# Theoretical Study of the Thermochemistry of Molecules in the Si−B−H−Cl System

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the $v_4' = 3$ level is 0.68 μs. Similarly, the lifetimes of levels with $v_1' = 1$ and $v_4' = 0$, 1, and 2 are 0.97, 0.66, and 0.14 μs, respectively.[26] This reduction in lifetime as a function of excitation of the bending mode is indicative of an increase in IVR or intersystem crossing.

Thus, if the continuum were associated with either of these processes rather than dissociation, one would expect the continuum absorption would be found under the entire $A^1\Sigma_u^- \leftarrow X^1\Sigma_g^+$ absorption region. Moreover, if one takes the decrease in radiative lifetimes as a measure of the crossing rate, the calculated broadening estimated from the uncertainty principle would be substantially less than a wavenumber.

The resolution of the doubled excimer pumped dye laser was not sufficient to excite single rotational levels of the $C_2N_2$ spectrum. The overall symmetry of the Q branch $A^1\Sigma_u^- \leftarrow X^1\Sigma_g^+$ $1_0^1 4_1^0$ band is $\Sigma \leftarrow \pi$. The peak of the Q branch will be at $J = 25$ for a thermally excited population of $C_2N_2$. The excitation laser was fixed at the Q band maximum. The $A^1\Sigma_u^- v_1' = 1, v_4' = 0$ level lies 47625 cm$^{-1}$ above the ground state. The $N = 16$ level of CN ($X^2\Sigma^+$) has 517 cm$^{-1}$ of rotational energy. This corresponds to a $C_2N_2$ dissociation threshold of 47108 ± 10 cm$^{-1}$ or 212.28 nm. The corresponding bond strength for $C_2N_2$ is 5.84 eV and $\Delta H_f°(CN)$ is 435.5 ± 2.0 kJ/mol.

Experiments on $C_2N_2$ photolysis at higher energy are well modeled by a statistical theory that conserves angular momentum.[12,13] The details of that calculation show that the rotational levels of the two CN fragments are not locked to one another. Rather the orbital angular momentum of the dissociating fragments takes on values which conserve total angular momentum while the rotational state of the partner can assume all energetically possible values with equal weight. Therefore, it is reasonable to assume that in the experiment described here the last observed rotational level of the CN fragment is an energetic upper limit set by the total energy available after dissociation.

By comparison with BrCN photolysis at the same wavelength, the quantum yield for dissociation of $C_2N_2$ excited on the $1_0^1 4_1^0$ line is about 0.05.

The first dissociative state is reached by the $2_0^1 4_0^3$ transition and lies 47070 cm$^{-1}$ above the ground-state origin. The next lowest level is excited via the $2_0^1 4_1^2$ band. This hot band is seen in

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(26) Huang, Y.; Barts, S. A.; Halpern, J. B., manuscript in preparation.

absorption and emission at about the same level as the $2_0^1 4_0^3$ transition. No CN is observed following excitation of any rotational line in the $2_0^1 4_1^2$ band. The frequency of the excited state $v_4'$ bending mode, 274 cm$^{-1}$, is comparable to the average amount of rotational energy at room temperature, 200 cm$^{-1}$. If the dissociation limit was between the $A^1\Sigma_u^-$ state 01020 and 01030 levels, it should have been possible to observe CN following absorption on some rotational lines of the $2_0^1 4_1^2$ band.

This is not the case. Thus, the dissociation limit should lie in the $2_0^1 4_0^3$ band. Unfortunately, the low CN quantum yield at threshold and the resolution of the photolysis laser make it impossible to directly determine where in this band dissociation is first seen.

The energy needed to excite the rotationless $2_0^1 4_0^3$ line, 47070 ± 100 cm$^{-1}$, can therefore be taken as an estimate for breaking the ethanedinitrile CC bond. The uncertainty includes a factor to compensate for the rotational energy of the parent $C_2N_2$. The dissociation threshold would then be 212.45 nm, the bond strength 5.84 eV, and $\Delta H_f°(CN)$ 435.2 ± 2.3 kJ/mol. This CN heat of formation is slightly lower than but within the error of the other two measurements. On the other hand, if rotation were ignored and it was assumed that the dissociation limit lay between excited states reached via the $2_0^1 4_0^3$ and $2_0^1 4_1^2$ bands, 435.2 ± 2.3 kJ/mol would be an upper limit.

Averaging the three determinations yields for the heat of formation of CN at 0 K

$$H_0^f(CN) = 435.4 \pm 2.0 \text{ kJ/mol}$$

and an average bond strength for fracture of the CC bond in $C_2N_2$ of 5.84 ± 0.02 eV. While this is close to the JANAF value, the agreement of our three measurements significantly reduces the uncertainty. It is worthwhile to recall that the uncertainty was based on a wide variation in measured values and the inability of the JANAF board to find a basis of choosing between them. Moreover, many workers have been using lower values recommended by the shock tube and the photodissociative excitation experiments.

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# Theoretical Study of the Thermochemistry of Molecules in the Si–C–H System

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Ab initio electronic structure calculations coupled with empirical corrections are used to obtain a self-consistent set of heats of formation for molecules in the series $H_nSi(CH_3)_m$ and $H_nSiCH_m$ ($n, m$ = 0–4). Heats of formation are also reported for silylethylenes and silylacetylenes in the series $H_2C{=}CHSiH_n$ and $HC{\equiv}CSiH_n$ ($n$ = 0–3), and for $H(CH_3)Si{=}CH_2$, $(CH_3)_2Si{=}CH_2$, and 1,2-dimethyldisilane. Gibbs free energies as a function of temperature and standard entropies are given for all molecules in the study.

## I. Introduction

The reactions of organosilicon compounds are of considerable interest in the field of organometallic chemistry[1-3] due both to the parallels with the analogous hydrocarbon chemistry and to

their own unique properties. Organosilicon compounds are also of key importance to gas-phase reactions occurring during the chemical vapor deposition (CVD) of silicon carbide (SiC). Typical starting compounds used in this process are mixtures of silane and hydrocarbons[4-7] or organochlorosilanes such as methyltrichloro-

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silane,[8-12] which are decomposed in hydrogen at high temperatures (typically above 1500 K) to produce SiC. Decomposition of these reactants leads to reactive silicon-containing species such as silylenes (SiXY; X, Y = H, Cl, or CH₃).[13,14] Silylenes are known to be highly reactive toward unsaturated hydrocarbons such as ethylene and acetylene, which are also formed during reactant pyrolysis.[15-17] These reactions can thus lead to the formation of gas-phase organosilicon species that may be reactive with the deposition surface.

Computational models are now available that can simulate the complex gas-phase chemistry occurring during CVD.[14,18] However, a base of thermodynamic data is required for their implementation. Although this data base exists for most of the species involved in silane and hydrocarbon decomposition, it is not available for many organosilicon compounds. The high-temperature decomposition of SiC precursors involves reactions of large numbers of species, many of which are short-lived and difficult to detect. It is thus difficult to experimentally obtain thermodynamic data for many of the species of interest.

In this paper, we report results of ab initio electronic structure calculations using the empirical bond-additivity correction (BAC) method[19,20] to determine thermodynamic parameters for compounds in the Si-C-H system. Data are reported for all compounds in the $H_nSi(CH_3)_m$ and $H_nSiCH_m$ systems. Several silylethylenes and silylacetylenes are also included, since these compounds are expected to be the initial products of rapid reactions between silylenes and unsaturated hydrocarbons.[16] This extends our previous investigations into the thermochemistry of gas-phase silicon compounds, which have so far included the Si-H-Cl,[21] $Si_2H_m$,[22] Si-H-F,[20] and Si-N-H-F[23] systems.

## II. Theoretical Methods

Detailed presentations of the theoretical methods used in these calculations have been already presented elsewhere.[19,20] A general discussion is provided here, however, for the reader who is not familiar with the computational technique.

Ab initio electronic structure calculations using the Gaussian series of codes developed by Pople et al.[24] were carried out to provide molecular geometries, vibrational frequencies, and electronic energies. In determining the equilibrium molecular geometry, restricted Hartree-Fock (RHF) theory was used for closed-shell molecules and unrestricted Hartree-Fock (UHF) theory for open-shell molecules. The electronic wave function is described by a 6-31G* split-valence basis set with polarization functions on the heavy atoms. Vibrational frequencies obtained at this level of theory are known to be systematically larger than

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**TABLE I: Parameters for Bond Additivity Corrections for BAC-MP4(SDTQ) Level of Theory**

| bond | $A$ | ref species | $\alpha^{a,b}$ |
|------|------|-------------|----------------|
| Si-C | 847.99 | $H_3SiCH_3$ | 2.5 |
| Si-H | 97.79 | $SiH_4$ | 2.0 |
| C-H | 38.61 | $CH_4$ | 2.0 |

$^a$ In $Å^{-1}$. $^b$ Based on related classes of compounds.

experimental values[25] and so were divided by a factor of 1.12.

Higher levels of theory incorporating electron correlation must be used to obtain accurate electronic energies. For this purpose, calculations employing fourth-order Møller-Plesset perturbation theory with single, double, triple, and quadruple excitations were performed (MP4(SDTQ)), using a split-valence basis set with polarization functions on all atoms (6-31G**). Molecules with as many as 11 heavy atoms have been treated at this level of theory with existing computer technology. The electronic energies obtained from MP4 calculations are not sufficiently accurate, however, to provide useful heats of formation. This is primarily a result of the finite basis set. The errors incurred are found to be systematic, however, and can be removed by the application of empirical correction factors. In the method used here these factors are called bond additivity corrections. Their values depend primarily on bond type and bond distance but are also a function of the identity of neighboring atoms. The form of the BAC for a molecule $X_k-X_i-X_j$ is given by

$$E_{BAC}(X_i-X_j) = f_{ij}g_{kij} \qquad (1)$$

where

$$f_{ij} = A_{ij} \exp(-\alpha_{ij}R_{ij}) \qquad (2)$$

$$g_{kij} = (1 - h_{ik}h_{ij}) \qquad (3)$$

$$h_{ik} = B_k \exp\{-\alpha_{ik}(R_{ik} - 1.4 \text{ Å})\} \qquad (4)$$

$A_{ij}$ and $\alpha_{ij}$ are empirically derived parameters that depend on the $X_i-X_j$ bond type and $R_{ij}$ is the bond distance (angstroms). The factor $B_k$ in eq 4 depends on the identity of atom $k$. For molecules with an additional heavy atom $l$ and structure $X_k-X_i-X_j-X_l$, an additional correction factor is required, leading to $E_{BAC} = f_{ij}g_{kij}g_{lji}$.

The values of $A_{ij}$ and $\alpha_{ij}$ used in these calculations are listed in Table I. The $A_{ij}$ factors were obtained by fitting the BAC-MP4 heats of formation for reference compounds to their respective experimental values; only compounds with well-established heats of formation were used as reference compounds. The correction for the Si-C single bond, $A_{SiC}$, was based on the heat of formation for the reference compound $Si(CH_3)_4$ measured by Steele[26] and preferred by Walsh.[27] For C-H bonds, the reference compound $CH_4$ was used to determine $A_{CH}$. As in previous calculations, the BACs for Si-H bonds were determined from the $SiH_4$ heat of formation.[20] The exponents $\alpha_{ij}$ were determined by comparison with correction factors obtained for related classes of molecules for which many reference compounds are available. Since thermodynamic data for compounds with multiply bonded Si-C bonds is limited, however, $\alpha_{SiC}$ was determined by assuming that this exponent should lie between the values of $\alpha_{SiSi}$ and $\alpha_{CC}$. Neighboring-atom $B_k$ factors used in this work are $B_H = 0.00$, $B_C = 0.31$, and $B_{Si} = 0.20$.

A correction was also made in the case of open-shell molecules for spin contamination of the ground state by excited electronic states. The error in the electronic energy caused by this effect was estimated using the approach of Schlegel[28] and is given by

$$E_{BAC}(\text{spins}^2) = E(\text{UMP3}) - E(\text{PUMP3}) \qquad (5)$$

where $E(\text{UMP3})$ is the third-order MP energy using the UHF wave function and $E(\text{PUMP3})$ is the projected UMP3 energy. This correction is generally small ($\leq 0.5$ kcal mol$^{-1}$) but may

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**TABLE II: Bond Additivity Corrections for the MP4(SDTQ) Level of Theory (kcal mol$^{-1}$)**

| species | Si-C bond length$^a$ (no.)$^b$ | BAC | Si-H bond length (no.) | BAC | C-H bond length (no.) | BAC | C-C bond length | BAC | Si-Si bond length | BAC | spin or UHF-unstable correction$^c$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| H₃SiCH₃ | 1.888 | 7.97 | 1.478 (3) | 4.82 | 1.086 | 4.40 | | | | | |
| | | | | | 1.086 (2) | 4.40 | | | | | |
| H₂Si(CH₃)₂ | 1.890 (2) | 7.87 | 1.481 (2) | 4.80 | 1.086 (2) | 4.40 | | | | | |
| | | | | | 1.087 (4) | 4.39 | | | | | |
| HSi(CH₃)₃ | 1.891 (3) | 7.78 | 1.483 | 4.78 | 1.087 (9) | 4.39 | | | | | |
| Si(CH₃)₄ | 1.893 | 7.67 | | | 1.087 (12) | 4.39 | | | | | |
| | 1.894 (3) | 7.67 | | | | | | | | | |
| H₂SiCH₃ | 1.894 | 7.84 | 1.480 (2) | 4.81 | 1.087 | 4.39 | | | | | 0.16 u |
| | | | | | 1.085 (2) | 4.41 | | | | | |
| HSi(CH₃)₂ | 1.896 (2) | 7.75 | 1.483 | 4.78 | 1.086 (4) | 4.40 | | | | | 0.14 u |
| | | | | | 1.088 (2) | 4.38 | | | | | |
| Si(CH₃)₃ | 1.898 (3) | 7.65 | | | 1.086 (6) | 4.40 | | | | | 0.13 u |
| | | | | | 1.089 (3) | 4.38 | | | | | |
| HSiCH₃ | 1.914 | 7.47 | 1.513 | 4.50 | 1.090 (2) | 4.36 | | | | | 3.55 s |
| | | | | | 1.084 | 4.41 | | | | | |
| Si(CH₃)₂ | 1.917 (2) | 7.35 | | | 1.085 (2) | 4.41 | | | | | 3.46 s |
| | | | | | 1.090 (2) | 4.37 | | | | | |
| | | | | | 1.092 (2) | 4.35 | | | | | |
| SiCH₃ | 1.917 | 7.40 | | | 1.094 | 4.33 | | | | | 0.59 u |
| | | | | | 1.087 (2) | 4.39 | | | | | |
| H₃SiCH₂ | 1.860 | 8.54 | 1.480 | 4.81 | 1.078 (2) | 4.47 | | | | | 0.66 u |
| | | | 1.447 (2) | 4.84 | | | | | | | |
| H₂Si(CH₃)CH₂ | 1.863 | 8.41 | 1.482 | 4.79 | 1.078 (2) | 4.47 | | | | | 0.65 u |
| | 1.888 | 7.89 | 1.480 | 4.81 | 1.086 (2) | 4.40 | | | | | |
| | | | | | 1.087 | 4.39 | | | | | |
| HSi(CH₃)₂CH₂ | 1.866 | 8.27 | 1.485 | 4.76 | 1.079 (2) | 4.46 | | | | | 0.64 u |
| | 1.890 (2) | 7.79 | | | 1.087 (6) | 4.39 | | | | | |
| Si(CH₃)₃CH₂ | 1.870 | 8.12 | | | 1.079 (2) | 4.46 | | | | | 0.63 u |
| | 1.895 | 7.64 | | | 1.087 (8) | 4.39 | | | | | |
| | 1.892 (2) | 7.69 | | | 1.088 | 4.38 | | | | | |
| H₂Si=CH₂ | 1.694 | 12.95 | 1.467 (2) | 4.93 | 1.076 (2) | 4.49 | | | | | 3.03 s |
| H(CH₃)Si=CH₂ | 1.693 | 12.79 | 1.471 | 4.90 | 1.076 (2) | 4.49 | | | | | 1.84 s |
| | 1.879 | 8.04 | | | 1.085 | 4.41 | | | | | |
| | | | | | 1.086 (2) | 4.40 | | | | | |
| (CH₃)₂Si=CH₂ | 1.693 | 12.61 | | | 1.077 (2) | 4.48 | | | | | 0.43 s |
| | 1.882 (2) | 7.92 | | | 1.085 (2) | 4.41 | | | | | |
| | | | | | 1.086 (4) | 4.40 | | | | | |
| HSiCH₂ | 1.767 | 10.79 | 1.475 | 4.86 | 1.078 | 4.47 | | | | | 7.45 u |
| | | | | | 1.076 | 4.49 | | | | | |
| SiCH₂ | 1.702 | 12.69 | | | 1.082 (2) | 4.44 | | | | | 2.84 s |
| H₃SiCH | 1.840 | 8.99 | 1.474 | 4.87 | 1.073 | 4.52 | | | | | 0.92 u |
| | | | 1.477 (2) | 4.83 | | | | | | | |
| H₂SiCH | 1.781 | 10.41 | 1.474 | 4.86 | 1.071 | 4.53 | | | | | 9.86 u |
| | | | 1.471 | 4.89 | | | | | | | |
| SiCH | 1.722 | 12.07 | | | 1.070 | 4.54 | | | | | 7.59 u |
| H₃SiC | 1.847 | 8.84 | 1.474 | 4.87 | | | | | | | 0.21 u |
| | | | 1.474 (2) | 4.87 | | | | | | | |
| H₂SiC | 1.797 | 10.00 | 1.473 (2) | 4.87 | | | | | | | 4.98 u |
| HSiC | 1.750 | 11.26 | 1.483 | 4.78 | | | | | | | 10.21 u |
| H₃SiC≡CH | 1.838 | 8.61 | 1.472 (3) | 4.88 | 1.058 | 4.65 | 1.194 | 14.78 | | | |
| H₂SiC≡CH | 1.821 | 8.99 | 1.473 (2) | 4.88 | 1.058 | 4.65 | 1.203 | 14.27 | | | 2.53 u |
| HSiC≡CH | 1.847 | 8.43 | 1.506 | 4.57 | 1.058 | 4.65 | 1.200 | 14.47 | | | 2.91 s |
| SiC≡CH | 1.816 | 9.12 | | | 1.059 | 4.65 | 1.216 | 13.60 | | | 4.53 u |
| H₂C=CHSiH₃ | 1.873 | 8.06 | 1.477 | 4.84 | 1.080 | 4.45 | 1.325 | 9.17 | | | |
| | | | 1.478 (2) | 4.83 | 1.077 | 4.48 | | | | | |
| | | | | | 1.078 | 4.47 | | | | | |
| H₂C=CHSiH₂ | 1.849 | 8.57 | 1.476 | 4.85 | 1.080 | 4.45 | 1.353 | 8.26 | | | 4.64 u |
| | | | 1.477 | 4.84 | 1.077 (2) | 4.48 | | | | | |
| H₂C=CHSiH | 1.882 | 7.90 | 1.512 | 4.51 | 1.079 | 4.46 | 1.334 | 8.88 | | | 2.31 s |
| | | | | | 1.078 (2) | 4.47 | | | | | |
| H₂C=CHSi | 1.843 | 8.70 | | | 1.086 | 4.40 | 1.367 | 7.81 | | | 6.08 u |
| | | | | | 1.076 | 4.49 | | | | | |
| | | | | | 1.077 | 4.48 | | | | | |
| CH₃SiH₂SiH₂CH₃ | 1.897 (2) | 7.79 | 1.483 (4) | 4.78 | 1.086 (6) | 4.40 | | | 2.357 | 5.72 | |

$^a$ In angstroms. $^b$ Number of bonds. $^c$ u, UHF-unstable correction; s, spin-contamination correction.

become large for molecules containing a high degree of unsaturation or low-lying electronic excited states. Closed-shell molecules that are UHF-unstable, such as SiH₂, also require an additional correction. The form of the correction is

$$E_{BAC}(\text{spin}_{UHF\text{-unstable}}) = K_{UHF\text{-I}}S(S + 1) \tag{6}$$

where $K_{UHF\text{-I}}$ is 10.0 kcal mol$^{-1}$ (based on the heat of formation of O₃) and $S$ is the spin obtained from the UHF/6-31G** calculation. Application of this correction yields reasonable heats of formation for singlet SiH₂ and CH₂. The BACs for all molecules in the study are given in Table II with the associated bond length, spin contamination, and UHF-unstable corrections.

The values of thermodynamic parameters are derived from the BAC-MP4(STDQ) energy, which, when combined with the

**TABLE III: Calculated $\Delta H^{\circ}_f(0)$ for Si–C–H Compounds at Various Levels of Theory (kcal mol$^{-1}$)**

| species | MP4 | BAC-MP2 | BAC-MP3 | BAC-MP4 SDQ | BAC-MP4 SDTQ |
|---|---|---|---|---|---|
| $H_3SiCH_3$ | 32.3 | -3.4 | -3.4 | -3.4 | -3.4 |
| $H_2Si(CH_3)_2$ | 33.7 | -17.9 | -18.0 | -18.1 | -18.0 |
| $HSi(CH_3)_3$ | 34.6 | -32.9 | -33.1 | -33.3 | -33.0 |
| $Si(CH_3)_4$ | 35.1 | -48.1 | -48.3 | -48.5 | -48.3 |
| $H_2SiCH_3$ | 66.9 | 35.3 | 36.0 | 36.0 | 36.0 |
| $HSi(CH_3)_2$ | 69.4 | 21.8 | 22.6 | 22.6 | 22.6 |
| $Si(CH_3)_3$ | 71.2 | 7.9 | 8.7 | 8.5 | 8.6 |
| $HSiCH_3$ | 79.6 | 52.8 | 51.9 | 51.3 | 50.9 |
| $Si(CH_3)_2$ | 80.1 | 37.3 | 36.9 | 36.3 | 35.7 |
| $SiCH_3$ | 97.1 | 76.6 | 76.7 | 76.3 | 76.0 |
| $H_3SiCH_2$ | 77.1 | 44.5 | 43.9 | 43.8 | 44.5 |
| $H_2Si(CH_3)CH_2$ | 78.5 | 29.9 | 29.2 | 29.1 | 29.8 |
| $HSi(CH_3)_2CH_2$ | 79.3 | 14.9 | 14.0 | 13.9 | 14.8 |
| $Si(CH_3)_3CH_2$ | 79.8 | -0.2 | -1.0 | -1.2 | -0.3 |
| $H_2Si=CH_2$ | 77.9 | 44.3 | 44.3 | 43.8 | 43.0 |
| $H(CH_3)Si=CH_2$ | 79.7 | 31.2 | 31.0 | 30.5 | 30.0 |
| $(CH_3)_2Si=CH_2$ | 81.4 | 18.4 | 17.9 | 17.5 | 17.1 |
| $HSiCH_2$ | 119.2 | 87.2 | 88.0 | 86.9 | 87.1 |
| $SiCH_2$ | 99.0 | 77.4 | 76.6 | 75.8 | 74.6 |
| $H_3SiCH$ | 123.7 | 94.2 | 93.7 | 93.8 | 94.7 |
| $H_2SiCH$ | 140.9 | 106.7 | 106.2 | 105.5 | 106.4 |
| $SiCH$ | 148.1 | 127.1 | 125.4 | 123.6 | 123.9 |
| $H_3SiC$ | 172.7 | 147.7 | 147.8 | 148.2 | 149.1 |
| $H_2SiC$ | 192.4 | 167.0 | 167.0 | 166.8 | 167.6 |
| $HSiC$ | 210.6 | 190.8 | 189.0 | 185.4 | 184.3 |
| $H_3SiC\equiv CH$ | 97.7 | 55.6 | 55.2 | 54.6 | 55.0 |
| $H_2SiC\equiv CH$ | 132.1 | 92.5 | 92.5 | 91.3 | 91.9 |
| $HSiC\equiv CH$ | 140.1 | 107.7 | 106.6 | 105.6 | 105.0 |
| $SiC\equiv CH$ | 157.0 | 127.7 | 127.1 | 125.1 | 125.1 |
| $H_2C=CHSiH_3$ | 69.5 | 25.8 | 24.6 | 24.5 | 24.4 |
| $H_2C=CHSiH_2$ | 105.7 | 61.8 | 61.7 | 60.7 | 61.1 |
| $H_2C=CHSiH$ | 112.5 | 78.4 | 76.9 | 76.5 | 75.6 |
| $H_2C=CHSi$ | 135.0 | 101.1 | 100.5 | 98.9 | 99.0 |
| $CH_3SiH_2SiH_2CH_3$ | 62.4 | -4.6 | -4.1 | -4.2 | -4.4 |

unscaled zero-point energy, yields the heat of formation at 0 K. Standard expressions from statistical mechanics are applied to calculate the entropy, heat capacity, and internal energy, using the HF/6-31G* geometries and scaled frequencies as input. We use the abbreviation BAC-MP4 to refer to heats of formation determined from the MP4(STDQ) energies.

Since the major source of error in the thermochemical data is the determination of the molecular heat of formation at 0 K, an estimate of this error was obtained, using the results of calculations made at lower levels of perturbation theory during the determination of the MP4(SDTQ) electronic energy.[19] Bond additivity corrections are applied to the MP2, MP3, and MP4(SDQ) electronic energies to obtain $\Delta H^{\circ}_f(0)$ at these levels of theory, resulting in the following definition for the estimated error:

$$\text{Error(BAC-MP4)} = \{1.0 \text{ kcal mol}^{-1} + (\Delta H_{BAC\text{-}MP4} -$$
$$\Delta H_{BAC\text{-}MP3})^2 + (\Delta H_{BAC\text{-}MP4} - \Delta H_{BAC\text{-}MP4SDQ})^2 +$$
$$0.25(E_{BAC}(\text{spin}_S^2) \text{ or } E_{BAC}(\text{spin}_{UHF\text{-}I}))^2\}^{1/2} \quad (7)$$

Thus, convergence of $\Delta H^{\circ}_f(0)$ to a fixed value as the level of theory increases from BAC-MP2 to BAC-MP4 results in a low value for the calculational error. Spin and UHF-unstable errors are also reflected in the error value and tend to increase as the molecule becomes more unsaturated. It should be noted that this error estimate does not account for possible inaccuracies in the values of reference heats of formation. In particular, since there are no reference data for molecules containing Si–C double bonds, there exists a potential systematic error for this class of compounds.

## III. Results and Discussion

The results of applying the BAC-MP4 method to compounds in the Si–C–H system are given in Tables III–V. Table III lists the values of $\Delta H^{\circ}_f(0)$ at different levels of theory, from which BAC-MP4 error estimates are calculated. Computed electronic energies, vibrational frequencies, moments of inertia, and $Z$ matrices are not given here but are available in the supplementary material (see paragraph at the end of the paper). Table IV gives

**TABLE IV: Calculated $\Delta H^{\circ}_f(298)$ for Si–C–H Compounds at the BAC-MP4(SDTQ) Level of Theory with Error Estimates[a] (kcal mol$^{-1}$)**

| | | |
|---|---|---|
| $H_3SiCH_3$ | $-7.3 \pm 1.0$ | $-6.96,^b -6.65,^c -6.9,^d -11.1^i$ |
| $H_2Si(CH_3)_2$ | $-23.2 \pm 1.0$ | $-22.6,^b -22.95^c -22.6\text{-}22.9,^d -25.6^i$ |
| $HSi(CH_3)_3$ | $-39.4 \pm 1.0$ | $39.05,^b -39.26^c 39.0 \pm 0.1,^d -39.3^i$ |
| $Si(CH_3)_4$ | $-55.7 \pm 1.0$ | $-55.74,^b -57.1,^e -55.74,^c -55.7,^d$ |
| | | $-52.1^i$ |
| $H_2SiCH_3$ | $33.1 \pm 1.0$ | $30.6 \pm 2.1,^b 34 \pm 3^f$ |
| $HSi(CH_3)_2$ | $18.3 \pm 1.0$ | $15 \pm 2,^b 19 \pm 3^f$ |
| $Si(CH_3)_3$ | $3.1 \pm 1.0$ | $-1 \pm 2,^b -12 \pm 2,^g 3 \pm 3^f$ |
| $HSiCH_3$ | $48.8 \pm 2.3$ | $44.0 \pm 2.9,^b 51.9,^h 48 \pm 2,^c 50.6,^i$ |
| | | $53 \pm 4,^j 53.1 \pm 1.1,^k 45.2^l$ |
| $Si(CH_3)_2$ | $32.2 \pm 2.4$ | $32\text{-}33,^l 26 \pm 2,^m 37 \pm 6,^j 32 \pm 2^c$ |
| $SiCH_3$ | $74.5 \pm 1.3$ | |
| $H_3SiCH_2$ | $41.5 \pm 1.4$ | |
| $H_2Si(CH_3)CH_2$ | $25.6 \pm 1.5$ | |
| $HSi(CH_3)_2CH_2$ | $9.3 \pm 1.5$ | |
| $Si(CH_3)_3CH_2$ | $-6.9 \pm 1.5$ | $-8.6 \pm 1.4^b$ |
| $H_2Si=CH_2$ | $40.7 \pm 2.4$ | $37.0 \pm 4.8,^b 43 \pm 3,^j 46.5,^i 21.8^t$ |
| $H(CH_3)Si=CH_2$ | $26.4 \pm 1.8$ | $21 \pm 5,^b 18^n$ |
| $(CH_3)_2Si=CH_2$ | $12.3 \pm 1.4$ | $5.0 \pm 4.8,^b -0.5 \pm 2,^p 15.5 \pm 5,^q$ |
| | | $46,^n 8.6 \pm 1.7^u$ |
| $HSiCH_2$ | $85.8 \pm 4.0$ | |
| $SiCH_2$ | $74.2 \pm 2.9$ | |
| $H_3SiCH$ | $92.7 \pm 1.8$ | |
| $H_2SiCH$ | $105.4 \pm 5.1$ | |
| $SiCH$ | $124.4 \pm 4.2$ | |
| $H_3SiC$ | $147.6 \pm 1.8$ | |
| $H_2SiC$ | $167.2 \pm 2.9$ | |
| $HSiC$ | $184.9 \pm 7.1$ | |
| $H_3SiC\equiv CH$ | $53.0 \pm 1.1$ | $63.2 \pm 4^r$ |
| $H_2SiC\equiv CH$ | $91.0 \pm 1.8$ | |
| $HSiC\equiv CH$ | $105.0 \pm 2.5$ | |
| $SiC\equiv CH$ | $125.8 \pm 3.2$ | |
| $H_2C=CHSiH_3$ | $20.7 \pm 1.0$ | $-2,^e 11.4^i$ |
| $H_2C=CHSiH_2$ | $58.2 \pm 2.6$ | |
| $H_2C=CHSiH$ | $73.5 \pm 2.3$ | |
| $H_2C=CHSi$ | $97.8 \pm 3.5$ | |
| $CH_3SiH_2SiH_2CH_3$ | $-10.9 \pm 1.1$ | $-11.0,^c -14.9,^m -10.5^s$ |
| $SiH_3$ | $47.4 \pm 1.0$ | |
| $SiH_2 (^1A_1)$ | $64.8 \pm 2.2$ | |
| $SiH$ | $91.0 \pm 1.1$ | |
| $Si$ | $107.4$ | |
| $CH_3$ | $34.9 \pm 1.2$ | |
| $CH_2$ (triplet) | $92.8 \pm 1.4$ | |
| $CH$ | $146.7 \pm 1.1$ | |
| $CHCH_2$ | $71.0 \pm 3.5$ | |
| $C_2H$ | $132.2 \pm 6.4$ | |
| $C$ | $171.2$ | |
| $H$ | $52.1$ | |

[a] Error estimates indicate only relative applicability of the calculational methods. See text for discussion. [b] Reference 42. [c] Reference 44. [d] Reference 30. [e] Reference 61. [f] Reference 46. [g] Reference 47. [h] Reference 50. [i] Reference 53. [j] Reference 52. [k] Reference 48. [l] Reference 54. [m] Reference 27. [n] Reference 57. [p] Reference 58. [q] Reference 60. [r] Reference 63. [s] Reference 45. [t] Reference 62. [u] Reference 59.

the computed values of $\Delta H^{\circ}_f(298)$ and BAC-MP4 error estimates, with relevant literature values for comparison. Table V lists $\Delta S^{\circ}(298)$ and values of $\Delta G^{\circ}_f$ at various temperatures.

**A. Heats of Formation and Bond Dissociation Enthalpies.** Heats of formation at several levels of theory are given in Table III for all the compounds in this study. The results show that, in almost all cases, $\Delta H^{\circ}_f(0)$ is essentially the same at all levels of theory or converges to an approximately constant value. This indicates that error estimates for the BAC-MP4 heats of formation, as measured by eq 7, are probably small. Table IV lists values of $\Delta H^{\circ}_f(298)$ for the various species; the calculated uncertainties are generally $\leq 2.5$ kcal mol$^{-1}$. Larger uncertainties are found in the values of some molecules such as HSiC that are highly unsaturated; the high uncertainty in these cases usually arises from spin contamination or UHF-unstable corrections, resulting in a large spin contribution (Table II) to the error estimate.

Several trends in the stability of Si–C–H compounds can be discerned from the data in Table IV. Figure 1 displays $\Delta H^{\circ}_f(298)$

**TABLE V: BAC-MP4 Thermochemical Parameters for Si-C-H Compounds at Various Temperatures (kelvin)**

| species | $\Delta H^{\circ}_f(298)^a$ | $S^{\circ}(298)^b$ | $\Delta G^{\circ}_f{}^a$ | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | 300 | 600 | 1000 | 1500 | 2000 | 2500 |
| $H_3SiCH_3$ | -7.3 | 61.8 | 3.9 | 16.2 | 33.7 | 55.6 | 79.2 | 103.5 |
| $H_2Si(CH_3)_2$ | -23.2 | 72.4 | -5.5 | 13.7 | 40.3 | 73.5 | 108.2 | 143.1 |
| $HSi(CH_3)_3$ | -39.4 | 83.6 | -15.3 | 10.5 | 45.9 | 90.1 | 135.4 | 180.7 |
| $Si(CH_3)_4$ | -55.7 | 93.1 | -24.7 | 8.2 | 53.2 | 109.1 | 165.9 | 222.3 |
| $H_2SiCH_3$ | 33.0 | 64.5 | 38.8 | 45.3 | 55.0 | 67.3 | 81.5 | 96.6 |
| $HSi(CH_3)_2$ | 18.3 | 74.8 | 30.6 | 44.1 | 63.1 | 86.9 | 112.5 | 138.6 |
| $Si(CH_3)_3$ | 3.1 | 84.8 | 22.3 | 42.7 | 71.1 | 106.7 | 143.6 | 180.8 |
| $HSiCH_3$ | 48.8 | 62.0 | 50.6 | 52.9 | 57.0 | 62.3 | 69.9 | 78.6 |
| $Si(CH_3)_2$ | 32.2 | 74.6 | 39.9 | 48.1 | 60.4 | 76.0 | 93.6 | 111.9 |
| $SiCH_3$ | 74.5 | 60.2 | 72.2 | 70.5 | 69.3 | 68.4 | 70.0 | 72.9 |
| $H_3SiCH_2$ | 41.5 | 67.6 | 46.3 | 51.5 | 59.2 | 68.9 | 80.4 | 92.8 |
| $H_2Si(CH_3)CH_2$ | 25.6 | 77.8 | 37.0 | 49.2 | 66.3 | 87.6 | 110.4 | 133.8 |
| $HSi(CH_3)_2CH_2$ | 9.3 | 86.2 | 28.0 | 47.7 | 74.8 | 108.5 | 143.4 | 178.5 |
| $Si(CH_3)_3CH_2$ | -6.9 | 96.6 | 18.4 | 44.9 | 81.3 | 126.3 | 172.3 | 218.0 |
| $H_2Si=CH_2$ | 40.7 | 59.9 | 43.2 | 46.2 | 51.3 | 57.8 | 66.5 | 76.1 |
| $H(CH_3)Si=CH_2$ | 26.4 | 70.3 | 35.4 | 45.2 | 59.4 | 77.4 | 97.3 | 117.8 |
| $(CH_3)_2Si=CH_2$ | 12.3 | 80.4 | 28.1 | 44.8 | 68.3 | 97.9 | 129.0 | 160.3 |
| $HSiCH_2$ | 85.8 | 60.6 | 83.4 | 81.3 | 79.3 | 77.0 | 77.2 | 78.6 |
| $SiCH_2$ | 74.2 | 56.0 | 68.5 | 63.1 | 56.7 | 49.3 | 44.6 | 41.3 |
| $H_3SiCH$ | 92.7 | 65.6 | 93.4 | 94.3 | 96.1 | 98.3 | 102.6 | 108.0 |
| $H_2SiCH$ | 105.3 | 62.5 | 102.4 | 99.4 | 95.9 | 91.6 | 89.6 | 88.8 |
| $SiCH$ | 124.4 | 54.9 | 114.3 | 104.2 | 91.1 | 75.0 | 61.6 | 49.6 |
| $H_3SiC$ | 147.6 | 61.8 | 144.8 | 142.5 | 140.1 | 137.3 | 136.7 | 137.3 |
| $H_2SiC$ | 167.2 | 60.3 | 160.2 | 153.4 | 144.9 | 134.7 | 126.9 | 120.5 |
| $HSiC$ | 184.8 | 58.2 | 173.8 | 162.8 | 148.5 | 131.2 | 116.6 | 103.6 |
| $H_3SiC\equiv CH$ | 53.0 | 64.1 | 54.6 | 56.7 | 60.2 | 64.7 | 71.4 | 79.1 |
| $H_2SiC\equiv CH$ | 91.0 | 66.9 | 87.1 | 83.3 | 79.0 | 73.8 | 70.9 | 69.2 |
| $HSiC\equiv CH$ | 105.0 | 64.4 | 97.2 | 89.4 | 79.6 | 67.9 | 58.8 | 51.0 |
| $SiC\equiv CH$ | 125.8 | 60.4 | 114.5 | 103.1 | 88.1 | 70.0 | 54.4 | 40.3 |
| $H_2C=CHSiH_3$ | 20.6 | 69.0 | 30.1 | 40.6 | 55.8 | 74.6 | 95.3 | 116.6 |
| $H_2C=CHSiH_2$ | 58.2 | 69.0 | 63.0 | 68.4 | 76.7 | 87.2 | 99.8 | 113.1 |
| $H_2C=CHSiH$ | 73.5 | 66.7 | 74.4 | 75.8 | 78.9 | 83.1 | 89.3 | 96.5 |
| $H_2C=CHSi$ | 97.8 | 66.0 | 94.1 | 90.9 | 87.7 | 84.1 | 83.1 | 83.3 |
| $CH_3SiH_2SiH_2CH_3$ | -10.9 | 88.0 | 12.8 | 37.9 | 72.5 | 115.2 | 161.1 | 208.5 |

$^a$ In kcal mol$^{-1}$.  $^b$ In cal mol$^{-1}$ K$^{-1}$.
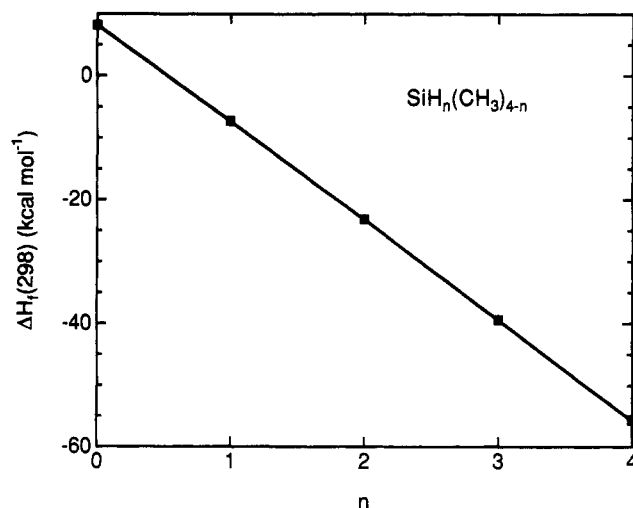


**Figure 1.** Calculated heats of formation for $SiH_n(CH_3)_{4-n}$ species as a function of $n$. As expected for closed-shell molecules, these species fall nearly on a straight line.

for the series of compounds $SiH_n(CH_3)_{4-n}$; the linear correlation observed shows that replacement of H atoms by methyl groups stabilizes the molecule by a fixed amount of approximately 16.0 kcal mol$^{-1}$ per methyl group. Similar trends are observed in the Si-H-F,[20] Si-H-Cl,[21] and $SiH_n(NH_2)_{4-n}$[23] series. This indicates that group additivity methods can be used to accurately predict heats of formation for larger methylsilanes, as has been shown by Luo and Benson.[29,30] For example, using this value for the methyl stabilization energy and the BAC-MP4 heat of formation

(29) Luo, Y.-R.; Benson, S. W. *J. Phys. Chem.* **1989**, *93*, 4643-4645.
(30) Luo, Y.; Benson, S. W. *J. Phys. Chem.* **1989**, *93*, 3791-3794.

**TABLE VI: Estimated $\Delta H^{\circ}_f(298)$ for Methyl-Substituted Disilanes**

| species$^a$ | this work$^b$ | O'Neal et al.$^c$ |
|---|---|---|
| $MeSiH_2SiH_3$ | 5.1 | 5.0 |
| $Me_2SiHSiH_3$ | -10.9 | -11.0 |
| $MeSiH_2SiH_2Me$ | $-10.9 \pm 1.1^d$ | -9.0 |
| $Me_3SiSiH_3$ | -26.9 | -26.9 |
| $Me_2SiHSiH_2Me$ | -26.9 | -24.9 |
| $Me_3SiSiH_2Me$ | -42.9 | -41.3 |
| $Me_2SiHSiHMe_2$ | -42.9 | -40.9 |
| $Me_3SiSiHMe_2$ | -58.9 | -57.5 |
| $Me_3SiSiMe_3$ | -74.9 | -75.0 |

$^a$ Me $\equiv CH_3$.  $^b$ Heats of formation based on BAC-MP4 heat of formation for $MeSiH_2SiH_2Me$ and assuming a methyl stabilization energy of 16.0 kcal mol$^{-1}$.  $^c$ Results of kinetics studies from ref 44.  $^d$ BAC-MP4 result.

for dimethyldisilane ($CH_3SiH_2SiH_2CH_3$) of $-10.9 \pm 1.1$ kcal mol$^{-1}$, heats of formation for other methyl-substituted disilanes can be estimated. Values obtained this way are given in Table VI.

In contrast to the $SiH_n(CH_3)_{4-n}$ series, a linear trend is not observed for either the $SiH_nCH_3$ (Figure 2) or $Si(CH_3)_n$ (Figure 3) series. This is again similar to trends observed for other silicon compounds, including $SiH_n$,[22] $Si(NH_2)_n$, and $SiH_nNH_2$[23] and $SiCl_n$[21] and $SiF_n$.[20] This behavior can be explained by the change that occurs in the electronic configuration of Si as bonding groups are added to it. For $Si(^3P)$, doublet-$SiCH_3$, and singlet-$Si(CH_3)_2$, the electronic configuration at the Si atom can be described as $s^2p^2$; bonding between the $CH_3$ groups and Si occurs with the unpaired 3p electrons. To add a third and fourth group, an electron must be promoted out of the 3s orbital into the empty 3p orbital. The configuration at Si for triplet-$Si(CH_3)_2$, $Si(CH_3)_3$, and $Si(CH_3)_4$ can thus be described as $sp^3$. The energy required to promote the 3s electron to the 3p level, which is essentially the singlet-triplet splitting for $Si(CH_3)_2$, shifts the line in Figure 3

**Figure 2.** Calculated heats of formation for $SiH_nCH_3$ species as a function of $n$. Squares: species on this line ($Si(^3P)$, $SiCH_3(^2A'')$, and $HSiCH_3$(singlet)) have an $s^2p^2$ electronic configuration at Si, causing their heats of formation to fall along a straight line. Triangles: species on this line ($HSiCH_3$(triplet), $H_2SiCH_3$, and $H_3SiCH_3$) have an $sp^3$ electronic configuration at Si, causing their heats of formation to fall along a different straight line.
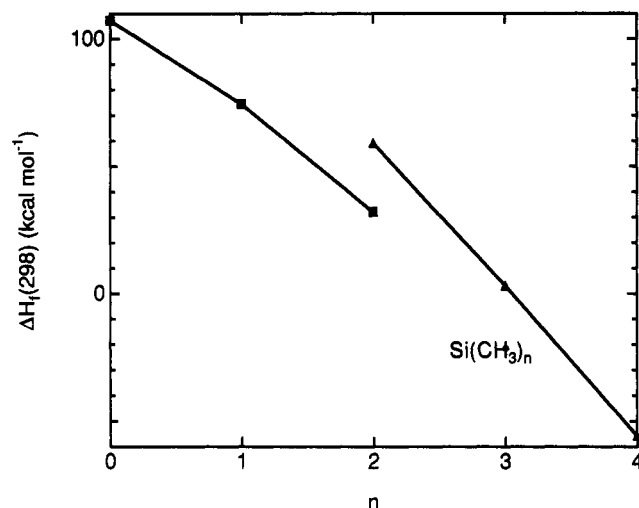


**Figure 3.** Calculated heats of formation for $Si(CH_3)_n$ species as a function of $n$. Squares: species on this line ($Si(^3P)$, $SiCH_3(^2A'')$, and $Si(CH_3)_2$(singlet)) have an $s^2p^2$ electronic configuration at Si, causing their heats of formation to fall approximately along a straight line. Triangles: species on this line ($Si(CH_3)_2$(triplet), $Si(CH_3)_3$, and Si-$(CH_3)_4$) have an $sp^3$ electronic configuration at Si, causing their heats of formation to fall along a different straight line.

upward for the latter three compounds.

Our calculations have also included the molecules $H_2C=Si-H(CH_3)$ and $H_2C=Si(CH_3)_2$, allowing the methyl stabilization effect in silylethylenes to be determined. The BAC-MP4 heats of formation for these compounds are 26.4 and 12.3 kcal mol$^{-1}$. With the heat of formation of $H_2Si=CH_2$ of 40.7 kcal mol$^{-1}$, we find that substitution of $CH_3$ for H on the Si atom stabilizes the molecule by 14 kcal mol$^{-1}$. This is somewhat less than the 16 kcal mol$^{-1}$ observed for methyl stabilization of saturated silanes.

Several of the molecules examined provide illustrations of some of the limitations of the BAC-MP4 method. One such limitation is that it is assumed that the HF/6-31G* geometry represents the energetic minimum for the molecule at the MP4/6-31G** level. It may be possible, however, that a geometry other than that determined by HF could produce a lower heat of formation. For the ground state of the $H_2SiC$ molecule, for example, HF theory found a nonplanar geometry, resulting in a BAC-MP4 heat of formation of 167.2 kcal mol$^{-1}$ at 298 K. However, restricting the geometry by imposing a planar geometry on the molecule gave
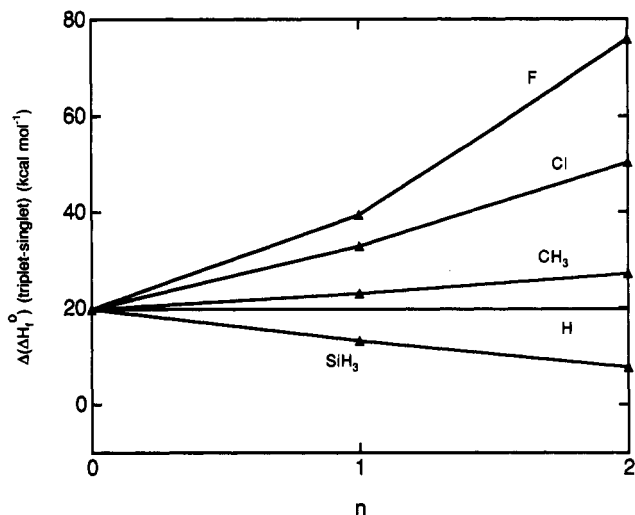


**Figure 4.** Singlet–triplet splittings for $SiH_{2-n}X_n$ molecules as a function of $n$. The plot illustrates the increase in the singlet–triplet splitting with increasing substituent electronegativity. The singlet–triplet splitting for $Si(SiH_3)_2$ was calculated from the following BAC-MP4 heats of formation: $\Delta H°_f(298)$(singlet) = 83.7 kcal mol$^{-1}$, $\Delta H°_f(298)$(triplet) = 91.5 kcal mol$^{-1}$.

a BAC-MP4 value of 164.4 kcal mol$^{-1}$, 2.8 kcal mol$^{-1}$ lower than the heat of formation obtained for the nonplanar case. For the sake of consistency with the other molecules in the study, we report the heat of formation for the non-planar geometry.

A second limitation is that the HF/6-31G* calculation may not always return the geometry of the global minimum on the potential energy surface, but rather that of a local minimum. No attempt is made to sample the entire geometric parameter space, which can be impractical for large molecules. Occasionally, multiple minima were found. This was the case in calculating the energy of the $H_2SiC$ triplet state, for which two different Si–C bond lengths were found. The molecule with the shorter bond (1.610) had a heat of formation of 244.9 kcal mol$^{-1}$, while the molecule with the longer Si–C bond (1.858) was the more stable, having a heat of formation of 228.4 kcal mol$^{-1}$.

In one instance, the HSiCH molecule, thermodynamic parameters could not be obtained because no local potential minimum was found. Imposition of two planes of symmetry to force the molecule to be linear produced two negative energy eigenvalues, indicating that the molecule prefers to bend. When allowed to do so, however, it rearranged to $SiCH_2$ with no barrier, indicating that this is the most stable configuration. Previous investigators have also observed this.[31] A shallow minimum has been obtained by including configuration interactions in determining the potential energy surface,[32] but this was not attempted here. Two excited-state triplet configurations were found for HSiCH, however. The trans configuration, containing an odd number of $\pi$ electrons in the molecular plane, is the lower energy configuration, having a heat of formation of 141.7 kcal mol$^{-1}$. The cis configuration has a heat of formation of 143.4 kcal mol$^{-1}$ and an even number of $\pi$ electrons in the molecular plane.

Singlet–triplet splittings in the methyl-substituted silylenes were also calculated as part of this study. These energy differences are of interest since silylene reactivity can be correlated with their size.[33] The singlet is the ground state for both methyl-substituted silylenes, with the triplet lying 23.0 ± 3.3 and 27.1 ± 3.5 kcal mol$^{-1}$ above the ground state for $HSiCH_3$ and $Si(CH_3)_2$, respectively. This is in good agreement with previous calculations of the $HSiCH_3$ heat of formation.[31,34,35] Note that the singlet–

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(32) Hoffmann, M. R.; Yoshioka, Y.; Schaefer III, F. W. *J. Am. Chem. Soc.* **1983**, *105*, 1084.

(33) Sosa, C.; Schlegel, H. B. *J. Am. Chem. Soc.* **1984**, *106*, 5847.

(34) Köhler, H. J.; Lischka, H. *J. Am. Chem. Soc.* **1982**, *104*, 5884–5889.

**TABLE VII: Calculated Bond Dissociation Enthalpies at 298 K (kcal mol⁻¹) for Selected Molecules**

| bond | BDE | bond | BDE | bond | BDE | bond | BDE |
|---|---|---|---|---|---|---|---|
| | | | (a) Si–H Bonds | | | | |
| H–SiH$_2$CH$_3$ | 92.4 | H–SiH$_2$CH$_2$ | 51.3 | H–SiH$_2$CH | 64.8 | H–SiH$_2$C | 71.7 |
| H–SiHCH$_3$ | 67.9 | H–SiHCH$_2$ | 97.2 | | | H–SiHC | 69.7 |
| H–SiCH$_3$ | 77.8 | H–SiCH$_2$ | 40.4 | | | | |
| H–SiH(CH$_3$)$_2$ | 93.5 | H–Si(CH$_3$)$_2$ | 66.0 | H–SiH(CH$_3$)CH$_2$ | 52.9 | | |
| H–Si(CH$_3$)$_3$ | 94.6 | | | H–Si(CH$_3$)$_2$CH$_2$ | 55.1 | | |
| H–SiH$_2$CH=CH$_2$ | 89.6 | H–SiHCH=CH$_2$ | 67.4 | H–SiCH=CH$_2$ | 76.3 | | |
| H–SiH$_2$C≡CH | 90.0 | H–SiHC≡CH | 66.1 | H–SiC≡CH | 72.9 | | |
| | | | (b) C–H Bonds | | | | |
| H–CH$_2$SiH$_3$ | 100.9 | H–CH$_2$SiH$_2$ | 59.8 | H–CH$_2$SiH | 89.1 | H–CH$_2$Si | 51.7 |
| H–CHSiH$_3$ | 103.2 | H–CHSiH$_2$ | 116.7 | | | H–CHSi | 102.3 |
| H–CSiH$_3$ | 107.0 | H–CSiH$_2$ | 113.9 | | | | |
| H–CH$_2$SiH$_2$CH$_3$ | 100.8 | H–CH$_2$SiHCH$_3$ | 60.2 | | | | |
| H–CH$_2$SiH(CH$_3$)$_2$ | 100.8 | H–CH$_2$Si(CH$_3$)$_2$ | 61.3 | | | | |
| H–CH$_2$Si(CH$_3$)$_2$ | 100.9 | | | | | | |
| | | | (c) Si–C Bonds | | | | |
| H$_3$Si–CH$_3$ | 89.6 | H$_3$C–SiH$_2$CH$_3$ | 91.1 | H$_3$C–SiH(CH$_3$)$_2$ | 92.6 | H$_3$C–Si(CH$_3$)$_3$ | 93.8 |
| H$_2$Si–CH$_3$ | 66.6 | H$_3$C–SiHCH$_3$ | 65.6 | H$_3$C–Si(CH$_3$)$_2$ | 63.9 | | |
| HSi–CH$_3$ | 77.1 | H$_3$C–SiCH$_3$ | 77.3 | | | | |
| Si–CH$_3$ | 67.7 | | | | | | |
| | | | | H$_3$C–Si(H$_2$)CH$_2$ | 50.1 | | |
| | | | | H$_3$C–SiH(CH$_3$)CH$_2$ | 51.9 | | |
| | | | | H$_3$C–Si(CH$_3$)$_2$CH$_2$ | 54.1 | | |
| H$_3$Si–CH$_2$ | 98.7 | | | H$_2$C–SiH$_2$CH$_3$ | 100.3 | | |
| H$_3$Si–CH | 101.5 | | | H$_2$C–SiH(CH$_3$)$_2$ | 101.7 | | |
| H$_3$Si–C | 71.0 | | | H$_2$C–Si(CH$_3$)$_3$ | 102.8 | | |
| H$_2$Si–CH$_2$ | 116.9 | H(CH$_3$)Si–CH$_2$ | 115.3 | (CH$_3$)$_2$Si–CH$_2$ | 112.7 | | |
| H$_2$Si–CH | 50.5 | | | | | | |
| H$_2$Si–C | 68.8 | | | | | | |
| HSi–CH$_2$ | 98.0 | | | H$_3$Si–CHCH$_2$ | 97.8 | | |
| Si–CH$_2$ | 126.0 | | | H$_2$Si–CHCH$_2$ | 77.6 | | |
| HSi–C | 77.4 | | | HSi–CHCH$_2$ | 88.5 | | |
| Si–CH | 129.7 | | | Si–CHCH$_2$ | 80.6 | | |
| | | | | H$_3$Si–CCH | 126.6 | | |
| | | | | H$_2$Si–CCH | 106.1 | | |
| | | | | HSi–CCH | 118.3 | | |
| | | | | Si–CCH | 113.8 | | |

triplet splitting in SiH$_2$ is 19.8 kcal mol⁻¹,[20] smaller than either of the methyl-substituted silylenes. The trend toward larger singlet-triplet splittings with increasing methyl substitution is correlated with the somewhat higher electronegativity of carbon relative to hydrogen;[36] this causes the bonds with Si to become more ionic.[37] Similar trends have been observed in chlorine- and fluorine-substituted silylenes.[37] These trends are displayed in Figure 4, which shows the increase in the singlet–triplet splitting with increasing electronegativity of the substituents. Note that the splitting actually decreases with increasing SiH$_3$ substitution, which is consistent with the lower electronegativity of silicon relative to hydrogen.

Table V gives entropies and free energies at selected temperatures. Polynomial fits to the dependence of the molecular enthalpy, entropy, and heat capacity, in the format used by the NASA[38] and CHEMKIN[39,40] thermochemical data bases, are given in Table XII of the supplementary material.

Bond dissociation enthalpies (BDEs) calculated from the heats of formation in Table IV reflect the trends observed in the heats of formation. Table VII lists BDEs for selected Si–H, C–H, and Si–C bonds. The Si–H and Si–C bond strengths exhibit a fairly regular high–low–high pattern with successive removal of either

hydrogen atoms or methyl groups. This trend is also observed for SiH$_n$,[21] SiCl$_n$,[21] and Si(NH$_2$)$_n$[23] species. The decrease in the Si–H or Si–C BDE after removal of the first H or CH$_3$ group can be correlated with the increased stability of the divalent silylene (SiXY) radical. This stabilization has been quantified by Walsh, who defines the divalent state stabilization energy as DSSE = BDE(R$_3$Si–R) – BDE(R$_2$Si–R). DSSEs observed here are relatively unaffected by methyl substitution on the Si atom (e.g., DSSE = 21.9 kcal mol⁻¹ for SiH$_4$,[20] 23.0 kcal mol⁻¹ for H$_3$SiCH$_3$, and 25.5 kcal mol⁻¹ for H$_2$Si(CH$_3$)$_2$).

The BDEs listed in Table VI also confirm what Walsh has remarked upon previously,[41] that Si–H bond strengths are remarkably constant in the organosilanes, with methyl substitution causing only minor changes. This is true of the radical species as well as the saturated compounds. The strength of the C–H bond in the methylsilanes is virtually unchanged from the hydrocarbon analogues[41] and is also independent of methyl substitution.

Several features of Si–C bonds are apparent from the data in Table VII as well. First, Si–C bond strengths, like those of Si–H bonds, are unaffected by methyl substitution at Si. Again, this is true of both radicals and saturated compounds. This behavior is quite different from NH$_2$ substitution, which increases the Si–N bond strength from 91.3 kcal mol⁻¹ in SiH$_4$ to 120 kcal mol⁻¹ in Si(NH$_2$)$_4$.[23] Second, removal of methyl hydrogens imparts greater strength to the Si–C bond, with $r$(Si–C) decreasing from 1.8880 Å in H$_3$SiCH$_3$ to 1.8396 Å in HSiCH$_3$ (Table II) as the BDE increases from 89.6 to 98.7 kcal mol⁻¹. The trend does not continue to H$_3$SiC, which has a substantially weaker Si–C bond than H$_3$SiCH. Finally, Si–C bonds in vinylsilanes (H$_2$C=CHSiH$_n$, $n$ = 0–3) and silylacetylenes (H$_n$SiC≡CH, $n$ = 0–3) are considerably stronger than Si–C bonds in the analogous silicon

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compound in which the organic moiety is a methyl group. For example, the Si-C bond strength in $H_3SiC\equiv CH$ is 126 kcal mol$^{-1}$, while in $H_3SiCH_3$ it is only 89.6 kcal mol$^{-1}$. This is consistent with trends observed in the hydrocarbon analogues of these compounds.[19]

The data also provide some insight into the characteristics of Si-C double bonds. Removal of two hydrogen atoms from $H_3SiCH_3$ to give $H_2Si=CH_2$ produces a large decrease in the bond length (to 1.694 Å) and an increase in the Si-C BDE to 116.9 kcal mol$^{-1}$. Although considerably weaker than the double bond in ethylene (173 kcal mol$^{-1}$), it is still a substantial increase in strength over the Si-C single bond. The strength of the Si-C $\pi$-bond ($D_\pi$) can also be determined from the thermodynamic data presented here. Walsh's definition of $D_\pi$ is[41]

$$D_\pi = D_\sigma(Si-H) + D_\sigma(C-H) - D(H-H) + \Delta H_{hyd} \quad (8)$$

which is based on reactions of the type $(CH_3)_3SiH \rightarrow (CH_3)_2$-$Si=CH_2 + H_2$. In this equation, $\Delta H_{hyd}$ is the hydrogenation energy of the $Si=C$ bond and $D_\sigma(Si-H)$ and $D_\sigma(C-H)$ are bond dissociation energies in $(CH_3)_3SiH$. From this definition, a value of 41.1 kcal mol$^{-1}$ is found for $D_\pi(H_2Si=CH_2)$, in good agreement with an earlier estimate.[42] The Si-C $\pi$-bond is thus weaker than the $\pi$-bond in $C_2H_4$ (66.1 kcal mol$^{-1}$)[19] but considerably stronger than that in $H_2Si=SiH_2$ (28.7 kcal mol$^{-1}$).[20] The strength of the $\pi$-bond is also essentially unaffected by methyl substitution, with $D_\pi$ equal to 40.5 and 39.5 kcal mol$^{-1}$ for $H(CH_3)Si=CH_2$ and $(CH_3)_2Si=CH_2$, respectively.

**B. Comparison of Heats of Formation with Literature Values.** Heats of formation for a number of organosilicon compounds are available in the literature, allowing comparisons to be made with some of the values reported here. Much of the data are for stable compounds such as the methylsilanes, but data are also available for the methylsilylenes and a few other unsaturated molecules. Thus, the effectiveness of the BAC-MP4 method can be evaluated for both saturated and unsaturated organosilicon compounds. Literature values of $\Delta H^\circ_f(298)$ are presented for comparison with BAC-MP4 calculated values in Table IV.

The thermochemistry of the methylsilanes ($SiH_n(CH_3)_{4-n}$) is reasonably well established and has been reviewed by Walsh.[42] As noted above, the BAC for the Si-C single bond was determined by adjusting the BAC-MP4 result for the heat of formation of $Si(CH_3)_4$ to the experimental value of -55.74 kcal mol$^{-1}$ preferred by Walsh.[42] Although there is a range of values in the literature for the $Si(CH_3)_4$ heat of formation, Walsh has argued strongly in favor of this value,[43] which was obtained by Steele using a combustion calorimetric method.[26] Calibration of $A_{SiC}$ with this value yields heats of formation that are within the experimental error of $\Delta H^\circ_f(298)$ for $H_3SiCH_3$, $H_2Si(CH_3)_2$, and $HSi(CH_3)_3$, as determined by equilibrium studies.[42] They are also in good agreement with recent theoretical estimates.[44] Thus, the BAC-MP4 predictions provide evidence in favor of Walsh's preferred value for the $Si(CH_3)_4$ heat of formation.

Thermodynamic data were also obtained for one of the higher silanes, $CH_3SiH_2SiH_2CH_3$. The BAC-MP4 heat of formation for this molecule (-10.9 ± 1.1 kcal mol$^{-1}$) is in good agreement with experimental data[44] and theoretical estimates[44,45] in the literature. Combining this heat of formation with group additivity (using the methyl stabilization energy of 16.0 kcal mol$^{-1}$ discussed above) permits the calculation of heats of formation for other methyl-substituted disilanes (Table VI). These values are also in good agreement with previous results.[44,45] Thus, the BAC-MP4 calculations lend further support to the heats of formation preferred by O'Neal et al.[44] In contrast, the values favored by Walsh, based on a $(CH_3)_3SiSi(CH_3)_3$ heat of formation of -83 ± 3 kcal mol$^{-1}$, appear to be systematically too low.[27]

Heats of formation for the methylsilyl radicals $SiH_2CH_3$, $SiH(CH_3)_2$, and $Si(CH_3)_3$ are available in the literature from several sources, although these molecules have not been as thoroughly studied as the methylsilylenes. Both Walsh[42] and Austin and Lampe[46] derived heats of formation for these radicals from the Si-H bond dissociation energies of the parent compounds. Their results are shown in Table IV with the experimental uncertainties. The results of both studies are consistent with the BAC-MP4 predictions; the agreement is particularly good with Austin and Lampe's results. A third experimental determination of $\Delta H^\circ_f(298)$ for $Si(CH_3)_3$ using the photoelectron-photoion coincidence technique[47] produced value of -12 ± 2 kcal mol$^{-1}$, which appears to be significantly in error based on comparison with our results and the two previously mentioned studies.

There has been considerable controversy in the literature regarding the heats of formation of the methylsilylenes. Reported values of the $HSiCH_3$ heat of formation vary from 44 to 53 kcal mol$^{-1}$, while that of $Si(CH_3)_2$ varies from 26 to 37 kcal mol$^{-1}$ (see Table IV). In addition, there is disagreement over the stability of $HSiCH_3$ with respect to its isomer $H_2Si=CH_2$. Because of the volume of literature concerning these subjects, it is worthwhile to briefly summarize the available results before comparing them to the BAC-MP4 predictions.

The earliest experimental determination of a methylsilylene heat of formation to our knowledge was that of Vanderwielen et al., who obtained a value of 53.1 ± 1.1 kcal mol$^{-1}$ for $HSiCH_3$ from measurements of methyldisilane decomposition kinetics.[48] This value does not account for changes in $C_p$ with temperature, although these should be small.[49] Neudorfl et al. also estimated the heat of formation from the activation energy for $HSiCH_3$ elimination from $H_3SiCH_3$.[50] The value they obtained of 51.9 kcal mol$^{-1}$ is in good agreement with that of Vanderwielen et al.; however, their analysis assumed that the activation energy for the insertion of $HSiCH_3$ into $H_2$ was the same as that for $SiH_2$ insertion into $H_2$, using John and Purnell's value of 5.5 kcal mol$^{-1}$.[51] Recent experiments and theoretical estimates of this activation energy put the value at 1.0 ± 0.7 kcal mol$^{-1}$.[16] Using this value yields a heat of formation of 55.0 kcal mol$^{-1}$, which is at the high end of the reported values (Table IV). Determination of $\Delta H^\circ_f(298)$ from ion cyclotron resonance (ICR) experiments[52] produced a value of 53 ± 4 kcal mol$^{-1}$ for $HSiCH_3$, in good agreement with the two earlier estimates. The authors of this study also derived the heat of formation of $Si(CH_3)_2$, finding 37 ± 6 kcal mol$^{-1}$. Finally, O'Neal et al. measured the decomposition kinetics of several methyldisilanes to obtain heats of formation for both $Si(CH_3)_2$ and $HSiCH_3$.[44] They also supported their experiments with semiempirical and ab initio calculations, resulting in "compromise" values of 48 ± 2 and 32 ± 2 kcal mol$^{-1}$ for the $HSiCH_3$ and $Si(CH_3)_2$ heats of formation, respectively.

Recent calculations at a high level of theory are in agreement with the experimental results just described. Gordon and Boatz performed ab initio calculations, using either isogyric reactions[53] (which conserve the number of unpaired spins) or isodesmic reactions[54] (which conserve the number of bonds between atom types) to make up for basis set deficiencies. Heats of formation of 50.6 and 32-33 kcal mol$^{-1}$ were predicted for $HSiCH_3$ and $Si(CH_3)_2$, respectively. In contrast, Walsh has performed a detailed analysis of existing experimental data, arguing that the ICR results represent upper limits and favoring values of 44 ± 3 kcal mol$^{-1}$ for $HSiCH_3$[55] and 25.7 ± 3 kcal mol$^{-1}$ for $Si(CH_3)_2$.[27]

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(55) Walsh, R. *Organometallics* **1988**, *7*, 75–77.

The BAC-MP4 method predicts heats of formation of 48.8 ± 2.3 kcal mol⁻¹ and 32.2 ± 2.4 kcal mol⁻¹ for HSiCH₃ and Si(C-H₃)₂, respectively. These values are in the middle of the range of experimental values (Table IV). Considering the experimental uncertainty and the estimate of error in our own calculations, the BAC-MP4 predictions can be considered in agreement with all of the reported values. However, the range of values may be narrowed if one accepts the argument[27] that the ICR results are upper limits to the heats of formation. Furthermore, the discrepancy between the values preferred by Walsh and those recommended by O'Neal et al. appears to turn on the value of the methyldisilane heats of formation used in the analysis of kinetic data.[27] As discussed above, our calculations support the values preferred by O'Neal et al.[44] Thus, we conclude that the compromise values of the methylsilylene heats of formation recommended by O'Neal are likely the best estimates available for these quantities.[44]

Silaethylene (H₂Si=CH₂) has also received considerable experimental and theoretical attention.[31,52] Walsh[56] has proposed a value of 37 ± 5 kcal mol⁻¹, while the ICR study of Shin and Beauchamp[52] produced a value of 43 ± 3 kcal mol⁻¹. Boatz and Gordon predict a value of 46.5 kcal mol⁻¹, again using an isogyric reaction.[53] The result of the BAC-MP4 method (40.7 ± 2.4 kcal mol⁻¹) appears to agree best with the experimental ICR data, although the uncertainty of Walsh's value includes our result. The major discrepancy between the BAC-MP4 prediction and that of Boatz and Gordon results from the fact that isogyric reactions do not fully correct for the Si–C double bond. Isogyric reactions conserve only unpaired spins and not bond types, while the BAC-MP4 correction to the electronic energy is a function of the HF/6-31G* bond length. The shorter Si–C bond in H₂Si=CH₂ thus results in a larger correction subtracted from the MP4-(STDQ) electronic energy, thereby accounting for the difference between the two calculations.

With regard to the stability of H₂Si=CH₂ relative to its isomer HSiCH₃, most high-level theoretical calculations predict a difference of 2–4 kcal mol⁻¹ between these two isomers, with H₂-Si=CH₂ the more stable of the two.[52,53] For example, a difference of 4.1 kcal mol⁻¹ is predicted by Boatz and Gordon;[53] Luke et al. predict a difference of 2.2 kcal mol⁻¹.[31] In contrast, two experimental studies using ICR have found larger differences. Shin et al. find 10 kcal mol⁻¹,[52] while Pau et al.,[57] studying the related compounds Si(CH₃)₂ and H(CH₃)Si=CH₂, report a difference of 28 kcal mol⁻¹ between those two isomers; the silaethylene is the most stable in both cases. Although the experimental values are much different from the predictions of theory, the value reported by Pau et al., is probably incorrect, since it is unlikely that methyl substitution could have so large an effect on the energy difference. The value obtained by Shin and supported with GVB+CI calculations, however, is in good agreement with the difference of 8.1 kcal mol⁻¹ obtained by the BAC-MP4 method. The greater stability predicted for H₂Si=CH₂ by BAC-MP4 compared to previous theoretical results again stems from the larger correction made for the Si–C double bond.

Literature values of the methyl-substituted silaethylenes are also available for comparison with our predictions. A determination of the (CH₃)₂Si=CH₂ heat of formation from measurements of Si(CH₃)₄ photolysis[58] yielded a value of 0.5 ± 2 kcal mol⁻¹, significantly below the BAC-MP4 result of 12.3 ± 1.4 kcal mol⁻¹. Walsh's recommended value[56] for this quantity is also lower than ours (5.0 ± 4.8 kcal mol⁻¹). Somewhat closer to the BAC-MP4 predictions is the value 8.6 ± 1.7 kcal mol⁻¹ obtained by Brix et al. from a study of the photolysis of 1,1-dimethyl-silacyclobutane.[59] In contrast, ICR experiments by Hehre and co-workers[57] yielded a value of 46 kcal mol⁻¹; their value for the

H(CH₃)Si=CH₂ heat of formation (18 kcal mol⁻¹) is also much lower than our prediction for this molecule (26.4 ± 1.8 kcal mol⁻¹). An analysis of existing kinetic, thermochemical, and mass spectroscopic data[60] obtained 15 ± 5 kcal mol⁻¹, in good agreement with our results. It thus appears that further experimental measurements are required to confidently assign this heat of formation.

Unfortunately, there are few data available for comparison with the heats of formation reported here for the vinylsilanes and silylacetylenes. The NBS tables of thermodynamic constants do list vinylsilane (H₂C=CHSiH₃), however.[61] The heat of formation reported at 298 K for this molecule is −2 kcal mol⁻¹, which is in serious disagreement with the BAC-MP4 prediction of 20.7 ± 1.0 kcal mol⁻¹. Dewar and Jie, using the AM1 method, estimate a heat of formation for vinylsilane (11.4 ± 13.3 kcal mol⁻¹) that is in somewhat better agreement with the BAC-MP4 result.[62] The heat of formation of silylacetylene (H₃SiC≡CH) has been reported by Rogers et al.[63] as 63.2 ± 4.0 kcal mol⁻¹. This value is based on the assumption of equivalent enthalpies of hydrogenation for H₃SiC≡CH and HC≡CH and is significantly different from the BAC-MP4 result of 53.0 ± 1.1 kcal mol⁻¹. Clearly, more experimental data are needed for these compounds.

There is one heat of formation reported for a radical of the type CH₂SiHₙ(CH₃)₃₋ₙ (n = 0–3). The heat of formation of the radical Si(CH₃)₃CH₂ is reported by Walsh[27] to be −8.6 ± 1.4 kcal mol⁻¹, based on Steele's value for the heat of formation of Si(CH₃)₄.[26] This is in good agreement with the BAC-MP4 prediction, which is −6.9 ± 1.5 kcal mol⁻¹.

## IV. Summary

Ab initio calculations of the electronic structure of Si–C–H molecules were combined with empirical corrections to yield a self-consistent set of thermodynamic data for these compounds. Heats of formation reported here in good agreement with experimental values in the literature for the saturated methylsilanes.[26,42] They also support the recommended values of O'Neal et al.[44] for the methylsilylenes, for which there is a substantial range of values in the literature. Finally, the BAC-MP4 results confirm the effectiveness of group additivity methods for the estimation of thermodynamic data for higher organosilanes.

*Note added in proof:* Walsh et al. have recently published experimental data from which they derive a heat of formation of −72.6 ± 1.3 kcal/mol for (CH₃)₃SiSi(CH₃)₃ (*J. Chem. Soc., Faraday Trans.* **1991**, *87*, 841). This value agrees with both experimental[44] and theoretical[45] estimates as well as with the BAC-MP4 prediction reported here. Combining this new value with earlier experimental data leads to revised estimates for the heats of formation of HSiCH₃ and Si(CH₃)₂ (48.0 and 33.5 kcal mol⁻¹, respectively) that are in good agreement with the BAC-MP4 predictions and other experimental and theoretical results discussed above. It thus appears that the controversy regarding the heats of formation of these species has been resolved.

We also note that the enthalpy for the reaction (CH₃)₃SiSi-(CH₃)₃ ↔ 2Si(CH₃)₃ reported by Walsh et al. in the article cited above may be combined with the BAC-MP4 prediction for the heat of formation of Si(CH₃)₃ to yield a heat of formation for (CH₃)₃SiSi(CH₃)₃. A value of 76.0 ± 4.3 kcal mol⁻¹ is obtained; although its uncertainty is somewhat high, it agrees with the BAC-MP4 prediction and Walsh et al.'s new experimental value.

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This provides additional evidence that the value $-1 \pm 2$ kcal mol$^{-1}$ reported by Walsh[42] is too low.

## Appendix

The supplementary material data are as follows: Table VIII presents the Z matrices[64] for each of the molecular species obtained from the HF/6-31G* geometry optimization calculations. Molecular geometries can be obtained from these matrices. Table IX gives the moments of inertia in atomic units (amu bohr$^2$), and Table X lists the scaled vibrational frequencies obtained at the same level of theory. Table XI presents the electronic energies resulting from the various perturbation-theory calculations using the 6-31G** basis set. The projected UHF (PUHF) and projected UMP2 (PUMP2) energies[28] are given for reference, although they are not used in the derivation of the BACs.

Table XII gives the coefficients for polynomial fits to $C_p$, $H$, and $S$ as a function of temperature ($300 \text{ K} \leq T \leq 2500 \text{ K}$) for the species considered in this paper. These fits are used with the CHEMKIN software package[39,40] and are defined by

$$C_p/R = a_1 + a_2 T + a_3 T^2 + a_4 T^3 + a_5 T^4$$

$$\frac{H}{RT} = a_1 + \frac{a_2 T}{2} + \frac{a_3 T^2}{3} + \frac{a_4 T^3}{4} + \frac{a_5 T^4}{5} + \frac{a_6}{T}$$

$$\frac{S}{R} = a_1 \ln T + a_2 T + \frac{a_3}{2} T^2 + \frac{a_4}{3} T^3 + \frac{a_5}{4} T^4 + a_7$$

**Registry No.** H$_3$SiCH$_3$, 992-94-9; H$_2$Si(CH$_3$)$_2$, 1111-74-6; HSi(CH$_3$)$_3$, 993-07-7; Si(CH$_3$)$_4$, 75-76-3; H$_2$SiCH$_3$, 51220-22-5; HSi(CH$_3$)$_2$, 24669-76-9; Si(CH$_3$)$_3$, 16571-41-8; HSiCH$_3$, 55544-30-4; Si(CH$_3$)$_2$, 6376-86-9; SiCH$_3$, 88867-57-6; H$_3$SiCH$_2$, 24669-75-8; H$_2$Si(CH$_3$)CH$_2$, 137626-39-2; HSi(CH$_3$)$_2$CH$_2$, 34377-79-2; Si(CH$_3$)$_3$CH$_2$, 19469-02-4; H$_2$Si=CH$_2$, 51067-84-6; H(CH$_3$)Si=CH$_2$, 38063-40-0; (CH$_3$)$_2$Si=CH$_2$, 4112-23-6; HSiCH$_2$, 137626-40-5; SiCH$_2$, 65632-07-7; H$_3$SiCH, 66605-30-9; H$_2$SiCH, 137626-41-6; SiCH, 68034-44-6; H$_3$SiC, 117768-71-5; H$_2$SiC, 74694-33-0; HSiC, 68034-43-5; H$_3$SiC≡CH, 1066-27-9; H$_2$SiC≡CH, 51286-34-1; HSiC≡CH, 99278-14-5; SiC≡CH, 116854-52-5; H$_2$C=CHSiH$_3$, 7291-09-0; H$_2$C=CHSiH$_2$, 117978-60-6; H$_2$C=CHSiH, 78442-50-9; H$_2$C=CHSi, 137626-42-7; CH$_3$SiH$_2$SiH$_2$CH$_3$, 870-26-8; H$_2$, 1333-74-0; C, 7440-44-0; Si, 7440-21-3.

*Supplementary Material Available:* Tables as described in the Appendix (26 pages). Ordering information is given on any current masthead page.

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# Vibrational Circular Dichroism and Infrared Spectra of 2-Methyloxirane and *trans*-2,3-Dimethyloxirane: Ab Initio Vibronic Coupling Theory with the 6-31G*$^{(0.3)}$ Basis Set

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The ab initio vibronic coupling theory (VCT) of Nafie and Freedman using a modified 6-31G* basis set (VCT/6-31G*$^{(0.3)}$ with and without electron correlation in the calculation of the magnetic dipole transition moments is applied to calculate IR and VCD intensities for (*S*)-2-methyloxirane and (*R,R*)-2,3-dimethyloxirane. The theoretical values are found to be in very good agreement with values obtained from published experimental IR and VCD spectra in the mid-IR region. Incorporation of electron correlation is found to have very little effect. The relative intensities of absorption and circular dichroism in the C–H stretching region of the IR spectrum are not as well reproduced using VCT/6-31G*$^{(0.3)}$, according to test results on a number of small model systems. Geometries obtained by complete optimization using the 6-31*$^{(0.3)}$ basis set are in better agreement with experimental geometries than those obtained with the conventional 6-31G* basis set. The circular dichroism in the mid-IR region of the two related systems is discussed in terms of the ab initio normal modes. Comparison of the two systems suggests almost complete correspondence of the signs of the Cotton effects of equivalent normal modes in this region of the spectrum. The computed VCD results suggest a revision of the assignments of two of the normal modes of the (*R,R*)-2,3-dimethyloxirane.

## Introduction

The vibonic coupling theory (VCT) formalism for infrared (IR) and vibrational circular dichroism (VCD) intensities developed by Nafie and Freedman[1] has recently been implemented at the ab initio level[2] and the complete IR and VCD spectra of (*S,S*)-2,3-dideuteriooxirane and the other deuterated isotopomers,[3] of ethanol and α–deuterioethanol,[4] and of a series of small model molecules, including hydrazine and hydrogen peroxide,[5] have appeared. VCT provides an alternative to the VCD formalism of Stephens,[6] which has seen widespread application in the recent literature.[7-18] Extensive testing by both Stephens and co-workers and Rauk and co-workers has established that very extensive basis sets are required to achieve reliable converged results with the ab initio implementations of either theory. The formalism of VCT

(vide infra) requires a summation over excited states for the description of the magnetic dipole transition moment. In the

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