

Supporting Information

Variable pressure ratios between the unknown acid AH under study and the reference compound, differing by at least a factor of three, were used, with total pressures in the range 2×10^{-5} to 8×10^{-5} Pa (as read on a Bayard Alpert ion gauge).

Relative (to N_2) sensitivities S_r of the Bayard Alpert gauge were either experimentally determined using a spinning rotor gauge (Leybold Vakuum GmbH, Cologne, Germany)ⁱ (Table S1) or estimated using the Bartmess and Georgiadis equation.ⁱⁱ

$$S_r = 0.36 \alpha + 0.30 \quad (1)$$

The molecular polarizability α was taken as α (ahc), calculated using the atomic hybrid component (τ) approach of Miller.ⁱⁱⁱ As τ (ahc) were not available for Si, Ge, and Sn, they were back-calculated⁴ from experimental S_r values in Table S1. We obtained (in $\text{\AA}^{3/2}$) $\tau_{Si}(\text{ahc}) = 3.372$, $\tau_{Ge}(\text{ahc}) = 5.244$, and $\tau_{Sn}(\text{ahc}) = 7.538$.

In general, negative ions were generated by proton abstraction from the neutral reactant by *t*-BuO⁻, which was obtained via dissociative electron capture at 0.1 eV (nominal) of *t*-BuONO, introduced in the spectrometer at a partial pressure of about 10^{-5} Pa. For compounds less acidic than *t*-BuOH, we used instead MeO⁻ generated according to Caldwell and Bartmess^{iv} from a mixture of *t*-BuONO and MeOH. In fact, as pointed out by a referee, methyl nitrite produces CH₃O⁻, but also the isobaric ion HNO⁻. On a few spectra recorded at sufficiently high resolution, we have observed that the intensity of HNO⁻ was about 50 % of that of CH₃O⁻ under our experimental conditions. Pertinent relative acidities in Table S2 were corrected accordingly, and the uncertainties were enlarged to ± 1 kJ/mol to take into account the possible range of HNO⁻ contribution to the total intensity at $m/z = 31$. 2-butyne was found to be less acidic than MeOH, consequently we used NH₂⁻ generated from NH₃ (at an electron energy of about 8 eV) for deprotonating the reactants.

All experimental data concerning equilibrium and bracketing measurements are reported in Tables S2-S6. Results concerning GeH_4 and MeGeH_3 have already been published.⁵ Each AH was measured against several RefH with known $\Delta_{\text{acid}}G^\circ(\text{RefH})$. When the overlap was considered satisfactory, a mean value for $\Delta_{\text{acid}}G^\circ(\text{AH})$ was calculated. For two reference acids (*n*-PrCHO, Table S5; $\text{CH}_2(\text{CO}_2\text{Et})_2$, Table S6), reevaluations of $\Delta_{\text{acid}}G^\circ(\text{RefH})$ were proposed, from check-experiments between acids considered as references. Most of the $\Delta_{\text{acid}}G^\circ(\text{RefH})$ given in the NIST data base²² are reported with an uncertainty of 8.4 kJ/mol (2 kcal/mol). When possible, we have tried to link our relative acidity measurements to only one absolute value. This is the case for all Si derivatives studied here, for which $\Delta_{\text{acid}}G^\circ$ were anchored to that of *t*-BuOH (Table S3). Though DeTuri and Ervin^v reported recently new determinations of gas-phase acidities of alcohols including *t*-BuOH, we chose to use the $\Delta_{\text{acid}}G^\circ$ (*t*-BuOH) value given in the NIST data base for the sake of consistency with the acidities of C, Ge and Sn derivatives which were anchored to the Bartmess acidity scale. It must also be mentioned that the gas-phase acidity for *t*-BuOH reported in the NIST data base is in better agreement with the G2 estimated value (1537 kJ/mol) than the value reported by DeTuri and Ervin⁵. The same methodology was applied to Ge derivatives (except MeGeH_3 and EtGeH_3) for which $\Delta_{\text{acid}}G^\circ$ (Table S4) were anchored to H_2S^{24} . In this approach, only one absolute $\Delta_{\text{acid}}G^\circ$ is fixed. All other $\Delta_{\text{acid}}G^\circ$, either those for AH, or those for RefH compounds serving as references, are optimized simultaneously by a multiple linear regression procedure, as used by Taft and coworkers,^{vi} following the Free and Wilson treatment.^{vii} Each experiment ($\Delta_{\text{exp}}\Delta_{\text{acid}}G^\circ$) is described by a series of presence (1), or absence (0) of $\Delta_{\text{acid}}G^\circ$ intervals, no constant term being included in the model. In Table S3, 22 optimized intervals involving 23 compounds, from *n*-PrOH to PrCHO, were determined from 42 overlapping experiments (98% of the variance in the data explained); in Table S4, 12 intervals involving 13

compounds, from $\text{CH}_2=\text{CH-GeH}_3$ to CF_3COMe , were determined from 22 overlapping experiments (99% of the variance explained).

Table S1. Experimental Relative Ion Gauge Sensitivities (S_r)

| Compound | S_r^a |
|---------------------------|-----------------|
| SiH_4 | 1.70 ± 0.02 |
| MeSiH_3 | 2.69 ± 0.02 |
| Me_2SiH_2 | 3.58 ± 0.02 |
| PhSiH_3 | 5.24 ± 0.06 |
| GeH_4 | 1.94 ± 0.02 |
| MeGeH_3 | 2.67 ± 0.02 |
| PhGeH_3 | 5.30 ± 0.08 |
| SnH_4 | 2.36 ± 0.02 |

^a Sensitivities relative to nitrogen; indicated uncertainty results from the standard deviations on the slopes of calibration curves [$P(\text{Bayard-Alpert})$ vs. $P(\text{spinning rotor})$].

Table S2. Experimental Gas-Phase Acidity of Propyne, Toluene, and 2-Butyne (kJ/mol, 298.15K)

| AH | RefH | $\Delta_{\text{acid}}G^0(\text{RefH})^a$ | $\Delta\Delta_{\text{acid}}G^0{}^b$ | $\Delta_{\text{acid}}G^0(\text{AH})^c$ |
|---|-------------------|--|-------------------------------------|--|
| $\text{HC}\equiv\text{C-CH}_3$ | MeOH | 1565 ± 8.4 | -4 ± 1 | |
| | PhCH ₃ | 1557 ± 8.4^d | 0.74 ± 0.28 | |
| | EtOH | 1551 ± 8.4 | 8.02 ± 0.21 | $1559 \pm 8.4 (1562 \pm 8.4)^e$ |
| PhCH ₃ | MeOH | 1565 ± 8.4 | -7 ± 1 | |
| | EtOH | 1551 ± 8.4 | 5.60 | $1557 \pm 8.4 (1564 \pm 8.4)^e$ |
| $\text{CH}_3\text{-C}\equiv\text{C-CH}_3$ | H ₂ O | 1607.1 ± 0.84^e | -10.63 ± 0.43 | |
| | pyridine | 1601 ± 8.4^e | -2.80 ± 0.38 | 1597 ± 8.4 |

^a Reference 22 unless otherwise indicated.

^b Gibbs energies for the reaction $\text{AH} + \text{Ref}^- \rightarrow \text{A}^- + \text{RefH}$ (338 K, no temperature correction).

^c This work unless otherwise indicated; the indicated uncertainty corresponds to the largest uncertainty on the reference acidities

^d Revised value, this work.

^e Reference 22.

Table S3. Experimental Relative Gas-Phase Acidities of Silane Derivatives (kJ/mol, 338 K) Obtained by the Free-Wilson Optimisation Procedure.

| AH | RefH | $\Delta_{\text{exp}}\Delta_{\text{acid}}G^0{}^a$ | $\Delta_{\text{est}}\Delta_{\text{acid}}G^0(\text{AH}/t\text{-BuOH})^b$ |
|--------------------|--------------------|--|---|
| MeSiH_3 | <i>n</i> -PrOH | -0.65 ± 0.03 | |
| | <i>i</i> -PrOH | 1.13 ± 0.07 | |
| | EtSiH ₃ | 2.80 ± 0.48 | |
| | <i>n</i> -PentOH | 3.90 ± 0.13 | 4.5 ± 1.1 |
| <i>i</i> -PrOH | <i>n</i> -PentOH | 2.81 ± 0.10 | |
| EtSiH ₃ | <i>t</i> -BuOH | 0.40 ± 0.22 | |

| | | | |
|---------------------------------------|---------------------------------------|--------------------------|----------------|
| | MeOCH ₂ CH ₂ OH | 1.34 ± 0.12 | |
| | Me ₂ CO | ≈ 9.9 ^c | 0.4 ± 0.6 |
| <i>n</i> -PentOH | <i>t</i> -BuOH | 2.46 ± 0.06 | |
| | MeOCH ₂ CH ₂ OH | 4.36 ± 0.02 | |
| <i>t</i> -BuOH | MeOCH ₂ CH ₂ OH | 2.00 | |
| | <i>t</i> -BuCH ₂ OH | 5.98 | |
| | <i>t</i> -PentOH | 6.45 ± 0.18 | 0 ^d |
| MeOCH ₂ CH ₂ OH | <i>t</i> -PentOH | 1.77 ± 0.05 | |
| | <i>t</i> -BuCH ₂ OH | 3.05 ± 0.07 | |
| <i>t</i> -PentOH | Et ₃ COH | 8.93 ± 0.21 | |
| <i>t</i> -BuCH ₂ OH | MeCO ₂ Me | 5.01 ± 0.05 | |
| | MeOCH ₂ CN | 6.47 ± 0.13 | |
| | Et ₃ COH | 8.15 ± 0.28 | |
| CH ₂ =CH-SiH ₃ | MeCO ₂ Me | 2.01 ± 0.25 | - 9.6 ± 1.6 |
| SiH ₄ | CH ₂ =CH-SiH ₃ | 0.31 ± 0.47 | |
| | MeCO ₂ Me | 1.39 ± 0.29 | |
| | MeOCH ₂ CN | 2.30 | |
| | Me ₂ CO | 2.92 ± 0.02 ^c | |
| | Et ₃ COH | 3.80 ± 0.29 | - 9.8 ± 1.8 |
| MeCO ₂ Me | MeOCH ₂ CN | 0.73 ± 0.26 | |
| | Et ₃ COH | 3.60 ± 0.36 | |
| MeOCH ₂ CN | Et ₃ COH | 0.70 ± 0.29 | |
| Et ₃ COH | PhCH ₂ OH | 5.98 ± 0.49 | |
| | Me ₂ CO | 10.61 ± 0.54 | |
| PhCH ₂ OH | Me ₂ CO | 5.09 ± 0.30 | |
| Me ₂ CO | Et(Me)CO | 2.10 ± 0.22 ^c | |
| PhC≡CH | Me ₂ CO | 0.39 ± 0.15 | |
| | Et(Me)CO | 1.26 ± 0.30 | |
| PhSiH ₃ | Me ₂ CO | - 0.27 ± 0.84 | |
| | Et(Me)CO | 0.00 ± 0.48 | |
| | PhC≡CH | - 0.70 ± 0.39 | - 25.4 ± 2.4 |
| Et(Me)CO | MeCHO | 5.94 ± 0.45 | |
| <i>n</i> -PrCHO | MeCHO | - 4.95 ± 0.91 | |
| | EtCHO | - 3.89 ± 0.16 | |
| CH≡C-SiH ₃ | Et(Me)CO | - 7.01 ± 0.62 | |
| | MeCHO | - 1.22 ± 0.68 | |
| | EtCHO | - 1.46 ± 0.79 | |
| | <i>n</i> -PrCHO | 1.72 ± 0.52 | - 33.3 ± 2.8 |

^a Gibbs energies for the reaction $\text{AH} + \text{Ref}^- \rightarrow \text{A}^- + \text{RefH}$; quoted uncertainties are the standard deviations for three to four measurements; when only one experiment was available, no uncertainty was reported.

^b Values relative to *t*-BuOH; quoted uncertainties are standard deviations obtained by the propagation of standard deviations on each optimized interval.

^c Some measurements with acetone did not give good overlaps with data established using other compounds. These data were not included in the Free-Wilson treatment. We have observed that tertiary alkoxyde ions gave rise to the reaction: $(\text{R}_1\text{CH}_2)\text{R}_2\text{R}_3 \rightarrow \text{R}_3\text{H} + \text{R}_1\text{-CH=C(O}^-\text{)R}_2$. This may explain some difficulties encountered in the corresponding acidity range.

^d Reference compound; $\Delta_{\text{acid}}G^0(t\text{-BuOH}, 298.15 \text{ K}) = 1540 \pm 8.4 \text{ kJ/mol}$ (taken from ref. 22)

Table S4. Experimental Relative Gas-Phase Acidities of Germane Derivatives (kJ/mol, 338 K) Obtained by the Free-Wilson Optimisation Procedure.

| AH | RefH | $\Delta_{\text{exp}}\Delta_{\text{acid}}G^0$ ^a | $\Delta_{\text{est}}\Delta_{\text{acid}}G^0(\text{AH}/\text{H}_2\text{S})$ ^b |
|---------------------------------|--------------------------|---|---|
| $\text{CH}_2=\text{CH-GeH}_3$ | pyrrole | 0.30 ± 0.11 | |
| | MeSH | 0.20 ± 0.15 | |
| | EtSH | 8.59 ± 0.45 | 24.4 ± 1.9 |
| GeH_4 | pyrrole | 0.25 ± 0.08 | |
| | MeSH | 0.50 ± 0.04 | |
| | EtSH | 7.59 ± 0.25 | 24.1 ± 1.8 |
| pyrrole | EtSH | 6.53 ± 0.29 | |
| MeSH | EtSH | 8.20 ± 0.38 | |
| EtSH | <i>n</i> -PrSH | 3.39 ± 0.04 | |
| | <i>n</i> -BuSH | 5.69 ± 0.13 | |
| | <i>n</i> -HexSH | 7.66 ± 0.25 | |
| <i>n</i> -PrSH | <i>t</i> -BuSH | 6.78 ± 0.17 | |
| <i>n</i> -BuSH | <i>n</i> -HexSH | 2.47 ± 0.38 | |
| <i>n</i> -HexSH | <i>t</i> -BuSH | 2.80 ± 0.21 | |
| PhGeH_3 | EtSH | -10.96 ± 0.46 | |
| | <i>n</i> -PrSH | -7.70 ± 0.04 | |
| | <i>t</i> -BuSH | -1.59 ± 0.22 | 5.1 ± 0.7 |
| H_2S | <i>n</i> -HexSH | -8.70 ± 0.08 | |
| | <i>t</i> -BuSH | -6.28 ± 0.04 | |
| | CF_3COMe | 8.41 ± 0.25 | 0 ^c |
| $\text{CH}\equiv\text{C-GeH}_3$ | H_2S | -8.43 ± 0.05 | |
| | CF_3COMe | 3.16 ± 0.27 | -7.4 ± 0.6 |

^a Gibbs energies for the reaction $\text{AH} + \text{Ref}^- \rightarrow \text{A}^- + \text{RefH}$; quoted uncertainties are the standard deviations for three to four measurements.

^b Values relative to H_2S ; quoted uncertainties are standard deviations obtained by the propagation of standard deviations on each optimized intervals.

^c Reference compound; $\Delta_{\text{acid}}G^0(\text{H}_2\text{S}, 298.15 \text{ K}) = 1442.4 \pm 1.3 \text{ kJ/mol}$ (taken from ref. 24)

Table S5. Experimental Gas-Phase Acidities of Methyl- and Ethylgermane (kJ/mol, 298.15 K)

| AH | RefH | $\Delta_{\text{acid}}G^0(\text{RefH})^a$ | $\Delta\Delta_{\text{acid}}G^0{}^b$ | $\Delta_{\text{acid}}G^0(\text{AH})^c$ |
|--------------------|---------------------------------|--|-------------------------------------|--|
| MeGeH ₃ | MeCHO | 1502 ± 8.4 | 0.52 ± 0.21 ^d | 1502 ± 8.4 |
| | EtCHO | 1501 ± 8.4 | 1.12 ± 0.12 ^d | |
| EtGeH ₃ | MeCHO | 1502 ± 8.4 | 0.95 ± 1.04 | 1500 ± 11 |
| | <i>n</i> -PrCHO | 1497 ± 8.4 ^e | 1.57 ± 0.30 | |
| | (<i>i</i> -Pr) ₂ CO | 1496 ± 11 | 1.74 ± 0.60 | |
| <i>n</i> -PrCHO | MeCHO | 1502 ± 8.4 | -4.95 ± 0.91 | 1497 ± 8.4 (1505 ± 14) ^a |
| | EtCHO | 1501 ± 8.4 | -3.89 ± 0.16 | |

^a Reference 22 unless indicated.^b Gibbs energies for the reaction AH + Ref⁻ → A⁻ + RefH (338 K, no temperature correction); this work unless indicated.^c This work unless otherwise indicated; the indicated uncertainty corresponds to the largest uncertainty on the reference acidities.^d Reference 24.^e Revised value, this work.**Table S6.** Experimental Gas-phase Acidities for Stannane Derivatives (kJ/mol, 298.15 K)

| AH | RefH | $\Delta_{\text{acid}}G^0(\text{RefH})^a$ | $\Delta\Delta_{\text{acid}}G^0{}^b$ | $\Delta_{\text{acid}}G^0(\text{AH})^c$ |
|---|--|--|-------------------------------------|--|
| SnH ₄ | CF ₃ COMe | 1431 ± 8.4 | 0.32 ± 0.41 | 1432 ± 8.4 |
| | CH ₂ (CO ₂ Et) ₂ | 1431 ± 8.4 ^d | 1.20 ± 0.18 | |
| CH ₂ (CO ₂ Et) ₂ | CF ₃ COMe | 1431 ± 8.4 | -0.24 ± 0.21 | 1431 ± 8.4 (1432 ± 8.4) ^a |
| EtSnH ₃ | CF ₃ COMe | 1431 ± 8.4 | 1.51 ± 0.02 | 1433 ± 8.4 |
| | CH ₂ (CO ₂ Et) ₂ | 1431 ± 8.4 | 2.25 ± 0.78 | |
| CH ₂ =CH-SnH ₃ | CF ₃ COMe | 1431 ± 8.4 | -0.16 ± 0.17 | 1431 ± 8.4 |
| | CH ₂ (CO ₂ Et) ₂ | 1431 ± 8.4 | 0.38 ± 0.18 | |
| CH≡C-SnH ₃ | CF ₃ COMe | 1431 ± 8.4 | << 0 | 1386 ± 12 ^e |
| | CH ₂ (CO ₂ Et) ₂ | 1409 ± 8.4 | < 0 | |
| | <i>m</i> -CF ₃ C ₆ H ₄ OH | 1391 ± 8.4 | < 0 | |
| | <i>p</i> -CF ₃ C ₆ H ₄ OH | 1381 ± 8.4 | > 0 | |
| PhSnH ₃ | HCOOH | 1415 ± 8.4 | << 0 | 1400 ± 16 ^f |
| | CF ₃ COMe | 1409 ± 8.4 | < 0 | |
| | CH ₂ (COMe) ₂ | 1409 ± 8.4 | -1.72 ± 1.29 | |
| | <i>m</i> -CF ₃ C ₆ H ₄ OH | 1391 ± 8.4 | 1.59 ± 0.39 | |

^a Reference 22, unless otherwise indicated^b Gibbs energies for reaction Ah + Ref⁻ → A⁻ + RefH (338 K, no temperature correction)^c This work; the indicated uncertainty corresponds to the largest uncertainty of the reference acidities, unless indicated.^d Revised value, this work.^e Bracketing, uncertainty estimated from the range (10 kJ/mol) between the two closest references and the absolute error on the reference acids (8.4 kJ/mol).^f The larger uncertainty is due to the discrepancy between the results obtained from the different references.**Table S7.** Variationally optimized exponents of the *d* and *f* polarization functions and the *s* and *p* diffuse functions for the augmentation of the valence basis set in ECP calculations of tin-containing compounds.

| ECP | <i>d</i> ^a | <i>d</i> ^b | <i>f</i> | <i>s</i> | <i>p</i> |
|-----------|-----------------------|-----------------------|----------|----------|----------|
| SKBJ | 0.205 | 0.212 | 0.286 | 0.0324 | 0.0324 |
| LANL2DZ | 0.215 | 0.204 | 0.273 | 0.0494 | 0.0286 |
| Stuttgart | 0.227 | 0.209 | 0.286 | 0.0463 | 0.0269 |

^a Values to be used with valence basis sets in geometry optimizations^b Values to be used with extended valence basis sets in single-point high-level calculations.

Table S8. Calculated and experimental vibrational frequencies for methylstannane.

| | | | Frequencies | Symmetry | Assignments |
|----------|-----------|------|-------------------|----------------|----------------------------|
| LANDL2DZ | Stuttgart | SKBJ | Exp. ^a | | |
| 3225 | 3224 | 3153 | 3005 | e | CH ₃ d-str. |
| 3123 | 3122 | 3068 | 2933 | a ₁ | CH ₃ s-str. |
| 1937 | 1927 | 1884 | 1875 | a ₁ | SnH ₃ s-str. |
| 1927 | 1912 | 1876 | 1875 | e | SnH ₃ d-str. |
| 1531 | 1535 | 1501 | 1417 | e | CH ₃ d-deform. |
| 1321 | 1323 | 1287 | 1209 | a ₁ | CH ₃ s-deform. |
| 830 | 835 | 823 | 774 | e | CH ₃ rock |
| 766 | 768 | 743 | 741 | e | SnH ₃ d-deform. |
| 748 | 746 | 721 | 695 | a ₁ | SnH ₃ s-deform. |
| 534 | 525 | 518 | 527 | a ₁ | SnC str. |
| 422 | 423 | 416 | 416 | e | SnH ₃ rock |
| 127 | 120 | 114 | 109 | a ₂ | Torsion |

^a Values taken from Shimanouchi, T. *Tables of Molecular Vibrational Frequencies Consolidated Volume I*, NBS 1972, 1.

Table S9. Calculated Ionization potential for Sn^a.

| ECP | IP (eV) |
|-----------|---------|
| SKBJ | 7.248 |
| LANL2DZ | 7.187 |
| Stuttgart | 7.206 |

^a The experimental value taken from Moore, C. E., *Atomic Energy Levels*, NSRDS-NBS, 1971, 35 is 7.342 eV.

Table S10. Calculated heat of formation ($\Delta_f H^0$ in kJ mol⁻¹) of tetramethylstannane.

| ECP | $\Delta_f H^0$ | Exp. ^a |
|-----------|----------------|-------------------------------------|
| SKBJ | -13 | -17.2; -45.3, -53.9, 73.3 |
| LANL2DZ | -28 | Proposed average value: -17.7 ± 2.2 |
| Stuttgart | 19 | |

^a Values taken from ref. 22

References

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