Fourier Transform-Ion Cyclotron Resonance Study of the Gas-Phase Acidities of Germane and Methylgermane; Bond Dissociation Energy of Germane

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An accurate gas-phase acidity for germane (enthalpy scale, equivalent to the proton affinity of GeH_3^-), $\Delta H_{acid}^{\circ}(GeH_4) = 1502.0 \pm 5.1$ kJ mol^{-1}, is obtained by constructing a consistent acidity ladder between GeH_4 and H_2S by using Fourier transform-ion cyclotron resonance spectrometry, and 0 and 298.15 K values for the first bond dissociation energy of GeH_4 are proposed: $D_0^{\circ}(H_3Ge-H) = 352 \pm 9$ kJ mol^{-1}; $D^{\circ}(H_3Ge-H) = 358 \pm 9$ kJ mol^{-1}, respectively. These results are compared with experimental and theoretical data reported in the literature. Methylgermane was found to be a weaker acid than germane by approximately 35 kJ mol^{-1}: $\Delta H_{acid}^{\circ}(MeGeH_3) = 1536.6$ kJ mol^{-1}. (J Am Soc Mass Spectrom 1993, 4, 54–57)

Films of amorphous materials, such as silicon, silicon–carbon, and silicon–germanium alloys, have been considered for use in photovoltaic generators [1]. Chemical vapor deposition (CVD) and glow discharge (GD) are the techniques generally used to obtain these materials.

Recently, germanium–carbon alloys have also been considered because they show good optoelectronic properties according to preliminary experimental data [2] and theoretical considerations [3]. Alkyl–germane and germane–hydrocarbon mixtures have been used as gaseous precursors.

When GD or CVD assisted by a decomposition agent (plasma enhanced or plasma assisted CVD) is used for deposition, knowledge of gas-phase radical and ionic reactions is useful in planning the film composition.

Relevant positive ion–molecule reactions were studied with the aim of modeling the formation of amorphous Ge–C alloys [4]. The formation of positive ions from germane has been studied from an energetics [5, 6] and kinetics [4, 7–9] point of view; however, the formation and reactions of negative ions derived from germane have been given less attention, although the importance of negatively charged species in silane-containing semiconductor-processing plasmas has been addressed in recent studies [10, 11].

Reed and Brauman [12] briefly described the formation of negative ions by dissociative electron capture on GeH_4 and GeD_4 with a view toward measuring the photodetachment energy of GeH_3^-. They report an upper bound of the adiabatic electron affinity (EA) of 1.74 ± 0.04 eV for the corresponding GeH_3 radical. A high-level calculation by Ortiz [13] gives $EA(GeH_3) = 1.49$ eV.

Knowledge of homolytic bond dissociation energies (D°) is also essential to understand amorphous Ge–H film growth [14]. In this regard the value of $D^{\circ}(H_3Ge-H)$ is controversial and is still under investigation both experimentally [6, 15] and theoretically [16].

The enthalpy of deprotonation of a neutral entity (AH) in the gas phase, corresponding to the proton affinity of the anion (referred to here as the enthalpy of acidity);

$$AH \rightarrow A^- + H^+ \qquad (1)$$

may be linked to the homolytic bond dissociation energy of the corresponding bond;

$$AH \rightarrow A^{\cdot} + H^{\cdot} \qquad (2)$$

by the thermodynamic relation

$$\Delta H^{\circ}_{acid}(AH) = D^{\circ}(A-H) + IE(H^{\cdot}) - EA(A^{\cdot}) \quad (3)$$

The ionization energy of the hydrogen atom IE(H·) is common to all acids and is very accurately known [17]. Thus, each of the three remaining quantities may be derived from the other two. Using the EA(GeH$_3$) value proposed by Reed and Brauman [12] and the $D^{\circ}(H_3Ge-H)$ value obtained by Noble and Walsh [18], Lias et al. [17] estimated the value of the gas-phase acidity of germane. The uncertainty with regard to this value arises mainly from the uncertainty with regard to $D^{\circ}(H_3Ge-H)$.

With the aim of improving the accuracy of the absolute acidity of germane, allowing in turn a new estimate of the H_3Ge-H bond dissociation energy, we constructed an acidity ladder between GeH$_4$ and H$_2$S, a reference acid of accurately known ΔH°_{acid}. Because methylgermane is a possible candidate for the production of Ge–C alloy film [19], among other organogermanes, we also investigated its ΔH°_{acid}.

Experimental

Chemicals

All reference compounds used in the present study are available commercially and were used without further purification. Germane [20] and methylgermane [21] were synthesized according to previously published procedures.

Gas-Phase Acidity Measurements

Negative ion–molecule reactions were monitored as previously described [22] by using the Fourier-transform-ion cyclotron resonance mass spectrometer constructed at the University of Nice–Sophia Antipolis, which has been described elsewhere [23]. Briefly, it consists of Bruker CMS 47 electronics, a Varian 15-in. electromagnet (50-mm pole gap, 1.6 T) and vacuum chamber, cell and gas inlet system purposely designed for ion–molecule reaction studies. Pressures were measured with a Bayard-Alpert ionization gauge (Alcatel, BN111). The gauge sensitivity was measured with a spinning rotor gauge (Leybold, Viscovac VM 210) [24]. Sensitivities relative to N$_2$ for the compounds used in the present study are presented in Table 1.

Negative ions, participating in the proton transfer equilibria, were generated by proton abstraction from the neutral reactant by t-BuO$^-$ or MeO$^-$ obtained by electron ionization at 0.1 eV of t-BuONO (Aldrich Chemical Co., Milwaukee, WI) or MeONO (generated

Table 1. Ionization gauge relative sensitivites (S_r) for the compounds used in the present study

Compound	$S_r{}^a$
GeH$_4$	1.94 ± 0.02
MeGeH$_3$	2.67 ± 0.02
MeSH	2.68 ± 0.02
EtSH	3.45 ± 0.03
t-BuSH	5.00^b
Pyrrole	3.55 ± 0.06
CF$_3$CH$_2$OH	2.27^c
n-PrSH	4.28 ± 0.02
n-C$_6$H$_{13}$SH	6.13 ± 0.12
H$_2$S	2.07 ± 0.07
n-BuSH	5.00^b
PhNH$_2$	4.44^c
EtCHO	3.01 ± 0.12
MeCHO	2.55 + 0.10

^{a}Sensitivities relative to nitrogen; experimental values with their standard deviation, unless otherwise stated.
^{b}Value calculated by using an additivity rule in the thiol series.
^{c}Values calculated from the polarizability [25].

in situ from a mixture of t-BuONO and MeOH [26]; MeO$^-$ was preferred to t-BuO$^-$ when GeH$_3^-$ was involved in the equilibrium because of mass interference. The intensities of the GeH$_3^-$ and MeGeH$_2^-$ ion signals, corresponding to the most abundant isotope ^{74}Ge, were divided by its relative abundance (0.365) [27] to estimate the total ion abundance. The relative intensities of isotopic peaks are in good agreement with the germanium isotopic composition.

Results and Discussion

Gas-Phase Acidities

To establish an accurate gas-phase acidity for germane, we constructed a homogeneous ladder between GeH$_4$ and H$_2$S that may be considered an anchor point. The relative gas-phase acidities [relative Gibbs energies $\Delta\Delta G^{\circ}_{acid} = \Delta G^{\circ}_{acid}(AH) - \Delta G^{\circ}_{acid}(RefH)$] referring to eq 4, where RefH is a reference acid, are presented in Table 2,

$$AH + Ref^- \rightleftharpoons RefH + A^- \qquad (4)$$
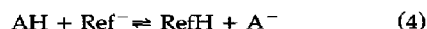
Experimental results concerning MeGeH$_3$ are also reported in Table 2. The nearest possible anchor point is HF. We have not considered this possibility with regard to the experimental problems associated with its use [28]. The increase in uncertainty due to the large number of necessary steps to link MeGeH$_3$ to other anchor points farther in acidity cancels the possible gain in accuracy inherent in this operation.

From the data in Table 2 we obtain a difference in gas-phase acidity of $\Delta\Delta G^{\circ}_{acid} = 24.4 \pm 1.1$ kJ mol^{-1} for GeH$_4$ relative to H$_2$S, at the temperature of the cell (338 K), by considering the possible ways of connecting the two compounds. Optimization of the various overlaps between steps by a least-squares method [29] leads to a result not significantly different. Relative

Table 2. Gas-phase proton transfer data for the reaction AH + Ref ⇌ RefH + A$^-$

AH	RefH	$\Delta\Delta G^{\circ\;a}_{\text{acid}}$ (kJ mol^{-1}, 338 K)
GeH$_4$	CF$_3$CH$_2$OH	< −12
	MeSH	0.50 ± 0.04
	EtSH	7.59 ± 0.25
	pyrrole	0.25 ± 0.08
MeSH	EtSH	8.20 ± 0.38
Pyrrole	EtSH	6.53 ± 0.29
EtSH	n-PrSH	3.39 ± 0.04
	n-BuSH	5.69 ± 0.13
	n-C$_6$H$_{13}$SH	7.66 ± 0.25
n-PrSH	t-BuSH	6.78 ± 0.17
n-BuSH	n-C$_6$H$_{13}$SH	2.47 ± 0.38
n-C$_6$H$_{13}$SH	t-BuSH	2.80 ± 0.21
	H$_2$S	8.70 ± 0.08
t-BuSH	H$_2$S	6.28 ± 0.04
MeGeH$_3$	PhNH$_2$	0.5
	MeCHO	0.52 ± 0.21
	EtCHO	1.12 ± 0.12

^{a}Mean and standard deviations for three to five measurements.

acidities of thiols are in good agreement with those found by Lias et al. [17]. A small discrepancy is observed for pyrrole.

The $\Delta G^{\circ}_{\text{acid}}$ values at 338 K have been corrected to 298.15 K, assuming constant $\Delta H^{\circ}_{\text{acid}}$ and $\Delta S^{\circ}_{\text{acid}}$ over the temperature range. The $\Delta S^{\circ}_{\text{acid}}$ values have also been estimated: For the GeH$_4$/H$_2$S couple, we used absolute entropies for neutrals [30] and the isoelectronic approximation [31] for the absolute entropies of ions. For MeGeH$_3$, we used the method proposed by Wetzel et al. [32] for estimating $\Delta S^{\circ}_{\text{acid}}$ of substituted silanes. We started with the isoelectronic value $\Delta S^{\circ}_{\text{acid}}(\text{GeH}_4) = 114.6$ J K^{-1} mol^{-1} and added R ln 3/4 for the difference in symmetry changes between MeGeH$_3$ and GeH$_4$ in eq 1. With regard to the reference values used for MeGeH$_3$, we used those reported by Lias et al. [17]. Uncertainties associated with the various approximations [31] involved in the temperature correction were added to the experimental uncertainties. The corresponding results are reported in Table 3. By using the $\Delta S^{\circ}_{\text{acid}}$ values used for the temperature corrections, $\Delta H^{\circ}_{\text{acid}}$ (298.15 K) was also calculated and

reported in Table 3. For the determination of the absolute gas-phase enthalpy of acidity $\Delta H^{\circ}_{\text{acid}}$ in eq 1, equivalent to the anion proton affinity, we need the corresponding data for the reference compounds. For MeGeH$_3$, we used the recent compilation by Lias et al. [17]. For GeH$_4$, the anchor point $\Delta H^{\circ}_{\text{acid}}$ (H$_2$S) is obtained by using eq 3.

In general, IE(H$^{\cdot}$) and EA are spectroscopic values, corresponding to 0 K; D° may be available at 0 or 298.15 K. The $\Delta H^{\circ}_{\text{acid}}$ (298.15 K) values calculated by Lias et al. [17] according to eq 3 (often referred to as D–EA values) are obtained from D° (298.15 K) under the assumption that the temperature dependence of EA(A$^{\cdot}$) and IE(H$^{\cdot}$) cancels out.

With the aim of increasing the accuracy of $\Delta H^{\circ}_{\text{acid}}(\text{H}_2\text{S})$, we considered the possibility of temperature correction. The 0 K enthalpy of acidity, $\Delta H^{\circ}_{\text{acid0}}(\text{H}_2\text{S}) = 1464.4 \pm 1.3$ kJ mol^{-1}, is obtained by using $D^{\circ}_0(\text{HS–H})$ [at the same temperature, from ΔH°_{f0} for H$^{\cdot}$(g), HS$^{\cdot}$(g), and H$_2$S(g)] [30] and the EA(HS$^{\cdot}$) value of Janousek and Brauman [33] in eq 3. The $\Delta H^{\circ}_{\text{acid0}}(\text{H}_2\text{S})$ was corrected to 298.15 K by using tabulated $H^{\circ}-H^{\circ}_0$ functions [30] for H$_2$S, H$^+$, and HCl (isoelectronic to HS$^-$). From this anchor point, we obtain a gas-phase enthalpy of acidity at 298.15 K for GeH$_4$ of 1502.0 ± 5.1 kJ mol^{-1}. The lower accuracy of the tabulated D–EA value [17] is mainly due to the uncertainty of $D^{\circ}(\text{H}_3\text{Ge–H})$ [18]. For MeGeH$_3$, the gas-phase enthalpy of acidity was obtained by averaging the data referred to MeCHO and EtCHO. On an absolute scale, the uncertainty (not quoted) is of the same order of magnitude as that for the reference compounds. Relative values for compounds of close acidities are much more precise. The gas-phase acidities $\Delta G^{\circ}_{\text{acid}}$ were obtained by using appropriate values of $\Delta S^{\circ}_{\text{acid}}$, calculated as described above.

The methyl substituent effect on the gas-phase acidity of simple molecules has been given some attention recently in reports dealing with alkanes [34] and silanes [32]. Ethane and methylsilane are weaker acids (enthalpy scale) than methane and silane by about 15 and 23 kJ mol^{-1}, respectively (careful building of an FT-ICR acidity ladder including SiH$_4$ and MeSiH$_3$ leads to a difference of only 14 kJ mol^{-1}) [35]. The acidity decrease was attributed to the destabilization of the anion by the methyl group. Methylation of GeH$_4$ produces a decrease in acidity of 35 kJ mol^{-1}.

Table 3. Gas-phase acidity of germane and methylgermane^a for the reaction AH + Ref$^-$ ⇌ RefH + A$^-$

AH	RefH	$\Delta\Delta G^{\circ\;b}_{\text{acid}}$	$\Delta\Delta H^{\circ\;b}_{\text{acid}}$	$\Delta H^{\circ}_{\text{acid}}(\text{RefH})^c$	$\Delta H^{\circ}_{\text{acid}}(\text{AH})$	$\Delta G^{\circ}_{\text{acid}}(\text{AH})$
GeH$_4$	H$_2$S	25.4 ± 1.4	32.7 ± 3.8	1469.3 ± 1.3^d	1502.0 ± 5.1	1467.9 ± 5.1
	PhNH$_2$	0.9	3.9	1533.0 ± 10.9		
MeGeH$_3$	MeCHO	1.2 ± 0.7	6.2 ± 3.9	1530.5 ± 12.1	1536.6	1503.2
	EtCHO	1.9 ± 0.6	8.0 ± 3.9	1528.4 ± 10.0		

^{a}In kJ mol^{-1}; $T = 298.15$ K; standard state: ideal gas at 0.1 MPa.
^{b}From data in Table 2 corrected at 298.15 K; see text.
^{c}From ref 17, unless otherwise stated.
^{d}Calculated from bond dissociation energy and electron affinity including temperature corrections; see text.

The explanation given for SiH_4 and CH_4 may reasonably be extrapolated to GeH_4.

Bond Dissociation Energies

Equation 3, which connects $\Delta H_{acid}^\circ(AH)$ to $D^\circ(AH)$, $EA(A^-)$, and $IE(H^-)$, is usually used to obtain $\Delta H_{acid}^\circ(AH)$ values at 298 K (under the assumption that the temperature dependences of $EA(A^-)$ and $IE(H^-)$ are equal) [17] by using $D^\circ(AH)$ values at the same temperature and spectroscopic $EA(A^-)$ and $IE(H^-)$ values corresponding to 0 K. Obviously, this relation may serve to obtain $D^\circ(A-H)$ at 298 K when $\Delta H_{acid}^\circ(AH)$ at 298 K and EA are known. In the present case, we have considered the possibility of applying eq 3 to data all referred to 0 K. This allows direct comparison with spectroscopic [6] or calculated [16] bond dissociation energies. Therefore, $\Delta H_{acid}^\circ(GeH_4)$ at 298 K was converted to $\Delta H_{acid0}^\circ(GeH_4)$ at 0 K using $H^\circ-H_0^\circ$ functions [30] for GeH_4, H^+, and AsH_3 (isoelectronic to GeH_3^-). We arrived at $\Delta H_{acid0}^\circ(GeH_4) = 1496.4$ kJ mol^{-1}. Using the $EA(GeH_3^-)$ of Reed and Brauman [12] equal to 167.9 ± 3.9 kJ mol^{-1}, we obtain $D_0^\circ(H_3Ge-H) = 352 \pm 9$ kJ mol^{-1}. The uncertainty is the sum of the uncertainties for EA and ΔH_{acid}°.

Using $H^\circ-H_0^\circ$ functions for GeH_4, AsH_3 (modeling GeH_3^-), and H^- [30], we propose a bond dissociation energy at 298 K: $D^\circ(H_3Ge-H) = 358 \pm 9$ kJ mol^{-1}. Neglecting temperature corrections when using eq 3 leads to $D^\circ(H_3Ge-H) = 359 \pm 9$ kJ mol^{-1}, a value not significantly different. Of note, the 0 K value is significantly lower than the 298 K value, a point not always recognized when thermochemical data of different origin are compared.

In a recent photoionization study of germane, Ruscic et al. [6] found $D_0^\circ(H_3Ge-H) < 358$ kJ mol^{-1} and recommended 348 ± 8 kJ mol^{-1} as a more probable value, in agreement with our 0 K data. High-level ab initio calculations [16] lead to $D_0^\circ(H_3Ge-H) = 355$ kJ mol^{-1}, in good agreement with these experimental results.

Gas-phase kinetics of hydrogen abstraction has been used to determine the first bond dissociation energy of germane. In such a study, Noble and Walsh [18] reported $D^\circ(H_3Ge-H) = 346 \pm 10$ kJ mol^{-1} (believed to be at 298.15 K). This value is lower than ours by 12 kJ mol^{-1}, although it is within the combined uncertainties. More recently, Agrawalla and Setser [15] proposed an even lower value of 326 ± 4 kJ mol^{-1} (at 0 K), in significant disagreement with all other values, in particular those derived from spectroscopic measurements.

From the first bond dissociation energy of germane, we can deduce the heat of formation of the germyl radical [6]. We obtain $\Delta H_{f0}^\circ(GeH_3) = 238 \pm 9$ kJ mol^{-1}. This 0 K value is again in agreement with the value calculated by Ruscic et al. [6] but disagrees strongly with the theoretical value of Binning and Curtiss [16]. At 298.15 K, we obtain 230 ± 9 kJ mol^{-1}, which compares with the Noble and Walsh [18] value of 218 ± 15 kJ mol^{-1}.

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