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Relative Energies of Silaethylene and Methylsilylene

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Abstract: The energy difference between silaethylene ($H_2Si{=}CH_2$) and methylsilylene (SiHMe) has been determined with ab initio quantum chemical techniques. Large basis sets and a variety of methods for the inclusion of electron correlation effects have been employed. In direct contrast to the recent theoretical and experimental results of Shin, Irikura, Beauchamp, and Goddard, which suggested silaethylene was 10 kcal/mol more stable than methylsilylene, we find the energy difference to be nearer 4 kcal/mol.

In a recent paper by Shin, Irikura, Beauchamp, and Goddard (SIBG),[1] experimental and theoretical methods were used to re-evaluate the thermochemistry of silaethylene ($H_2Si{=}CH_2$) and methylsilylene (SiHMe). Previous theoretical studies, using moderate size basis sets and including various amounts of electron correlation, had established that the energy difference between these isomers was small, somewhat less than 4 kcal/mol, with silaethylene likely being the most stable isomer.[2] This was in essential agreement with thermochemical estimates from gas-phase kinetic studies,[3] which, with assumptions about Si=C π-bond energies and assuming a constant increment of 16 kcal/mol in ΔH_f upon substitution of H by Me in methylsilanes being transferable to silylenes, predicts $\Delta H_f(H_2Si{=}CH_2) = 39$ kcal/mol and $\Delta H_f(\mathrm{SiHMe}) = 42$ kcal/mol. That is, silaethylene is more stable than methylsilylene by around 3 kcal/mol.

The estimate of the heat of formation of methylsilylene also depended on the heat of formation of silylene,[3] $\Delta H_f(SiH_2) = 58$ kcal/mol, which has lately been revised. A number of recent theoretical and experimental studies,[4] have shown that the correct value of $\Delta H_f(SiH_2)$ should be either 65.5 ± 1.5 or 69 ± 3 kcal/mol, with the former seeming the most likely. Using the value $\Delta H_f(SiH_2) = 69$ kcal/mol obtained in their own work[4a] and retaining the assumption of a constant increment of 16 kcal/mol in ΔH_f of silylenes upon substitution of H by Me,[3] SIBG revised the value of $\Delta H_f^\circ(\mathrm{SiHMe})$ to be 53 kcal/mol or about 14 kcal/mol above that of silaethylene. With this as motivation, SIBG examined the deprotonation energetics of methylsilyl cation, $CH_3SiD_2^+$, using ion cyclotron resonance, which, in conjunction with the known heat of formation of methylsilyl cation, yielded heats of formation of silaethylene and methylsilylene. Their data resulted in an energy difference of 10 ± 3 kcal/mol between $H_2Si{=}CH_2$ and SiHMe and was backed up by ab initio correlation consistent configuration interaction (CCCI) studies, which found a difference of 11.6 kcal/mol. In the present work much larger basis sets and higher level correlation treatments than those used by SIBG are used to demonstrate that the energy difference between the isomers is very likely to be close to the original estimates of 3 kcal/mol.

The basis sets used here were McLean and Chandler's[5] triple-ζ (TZ) contraction of Huzinaga's 12s9p primitive set for silicon[6] and Dunning's[7] triple-ζ (TZ) contraction of Huzinaga's 9s5p set for carbon. To this we appended two sets of cartesian d functions (TZ2P) to both silicon and carbon with $\alpha_d(\mathrm{Si}) = 1.0, 0.25$ and $\alpha_d(\mathrm{C}) = 1.5, 0.35$. The hydrogen basis set is Dunning's[7] standard double-ζ (DZ) contraction of Huzinaga's primitive 4s set, with a single set of p functions added to hydrogen ($\alpha_p(\mathrm{H}) = 0.75$). The hydrogen s functions have been scaled by the standard factor 1.2. The technical designation of this basis set is Si(12s9p2d/6s5p2d), C(9s5p2d/5s3p2d), and H(4s1p/2s1p) and will henceforth be abbreviated as TZ2P. The structures of silaethylene and methylsilylene have been precisely optimized at both the self-consistent field (SCF) and configuration interaction[8] with all single and double excitation (CISD) levels of theory by analytic gradient techniques[9-11] in conjunction with the TZ2P basis sets. Conversion of our theoretically determined energy differences to 0 K enthalpy differences is accomplished through the use of SCF/TZ2P vibrational frequencies, determined analytically.[12] Final energy predictions are determined with an extended (EXT) basis set, which, in addition to the TZ2P basis set, contains diffuse s and p functions on both silicon and carbon, with $\alpha_s(\mathrm{Si}) = 0.0347$, $\alpha_p(\mathrm{Si}) = 0.0230$, $\alpha_s(\mathrm{C}) = 0.0474$, and $\alpha_p(\mathrm{C}) = 0.0365$ determined in an even-tempered sense from the TZ2P basis set, and a set of Cartesian f functions, with $\alpha_f(\mathrm{Si}) = 0.32$ and $\alpha_f(\mathrm{C}) = 0.80$ as recommended by Frisch, Pople, and Binkley.[13]

Aside from the CISD method, a variety of techniques for including the effects of electron correlation have been employed. The simplest of these is appendage of the Davidson correction[14] for unlinked quadruple excitations to the CISD energies (CISD+Q). Others include the use of second-order (MP2)[15] and full fourth-order Möller–Plesset perturbation theory (MP4(SDTQ))[16] and coupled-cluster single- and double-excitation

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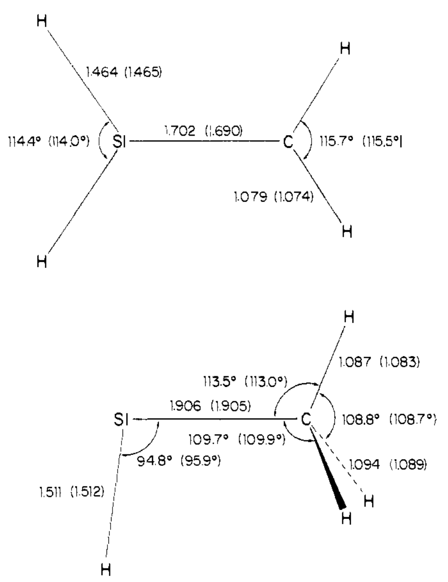

Figure 1. Optimized geometries of silaethylene and methylsilylene at the configuration interaction with all single- and double-excitation (CISD) and self-consistent field (in parentheses) levels of theory by using the TZ2P basis set. Bond lengths are in angstroms and angles in degrees.

(CCSD)[17] and coupled-cluster single-, double-, and linearized triple-excitation (CCSDT-1) techniques.[18,19] The CCSDT-1 model, in particular, has recently been shown to yield results that approach full-CI in quality, especially for properties evaluated near ground-state equilibrium structures, such as those in the present study.[20,21] The CISD+Q, MP4, CCSD, and CCSDT-1 energies reported, both with the TZ2P and EXT basis sets, have been determined at the CISD/TZ2P-optimized geometries. To limit the size of the configuration space at a negligible cost in accuracy, the six core orbitals (Si(1s,2s,2p) and C(1s)-like) have been omitted from the correlation treatment, as have the six highest lying orbitals (those with orbital eigenvalues above 12.0 hartrees for both H_2SiCH_2 and SiHMe). The MPn energies were determined with frozen inner shells.

The optimized geometries of silaethylene and methylsilylene obtained at both the CISD/TZ2P and SCF/TZ2P levels of theory are shown in Figure 1 (the SCF values are in parentheses). Note that the structures change very little upon reoptimization at the CISD level of theory. Only one bond distance, the Si–C double bond in silaethylene, changes by more than 0.005 Å upon reoptimization at the CISD level of theory, and there the change is only 0.012 Å. Similarly, all bond angles, except the H–Si–C angle in methylsilylene (1.1°), change by 0.5° or less. The geometries agree very well with those obtained in previous studies by smaller basis sets at various levels of theory.[2]

The total and relative energies of silaethylene and methylsilylene at the SCF/TZ2P-optimized geometries with SCF, CISD, and CISD+Q methods and at the CISD/TZ2P-optimized geometry with both the TZ2P and EXT basis sets and all of the correlated methods described above are shown in Table I. The relatively small change in geometry upon reoptimization with the CISD wave function is reflected, too, in the very small changes in total and relative energies at the two geometries. Changes in SCF, CISD, and CISD+Q total energies between the two geometries are, in all cases, less than 0.2 kcal/mol, and relative energies change by less than 0.13 kcal/mol. Given this, it seems extremely unlikely that further refinement of the geometries at still higher levels of theory would result in any major changes in the relative energies of silaethylene and methylsilylene. Thus, all subsequent studies have been performed at the CISD/TZ2P geometry.

Table I. Total Energies (Hartrees) and Relative Stabilities (kcal/mol) of Silaethylene and Methylsilylene at Various Levels of Theory

method	silaethylene	methylsilylene	ΔE
SCF/TZ2P[a]	−329.079 00	−329.082 36	−2.1
CISD/TZ2P[a]	−329.345 69	−329.345 21	0.3
CISD+Q/TZ2P[a]	−329.374 37	−329.373 10	0.8
SCF/TZ2P[b]	−329.078 86	−329.082 28	−2.1
CISD/TZ2P[b]	−329.345 82	−329.345 28	0.3
CISD+Q/TZ2P[b]	−329.374 70	−329.373 23	0.9
MP2/TZ2P[b]	−329.341 17	−329.334 56	4.1
MP4(SDTQ)/TZ2P[b]	−329.382 74	−329.378 77	2.5
CCSD/TZ2P[b]	−329.372 12	−329.371 85	0.2
CCSDT-1/TZ2P[b]	−329.384 62	−329.381 40	2.0
SCF/EXT[b]	−329.082 27	−329.084 78	−1.6
CISD/EXT[b]	−329.367 66	−329.366 05	1.0
CISD+Q/EXT[b]	−329.399 08	−329.396 46	1.6
MP2/EXT[b]	−329.365 20	−329.357 78	4.7
MP4(SDTQ)/EXT[b]	−329.408 84	−329.403 62	3.3
CCSD/EXT[b]	−329.396 38	−329.394 92	0.9

[a] At the SCF/TZ2P-optimized geometry. [b] At the CISD/TZ2P-optimized geometry.

Concentrating on the results obtained with the TZ2P basis set, we see that all of the correlated methods used here, except the least rigorous MP2 methods, find silaethylene to be between 0.2 and 2.5 kcal/mol more stable than methylsilylene. It is worth noting that the CCSD and CISD relative energies are nearly identical but that the inclusion of triple excitations in a linearized fashion via CCSDT-1 yields an additional 1.8 kcal/mol stabilization of the multiply bonded silaethylene isomer, and results in an energy difference (2.0 kcal/mol) more in line with the MP4 result of 2.5 kcal/mol. As mentioned earlier, CCSDT-1 energies, particularly for equilibrium structures, have been shown to be of near full-CI quality, thus we consider 2.0 kcal/mol to be our most accurate value with this basis set.

Our final energy predictions, obtained with the EXT basis set, differ only slightly from those obtained with the TZ2P basis set. Addition of f functions and a set of diffuse s and p functions to the heavy atoms stabilizes silaethylene by an additional 0.5 kcal/mol at the SCF level of theory and by 0.6–0.8 kcal/mol by correlated techniques. Unfortunately, determination of the CCSDT-1 energy with this basis set is impractical, but we can obtain a good estimate by adding on the 1.8 kcal/mol difference between CCSDT-1 and CCSD relative energies, obtained with the TZ2P basis set, to the 0.9 kcal/mol CCSD/EXT value. Thus, we obtain a CCSDT-1/EXT estimate of 2.7 kcal/mol, which is very similar to the 3.3 kcal/mol predicted by MP4. If we add to this the difference in zero-point vibrational energy of 0.9 kcal/mol (ZPVE(H_2SiCH_2) = 26.7 kcal/mol; ZPVE(SiHMe) = 27.6 kcal/mol), we obtain a final prediction for the CCSDT-1/EXT 0 K enthalpy difference between silaethylene and methylsilylene of 3.6 kcal/mol.

Given the large basis sets we have used here, the insensitivity of the geometry and relative energies to the method of optimization, the excellent agreement of all the electron correlated results, and the proven accuracy of the CCSDT-1 model, it seems highly unlikely to us that the exact energy difference between silaethylene and methylsilylene could differ from our best value of 3.6 kcal/mol by more than 3 kcal/mol. This places us firmly outside the error bars given for the experimental results of SIBG, 10 ± 3 kcal/mol, and a full 8 kcal/mol below their theoretical value of 11.6 kcal/mol, determined with a much smaller basis set and including a much smaller fragment of the correlation energy. (For comparison, our SCF energy of SiHMe with the EXT basis set is *below* any of their *correlated* energies.) It seems that the combination of small basis sets and correlation consistent CI methods gives a wildly unbalanced description of these two isomers.

A similar problem has recently arisen for the singlet–triplet splitting of the CHF molecule. There the CCCI method[22] gives

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a value of ΔE(S–T) at least 5 kcal/mol above both experiment[23] and higher level theoretical studies.[24,25]

Evidence directly conflicting with that of SIBG concerning the heat of formation of methylsilylene, and indirectly supporting a lower value for the energy difference between $H_2Si{=}CH_2$ and SiHMe, comes from a recent kinetic study of decomposition reactions of various methylated disilanes by Walsh.[26] Therein, he provides evidence to support a value of ΔH_f°(SiHME) = 43.9 ± 3 kcal/mol, compared to 53 ± 4 kcal/mol found by SIBG. Combined with Walsh's earlier estimate[3] for the heat of formation of $H_2Si{=}CH_2$, ΔH_f° = 39 kcal/mol, one can infer an energy difference of about 5 kcal/mol, in agreement with our high-level ab initio results.

SIBG also estimated the Si=C π-bond energy in silaethene by calculating the internal rotation barrier. Unfortunately, these authors incorrectly assumed coplanarity of the $CSiH_2$ moiety in the twisted structure, leading to a rotational barrier that is too high by 23 kcal/mol.[27]

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Heats of Formation of Alkyl Radicals from Appearance Energies

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Abstract: Heats of formation of alkyl radicals have been measured by monoenergetic electron impact on 24 selected precursor molecules as follows: ethyl 27.8; *n*-propyl 22.7; *sec*-propyl 19.1; *n*-butyl 18.1; *sec*-butyl 15.3; isobutyl 15.8; *tert*-butyl 9.5; and neopentyl 10.1 (all kcal mol^{-1}). These values are in good agreement with results from equilibrium measurements using ESR spectroscopy.

Recent investigations show that the heats of formation of C_2–C_4 alkyl radicals, and consequently the strength of C–H bonds in alkanes, are appreciably higher than the values accepted earlier. A revision of $\Delta H_f[C_2H_5^\bullet]$ upward from 25.9[1] to 28.0 kcal mol^{-1},[2] in good agreement with two recent values of 28[3] and 28.4 kcal mol^{-1},[4] has removed inconsistencies associated with the earlier value. The largest remaining disagreements among the ΔH_f data are for *s*-Pr and *t*-Bu radicals; recent values for the former are 22.3,[5] 19.0,[6] and 19.2[2] kcal mol^{-1}, and for the latter 12.4,[5] 9.0,[6] 9.1,[7] 9.2,[8] and 9.4[2] kcal mol^{-1}. For both radicals, the heats of formation, derived by Tsang[5] from his own work and a critical survey of the literature, are about 3 kcal mol^{-1} higher than others recently derived. The consequences of this discrepancy has been commented upon by McMillen and Golden.[1]

In a recent study by Castelhano and Griller,[2] using equilibrium constants for the system

$$CH_3^\bullet + RI \rightleftarrows CH_3I + R^\bullet$$

measured by electron paramagnetic resonance spectroscopy, heats of formation of the following alkyl radicals have been reported: C_2H_5 28.0, *n*-Pr 22.8, *s*-Pr 19.2, *s*-Bu 15.0, c-pentyl 25.1, *t*-Bu 9.4 kcal mol^{-1}. From these data the authors proposed C–H bond dissociation energies in alkanes as follows: primary C–H ~100, secondary C–H ~96, and tertiary C–H ~94 kcal mol^{-1}.

In view of the fundamental importance of these bond dissociation energies to experimental and theoretical kinetics, we have measured the heats of formation of C_2–C_4 alkyl radicals by an independent method, using the appearance energy (AE) for the ionic reaction:

$$R_1R_2 + e \rightarrow 2e + R_1^+ + R_2^\bullet$$

$$AE[R_1^+] \geq \Delta H_f[R_1^+] + \Delta H_f[R_2^\bullet] - \Delta H_f[R_1R_2]$$

in which the compound R_1R_2 is chosen such that $\Delta H_f[R_1^+]$ is a well-established value, and that $\Delta H_f[R_1R_2]$ is either known experimentally or can be calculated accurately. Recent work in these laboratories has shown that this method can give good values for the heats of formation of radicals and other neutral species[9-14] provided that certain conditions are met which reduce the inequality in the above equation to near zero; i.e., the ionic reaction

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