since in the vinyl derivatives it evolves from a typical C=C double bond to a linkage with very small double bond character. This lengthening is less pronounced in ethynyl derivatives where the C≡C triple bond becomes essentially a C=C double bond. These bonding changes are clearly mirrored in the topology of the electron density. As illustrated in Table 2, the charge density at the C—C bond critical point becomes significantly smaller upon C_β protonation, and the energy density less negative. Consistently, the C—C stretching frequency (see Table 3) appears shifted to the red. Also, interestingly, the effects are not negligible as far as the bonding ability of C_α is concerned and, as reflected by the values of the charge density in Table 2, the C_α–heteroatom linkage also becomes slightly weaker. As a consequence of this decrease in the bonding charge density, the bond becomes slightly longer and its stretching frequency (see Table 3) appears slightly shifted to the red.

The important finding is that in all cases C_α protonation is followed by a molecular fragmentation and the corresponding protonated species can be viewed systematically as a complex between ethylene or acetylene and a XH_3^+ (X = Si, Ge, Sn) cation. This is ratified by bond distances, charge densities, energy densities and stretching frequencies. As illustrated in Fig. 1, the protonation at C_α of the ethynyl derivatives leads to a C_s structure, where the symmetry plane bisects the C—C bond of the $H_2C{=}CH_2$ moiety and contains one of the hydrogen atoms of the XH_3^+ fragment. This is consistent with the formation of a tightly bound complex between the XH_3^+ cation and the π-system of the ethylene molecule. This picture is also consistent with the fact that in the complex the C—X stretching frequency is replaced by a vibrational mode in the 200–300 cm^{-1} region, which corresponds to the displacement of the XH_3^+ cation along an imaginary axis which would connect the heteroatom with the middle point of the C—C bond. Also, the value of the charge density is typical of weak interactions of electrostatic and polarization nature. It can also be observed that the C—C bond becomes slightly weaker than that of the neutral system, and also weaker than that of a $H_2C{=}CH_2$ isolated molecule, reflecting the interaction of the π system with the XH_3^+ cation. In fact, the C—C distance in the complex is about 1.36–1.37 Å, whereas in ethylene it is 1.331 Å. Consistently, the C—C stretching frequency in the C_α-protonated form (see Table 3) is red shifted with respect to that in ethylene (1720 cm^{-1}, at the same level of theory).

The C_α-protonated species of the ethynyl derivatives are also C_s structures, although in these cases the symmetry plane contains the C—C bond of the HCCH moiety and one of the X—H bonds of the XH_3^+ subunit (see Fig. 1). It can also be observed that the interaction between the XH_3^+ and the HCCH subunits results in a

Table 2. Bonding characteristics in terms of the charge densities, $\rho(\mathbf{r})$ (a.u.), and energy densities, $H(\mathbf{r})$ (a.u.), at the bond critical points

	C—C bond		C—X bond	
System	$\rho(\mathbf{r})$	$H(\mathbf{r})$	$\rho(\mathbf{r})$	$H(\mathbf{r})$
$H_2C{=}CH{-}SiH_3$	0.339	−0.375	0.117	−0.066
$[H_3C{-}CH{-}SiH_3]^+$	0.292	−0.285	0.101	−0.048
$[H_2C{=}CH_2{\cdots}SiH_3]^+$	0.329	−0.349	0.056	−0.024
$H_2C{=}CH{-}GeH_3$	0.342	−0.381	0.127	−0.071
$[H_3C{-}CH{-}GeH_3]^+$	0.295	−0.290	0.113	−0.055
$[H_2C{=}CH_2{\cdots}GeH_3]^+$	0.329	−0.348	0.052	−0.009
$H_2C{=}CH{-}SnH_3$	0.341	−0.381	0.034	−0.027
$[H_3C{-}CH{-}SnH_3]^+$	0.296	−0.291	0.026	−0.022
$[H_2C{=}CH_2{\cdots}SnH_3]^+$	0.332	−0.357	0.027	−0.019
$HC{\equiv}C{-}SiH_3$	0.402	−0.671	0.117	−0.061
$[H_2C{=}C{-}SiH_3]^+$	0.384	−0.568	0.097	−0.042
$[HC{\equiv}CH{\cdots}SiH_3]^+$	0.402	−0.648	0.062	−0.030
$HC{\equiv}C{-}GeH_3$	0.403	−0.679	0.128	−0.067
$[H_2C{=}C{-}GeH_3]^+$	0.386	−0.582	0.107	−0.048
$[HC{\equiv}CH{\cdots}GeH_3]^+$	0.403	−0.588	0.055	−0.013
$HC{\equiv}C{-}SnH_3$	0.399	−0.689	0.031	−0.023
$[H_2C{=}C{-}SnH_3]^+$	0.386	−0.603	0.031	−0.020
$[HC{\equiv}CH{\cdots}SnH_3]^+$	0.398	−0.609	0.026	−0.016

Table 3. Calculated harmonic frequencies[a] (cm^{-1})

System	C—C bond	C—X bond	X—H
$H_2C{=}CH{-}SiH_3$	1680 (1617, 1596)[b]	620 (707)[b]	2238, 2250 (2175, 2195)[b]
$[H_3C{-}CH{-}SiH_3]^+$	1226	546	2225, 2313, 2347
$[H_2C{=}CH_2{\cdots}SiH_3]^+$	1369	329	2310, 2350, 2375
$H_2C{=}CH{-}GeH_3$	1686 (1595)[c]	543 (639)[c]	2054, 2080 (2080, 2090)[c]
$[H_3C{-}CH{-}GeH_3]^+$	1233	479	2050, 2132, 2164
$[H_2C{=}CH_2{\cdots}GeH_3]^+$	1365	264	2105, 2150, 2173
$H_2C{=}CH{-}SnH_3$	1675 (1600)[b]	546	1876, 1890 (1892, 1910)[b]
$[H_3C{-}CH{-}SnH_3]^+$	1229	345	1934, 1956, 1973
$[H_2C{=}CH_2{\cdots}SnH_3]^+$	1371	221	1964, 1986, 1995
$HC{\equiv}C{-}SiH_3$	2165 (2056)[d]	642 (679)[d]	2261, 2265 (2193)[d]
$[H_2C{=}C{-}SiH_3]^+$	1822	536	2250, 2325, 2355
$[HC{\equiv}CH{\cdots}SiH_3]^+$	1986	361	2311, 2354, 2369
$HC{\equiv}C{-}GeH_3$	2180 (2060)[e]	546 (530)[e]	2091, 2110 (2112, 2127)[e]
$[H_2C{=}C{-}GeH_3]^+$	1833	393	2080, 2149, 2179
$[HC{\equiv}CH{\cdots}GeH_3]^+$	2003	273	2115, 2173, 2181
$HC{\equiv}C{-}SnH_3$	2142	441	1910, 1918
$[H_2C{=}C{-}SnH_3]^+$	1806	293	1947, 1976, 1987
$[HC{\equiv}CH{\cdots}SnH_3]^+$	2020	229	1966, 1991, 1997

[a] Experimental values, when available, are given in parenthesis.
[b] Values taken from Ref. 23.
[c] Values taken from Ref. 24.
[d] Values taken from Ref. 26.
[e] Values taken from Ref. 25.

certain distortion of the latter which is not linear, the HCC angle being around 167°. Similarly to what has been discussed above for the vinyl derivatives, these protonated structures can be viewed as tightly bound complexes between acetylene and XH_3^+ (X = Si, Ge, Sn) cations. Also in these cases, the C—X stretching frequency of the neutral is replaced by a vibrational mode which corresponds to the separation-approaching movement of both building blocks along the imaginary axis which would connect the heteroatom and the middle point of the C—C bond. It is worth noting, however, that the corresponding vibrational frequency is slightly higher as it corresponds, as we shall show later, to a slightly stronger interaction between the two building blocks. Also in this case, the C—C bond becomes slightly activated and its stretching frequency appears red shifted with respect to isolated acetylene and the bond length (for the acetylene molecule $r_{cc} = 1.205$ Å, $\nu_{CC} = 2087\ cm^{-1}$, at the B3LYP/6–31 G* level of theory).

Finally, for both kind of systems, the atomic charges obtained by means of NBO analysis[27] clearly shows that most of the positive charge of the protonated species is located on the XH_3 moiety, whereas the other building subunit, C_2H_4 or C_2H_2, exhibits a small positive net charge. We also estimated the interaction energy between the two building blocks. The results are summarized in Table 4 and clearly show that this interaction is much stronger for acetylene than for ethylene, because in the former case the interaction involves a C≡C triple bond, which should be more polarizable.

The calculated proton affinities indicate that, as expected, the vinyl derivatives are stronger bases than the ethynyl derivatives. In both series of compounds the intrinsic basicity of the system increases in the order Si < Ge < Sn. As a consequence, although in general they behave as moderate carbon bases, the vinylstannane derivative is predicted to be $>20\ kJ\ mol^{-1}$ more basic than ammonia. It is also worth noting that the intrinsic basicity of C_β is almost the same in vinyl as in ethynyl derivatives.

CONCLUSIONS

Our results show that vinyl-and ethynylsilanes, -germanes and-stannanes are carbon bases of moderate strength in the gas phase, with the only exception of vinylstannane, which is predicted to be about 20 $KJ\ mol^{-1}$ more basic than ammonia. The most important conclusion is that C_α protonation is followed by C—X bond cleavage, so that the most stable protonated form corresponds to a tightly bound complex between ethylene

Table 4. Interaction energies, D_e and D_0 ($kJ\ mol^{-1}$), between the two building blocks (ethylene or acetylene and XH_3^+) of the C_α-protonated species

System	D_e	D_0
$[H_2C{=}CH_2{\cdots}SiH_3]^+$	188	174
$[H_2C{=}CH_2{\cdots}GeH_3]^+$	167	154
$[H_2C{=}CH_2{\cdots}SnH_3]^+$	127	116
$[HC{\equiv}CH{\cdots}SiH_3]^+$	238	226
$[HC{\equiv}CH{\cdots}GeH_3]^+$	215	204
$[HC{\equiv}CH{\cdots}SnH_3]^+$	178	170

(or acetylene) and the corresponding XH_3^+ cation. This implies that dissociative proton attachments can be observed not only when the basic center is a very electronegative atom, but also for active centers of low electronegativity, provided that the other atoms bonded to it are much less electronegative than the basic center itself, and that the fragments formed as products of the dissociation are intrinsically stable.

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