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Electron affinity of $X_nGe(OMe)_{3-n}$ radicals (X = H, F; $n = 0-2$) and the Ge–H bond dissociation energy

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Abstract

The recent observation of a number of gas-phase germyl anions of the type $X_nGe(OMe)^-_{3-n}$ (X = H, F; $n = 0-2$), suggests that these species are very stable and relatively unreactive in ion/molecule reactions. We report the electron affinity of the corresponding $X_nGe(OME)_{3-n}$ radicals calculated at the QCISD(T) level using basis sets developed by the generator coordinate method and adapted to effective core potentials. These calculations show the electron affinity increasing in the order GeH_3 (1.55 eV) < H_2GeOMe (1.75 eV) < $HGe(OMe)_2$ (1.95 eV) < $Ge(OMe)_3$ (2.32 eV) < $FGe(OMe)_2$ (2.67 eV) < F_2GeOMe (3.12 eV), and are estimated to be within 0.10–0.15 eV (for the radicals at the upper end) of the true adiabatic values. Ge–H bond energies have also been calculated for some of the simpler systems and the 81.1 kcal mol^{-1} $BDE_{0\ K}$ calculated for $H_3Ge–H$ is in very good agreement with the recommended experimental value of 82 ± 2 kcal mol^{-1}. (Int J Mass Spectrom 210/211 (2001) 173–180) © 2001 Elsevier Science B.V.

Keywords: Germyl anions; Electron affinity; Ge–H bond energies; Gas-phase acidities

1. Introduction

The properties of simple germanium-containing anions are presently of considerable interest to chemistry and material sciences. Germyl anions find increasing application as selective reagents in organic synthesis [1] whereas germanates containing GeO_4 building units are being explored as possible unique framework topologies for zeolites [2]. In the meantime, cluster anions of Ge are considered as typical examples of Zintl ions and as such they can provide valuable structural information [3]. Last, unraveling the mechanism and the role of anionic species in sol-gel processes leading to Ge-containing polymeric materials are key questions in the search for new materials [4].

In spite of the diversity of modern Ge chemistry, there is still little data regarding such fundamental properties as bond energies, electron affinities, and proton affinities of organogermane species. For example, the Ge–H bond energy in GeH_4 was claimed to amount to 82.7 ± 2.4 kcal mol^{-1} from gas-phase kinetic measurements [5]. Further kinetic studies [6] and laser induced photoacoustic experiments [7] re-

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veal negligible changes of the Ge–H bond energy in alkyl substituted germanes, but highly electronegative substituents like iodine lead to a weaker Ge–H bond energy of 79.3 ± 2.4 kcal mol^{-1} [8]. On the other hand, a somewhat lower bond dissociation energy of 78.0 ± 1 kcal mol^{-1} for H_3Ge–H has been derived from state-to-state kinetics using infrared chemiluminescence [9]. By comparison, Ge–X (X = C, O, halogens) bond dissociation energies remain poorly known. Few experimental values are also available for the electron affinity of Ge species. An upper limit of 1.74 ± 0.04 eV has been established for the electron affinity of $^{\cdot}GeH_3$ based on threshold photodetachment experiments [10]. Methyl substitution on Ge decreases the electron affinity and a value of 1.38 ± 0.03 eV has been experimentally determined for $^{\cdot}GeMe_3$ [11]. More recently, photoelectron spectroscopy has been used to obtain the electron affinity of Ge clusters because of their relevance to semiconductors [12].

We have previously shown that the ion/molecule reaction of F^-, or MeO^-, with $Ge(OMe)_4$ gives rise to germyl anions such as $Ge(OMe)_3^-$ and $FGe(OMe)_2^-$ as a result of fragmentation of the primary reaction products, $FGe(OMe)_4^-$ and $Ge(OMe)_5^-$ [13]. We have also reported that germyl anions such as $HGe(OMe)_2^-$ and H_2GeOMe^- can be generated in the cell of a Fourier transform ion cyclotron resonance (FTICR) spectrometer by infrared multiphoton dissociation of the primary ion/molecule reaction products, and fluorine substituted germyl anions by reaction of $Ge(OMe)_3^-$ and $FGe(OMe)_2^-$ with BF_3 [13]. Since the experimental determination of the electron affinity of these different species in a FTICR spectrometer has not been a trivial matter, we have resorted to complement our earlier results with theoretical calculations aimed at characterizing gas-phase ionic organogermanium species [13,14]. We have initially explored the use of density functional techniques coupled with basis sets adapted to a pseudopotential by the generator coordinate method to calculate the proton affinity of GeX_3^- (X = H, F, OH) and the electron affinity of $^{\cdot}GeH_3$ and $^{\cdot}GeF_3$ [14]. These calculations suggest that the electron affinity of $^{\cdot}GeF_3$ is considerably higher than that previously estimated from appearance potential measurements [15]. An independent theoretical study pertaining to the electron affinity of GeF_n species has reached a similar conclusion [16]. This article reports the results of systematic theoretical calculations on the newly observed germyl anions $X_nGe(OMe)_{3-n}^-$ (X = H, F; $n = 0$–2) and the trend of electron affinities in Ge species as a special dedication to the long-standing interest and seminal contributions of Nico Nibbering and his group to the characterization of the reactivity and structure of negative ions [17]. These present calculations have been carried out at the QCISD(T) level with basis sets developed by the methodology outlined in our earlier article [14]. We have also extended our calculations to estimate Ge–H bond energies for some of these systems.

2. Computational methodology

The computational procedure relies on a method that we have developed in recent years and that makes use of the discrete version of the generator coordinate method (GCM). The general methodology has been previously described [14,18], and consists of obtaining an optimized set of discrete parameters for the atoms by using the generator coordinate method to vary the space of the generator coordinate. The method has been adapted to the GAUSSIAN 94 program [19] and involves an initial analysis of the best representation for the basis functions using as a criterion the ground state electron energy of the atoms. It is now well established that this method can outperform the G2 method in estimating proton affinities [20] at a considerable reduction of computational cost.

For the present calculations, the general procedure involves three steps: (1) obtaining the valence basis sets from the 7*s*, 5*p*, and 1*d* set of functions adapted to the pseudopotential (ECP) of Stevens et al [21] for C, O, F, and Ge, and 4*s*/1*p* for H; (2) Contraction of the basis sets obtained in (1) with reoptimization of the exponents of the primitive functions (4111/311/1 functions for C, O, F, and Ge, and Ge, and 311/1 for H) leading to what we define as GCM/ECP basis set; and (3) addition of diffuse functions (*s* and *p* type) to correct the valence region, and additional polarization

Table 1
Optimized geometric parameters for the germyl radicals and anions obtained (bond distances in angstroms and angles in degrees)

	R			θ					δ^a
System	Ge–H	Ge–O	Ge–F	∠HGeH	∠HGeO	∠OGeO	∠FGeO	∠FGeF	∠(XYZ)Ge
GeH_3^-	1.612			92.8					52.6
GeH_3	1.530			110.8					
									33.1
$H_2Ge(OMe)^-$	1.628	1.903		90.7	95.3				51.26
$H_2Ge(OMe)$	1.545	1.780		112.2	104.6				35.6
	1.533				108.1				
$HGe(OMe)_2^-$	1.601	1.905			91.7	101.0			51.1
$HGe(OMe)_2$	1.533	1.781			104.3	113.4			
									37.9
$Ge(OMe)_3^-$		1.880				94.8			52.0
$Ge(OMe)_3$		1.773				105.5			
									37.8
$FGe(OMe)_2^-$		1.894	1.802			99.5	93.8		49.7
$FGe(OMe)_2$		1.770	1.719			114.7	103.4		
									36.7
$F_2Ge(OMe)^-$		1.864	1.835				96.4	94.1	49.7
		1.753	1.719				105.9	107.1	37.8
			1.733				108.5		

[a] δ represents the smallest angle between the XYX atoms and Ge. As this angle increases, the structure of the corresponding species assumes a more pyramidal geometry.

functions (*p* for H, and *d* and *f* for C, F, O, and Ge), for more refined energy calculations. This results in a (41111/3111/11/11) set for C, O, F, and Ge, and a (3111/11) set for H and is referred to as our (GCM+/ECP) basis set.

The highest level of energy calculations used in this work is identified as QCISD(T)/(GCM+/ECP), and is obtained from the additivity approximation [13,22],

$$
\begin{aligned}
&E\ [\text{QCISD(T)/GCM+/ECP}] \\
&\approx E\ [\text{QCISD(T)/(GCM/ECP)}] \\
&+ E\ [\text{MP2/(GCM+/ECP)}] \\
&- E\ [\text{MP2/(GCM/ECP)}] + \text{ZPE/(GCM/ECP)}
\end{aligned}
$$

Molecular geometries were initially optimized with the basis set outlined in step (2) and vibrational frequencies calculated at the HF/(GCM/ECP) level. The zero-point energies (ZPEs) obtained from these frequencies were scaled by 0.8929 in the final energy calculations. Using the structures obtained at the HF/(GCM/ECP) level and the calculated force constants a new geometry optimization was performed at the MP2/(GCM/ECP) level resulting in a lower computational cost for calculating molecular geometries at MP2 level. The more refined energy calculations, namely *E* [QCISD(T)/(GCM/ECP)] and *E* [MP2/GCM+/ECP], were then carried out with the latter geometry.

3. Results and discussion

3.1. Structure of germyl anions

Table 1 lists the most relevant geometric parameters for the radical and anionic species of GeH_3, H_2GeOMe, $HGe(OMe)_2$, $Ge(OMe)_3$, F_2GeOMe, and $FGe(OMe)_2$, where the GeH_3 system has been included for comparison purposes. Some representative structures can be visualized in Figs. 1 and 2. Since several different conformers are possible for the radicals and anions containing one or more methyl groups, calculations were carried out with and without

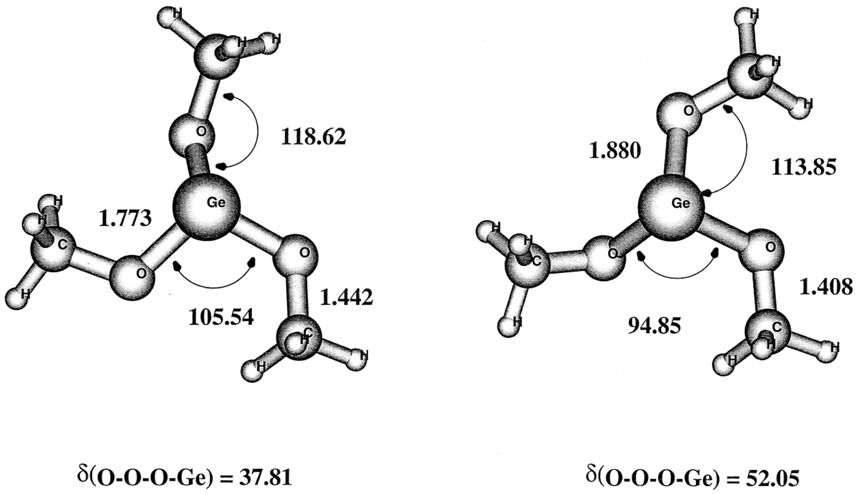

Fig. 1. Structure and important geometric parameters for the neutral and anionic $Ge(OMe)_3$ species.

symmetry restrictions. The structures represented in Table 1 are those corresponding to the individual energy minimum for each species.

The pyramidal structure calculated for $^{\cdot}GeH_3$ is very similar to that previously reported by earlier theoretical reports [23] and agrees with the experimental conclusions derived from the electronic [24] and ESR [25] spectra of this radical. Our calculated Ge–H bond distance of 1.530 Å is within 0.01 Å of our previous density functional theory (DFT) calculation [14] and of other recent high calculations [26]. Likewise, our calculated ∠HGeH angle of 110.8° is identical to those obtained in similar high level calculations [14,26]. By comparison, the $^{\cdot}Ge(OMe)_3$ radical is predicted to be even more pyramidal with an ∠OGeO angle of 105.5° in close agreement with the ∠FGeF angle of 106.8° predicted for $^{\cdot}GeF_3$ in our previous report [14]. For the $^{\cdot}XGe(OMe)_2$ ($X = H, F$) radical, the ∠OGeO angle is predicted to become considerably larger.

The corresponding germyl anions are characterized by a significant lengthening of the bonds (more than 0.1 Å for Ge–O and Ge–F) in agreement with the idea of increasing electron repulsion and overall expansion of the resulting anion. For the symmetrical cases like GeH_3^- and $Ge(OMe)_3^-$ it is also noticeable that the corresponding ∠HGeH and ∠OGeO angles become close to the limit expected for pure *p*-type bonding by the central Ge. The considerable closing of the ∠HGeH angle in GeH_3^- had already been predicted in a very early ab initio calculation [27].

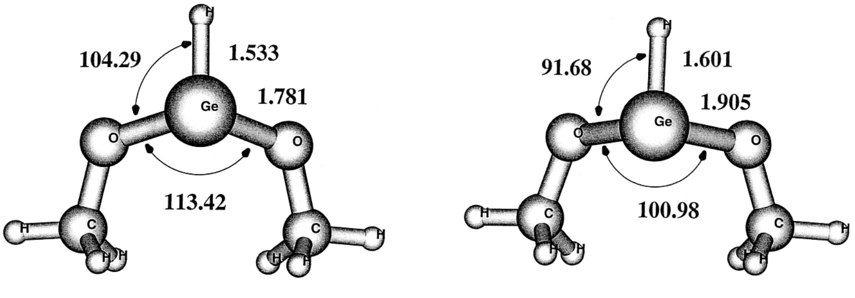

Fig. 2. Structure and important geometric parameters for the neutral and anionic $HGe(OMe)_2$ species.

Table 2
Electronic energies (in a.u.) and zero-point energies (in kcal mol^{-1}) of radicals and anions used for electron affinity and bond energy calculations

	MP2 GCM/ECP	QCISD(T) GCM/ECP	MP2 GCM+/ECP	ZPE HF/GCM/ECP	QCISD(T) (GCM+/ECP) + ZPE (in a.u.)[a]
GeH_3	−5.508 79	−5.522 42	−5.537 21	13.30	−5.532 43
GeH_3^-	−5.544 83	−5.572 37	−5.578 08	11.75	−5.588 89
GeH_4	−6.139 81	−6.155 63	−6.173 66	19.56	
					−6.161 65
$HGe(OMe)_2$	−51.049 03	−51.126 12	−51.203 36	60.27	−51.194 69
$HGe(OMe)_2^-$	−51.106 91	−51.187 26	−51.268 85	58.32	−51.266 21
$H_2Ge(OMe)_2$	−51.681 01	−51.761 94	−51.837 31	66.25	
					−51.823 97
H_2GeOMe	−28.275 70	−28.328 85	−28.360 03	37.05	−28.360 46
H_2GeOMe^-	−28.323 83	−28.380 95	−28.417 88	35.43	−28.424 58
H_3GeOMe	−28.906 63	−28.963 17	−28.992 40	43.09	
					−28.988 32
$FGe(OMe)_2$	−74.478 73	−74.562 84	−74.859 75	56.65	−74.863 25
$FGe(OMe)_2^-$	−74.564 79	−74.651 31	−74.953 09	54.97	
					−74.961 40
F_2GeOMe	−75.488 92	−75.536 96	−75.674 53	30.68	−75.679 00
F_2GeOMe^-	−75.591 80	−75.642 84	−75.784 97	29.64	
					−75.793 84
$Ge(OMe)_3$	−73.430 21	−73.528 16	−74.048 42	82.95	−74.028 34
$Ge(OMe)_3^-$	−73.498 52	−73.598 37	−74.128 60	81.13	−74.113 02

[a] ZPE is scaled by 0.8929 for the final energy calculations.

3.2. Electron affinity of the radicals

Table 2 lists the energies calculated at different levels as explained in Sec. 2. The last column of Table 2 displays the results obtained at our highest level of calculation, namely QCISD(T)/(GCM+/ECP), corrected by the zero-point energies of each species. The corresponding electron affinities for the different radical can then be calculated from our highest level calculations and the results are shown in Table 3.

Table 3
Calculated electron affinities[a]

Radical	EA/eV
GeH_3	1.55
H_2GeOMe	1.75
$HGe(OMe)_2$	1.95
$Ge(OMe)_3$	2.32
$FGe(OMe)_2$	2.67
F_2GeOMe	3.12

[a] $EA\ (R^{\cdot}) = E(R^-) - E(R^{\cdot})$ obtained from the last column in Table 2.

The calculated value of 1.55 eV for the electron affinity of $^{\cdot}GeH_3$ is identical to that reported in our earlier article [14]. This value is 0.05 eV lower than that obtained at the G2 level and both values are below the experimental upper limit of 1.74 ± 0.04 eV [10]. Nevertheless, it is important to emphasize the inherent difficulty in establishing adiabatic electron affinities from threshold photodetachment experiments when the neutral and the anion display significant differences in geometry as in the present case. On the other hand, it is reasonable to assume that calculated electron affinities either at the G2 level or using our methodology should yield values within 0.1 eV of the true electron affinity of simple species such as $^{\cdot}GeH_3$. The progressive substitution of hydrogens by methoxy groups around the central Ge atom leads to an increase in electron affinity as might be expected by the electronegative nature of the substituent. While there are no experimental numbers yet for these species, recent experiments in our laboratories [28] reveal that no apparent photodetachment is observed in $Ge(OMe)_3^-$ ions when irradiated with 532 nm laser light (2.33 eV). This observation suggests that our theoretical prediction is a lower limit to the electron affinity of the $^{\cdot}Ge(OMe)_3$ radical.

The effect of fluorine substitution on the electron affinity of germyl radicals can be analyzed by comparison with other GeF_n species. We have previously estimated a value of 3.51 eV for the electron affinity of $^{\cdot}GeF_3$ at the same level of calculation as reported here [14]. Density functional methods yield somewhat higher values for this radical [14,29] but direct comparison with experiment is difficult since very conflicting values of 1.1 [30], 1.6 [31], and 3.1 eV [32] have been claimed from appearance potential measurements. The electron affinity calculated by us for $^{\cdot}FGe(OMe)_2$ and $^{\cdot}F_2GeOMe$ reveal a smooth trend of increasing electron affinity upon progressive substitution of methoxy groups in $^{\cdot}Ge(OMe)_3$ with the more electronegative fluorine atoms.

A key question in these electron affinity calculations is the reliability of our values obtained with respect to the true electron affinities. A reasonable guideline is provided by comparison of results obtained by different methods with known experimental values. For example, the electron affinity of GeF has recently been calculated by different density functional approaches [29] using a DZP^{++} basis set and the results are typically within 15% of the 1.02 eV value derived from negative ion photoelectron spectroscopy [12c]. On the other hand, calculations [33] on Ge_n clusters ($n = 2, 3$) reveal that both B3LYP and CCSD(T) employing 6-311+G(3*df*) basis sets yield electron affinities within 0.1 eV of the experimental values [12a]. Thus, we feel confident that our present values are probably within 0.10–0.15 eV of the true adiabatic electron energies.

3.3. Ge–H bond energies

Table 4 lists the the Ge–H bond energies calculated in this work for GeH_4, H_3GeOMe, and $H_2Ge(OMe)_2$ both at 0 and 298 K. These results show the D_0(Ge–H) to hover in the 80–81 kcal mol^{-1} range for these simple germanes, whereas the BDE (298 K) is predicted to be in the range of 81–83 kcal mol^{-1}. These results are particularly enlightening in view of the controversy surrounding this important thermochemical parameter.

Table 4
Bond dissociation energies (in kcal mol^{-1})[a]

	BDE (0 K)	BDE (298 K)	Experimental
$H_3Ge–H$	81.1	82.5	82 ± 2[b]
$H_2Ge(OMe)–H$	80.0	81.5	
$HGe(OMe)_2–H$	81.1	82.6	

[a] BDE at 298 K = $\Delta E + \Delta H_{vib}(\text{thermal}) + \Delta H_{rot}(\text{thermal}) + \Delta H_{trans}(\text{thermal})$.

[b] Recommended value for $D_0(H_3Ge–H)$ from [35]. See text for a discussion regarding previous experimental and theoretical values.

Our calculated $H_3Ge–H$ bond energy at 298 K is in excellent agreement with the experimental value of 82.7 ± 2.4 kcal mol^{-1} obtained by Walsh and coworkers [5] from the gas-phase kinetics of iodine and monogermane. Our calculated $D_0(H_3Ge–H)$ is also in good agreement with the value of 82 ± 2 kcal mol^{-1} obtained from photoionization experiments on GeH_4 [34] that has been proposed as the recommended value in the recent classical review on R–H bond dissociation energies [35]. Higher values for $D_0(H_3Ge–H)$, namely 84.1 ± 2.1 kcal mol^{-1}, and $BDE_{298\ K}$ = 85.6 ± 2.1 kcal mol^{-1}, have been derived from the gas-phase acidity of monogermane [36] and the electron affinity determined from photodetachment experiments on GeH_3 [10]. By comparison, other high quality calculations yield results just outside the quoted experimental uncertainty. For example, Binning and Curtiss predict $D_0(H_3Ge–H) = 84.8$ kcal mol^{-1} [37] from calculations at the MP4 level with basis sets specially developed for Ge. Likewise, the G2 calculations of Radom and co-workers [38] predict $D_0(H_3Ge–H) = 84.7$ kcal mol^{-1} and $BDE_{298\ K} = 86.1$ kcal mol^{-1}. Interestingly enough, a very thorough study of the effects of correlation energy on the calculation of bond energies has led to the proposal that $D_e(H_3Ge–H)$ should be in the range of 91.1–93.0 kcal mol^{-1} [39]. These latter values seem unrealistic when compared with the available experimental data. Finally, it is interesting to notice that a significant variation of $BDE_{298\ K}$ has been reported for $H_3Ge–H$ from calculations performed at different

Table 5
Proton affinity of simple germyl anions (in kcal mol^{-1})

A^-	AH	Calculated PA (298 K)	Experimental PA (298 K)
$GeH_3{}^-$	GeH_4	360.3	359.0 ± 1.3[a]
H_2GeOMe^-	H_3GeOMe	355.0	
$HGe(OMe)_2^-$	$H_2Ge(OMe)_2$	351.5	

[a] See [36].

levels with a TZDP++ basis set: 76.8 (MP2), 76.5 (PMP2), 78.8 (MP3), 79.3 (MP4), 79.3 [CCSD(T)], and 81.9 (B3LYP) kcal mol^{-1} [40].

The values reported in Table 4 do not include the high level corrections (HLC) that have been shown to be necessary for calculating accurate bond energies within the G2 theory [41]. Since our method makes use of a different basis set, we have compared the effect of the HLC. in these calculations. For CH_4, our methodology estimates the C–H bond dissociation energy at 298 K to be 101.4 kcal mol^{-1} without HLC (102.2 kcal mol^{-1} by G2 without HLC) and 104.9 kcal mol^{-1} with high level corrections (105.8 kcal mol^{-1} by G2 with HLC) in excellent agreement with the experimental value of 104.9 kcal mol^{-1} [35]. If this high level correction of 3.5 kcal mol^{-1} is used for the case of GeH_4 the resulting bond dissociation energy at 298 K would amount to 86.1 kcal mol^{-1}, in perfect agreement with the value obtained by G2 calculations [38] that automatically include these corrections. Thus, our calculations and G2 calculations agree very well with the presently acceptable bond dissociation energy H_3Ge–H [35] without the need for high level corrections. While we have not explored the possible reasons as to why high level corrections seem inadequate for species like GeH_4, these findings suggest the need for further theoretical and experimental work on these bond dissociation energies.

3.4. Proton affinity of germyl anions

Table 5 lists the calculated proton affinity for some selected germyl anions. The excellent agreement observed between our calculated value for GeH_3^- and the experimental value [36] suggests that our calculated proton affinities for these systems are probably within 1.5 kcal mol^{-1} of the experimental values.

4. Conclusions

The present calculations reveal that simple germyl anions are very stable species and their corresponding radicals are characterized by substantial positive electron affinities. We have also shown that the computational methodology adopted in our line of work yields accurate thermochemical values involving negative ions at a much cheaper computational cost.

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