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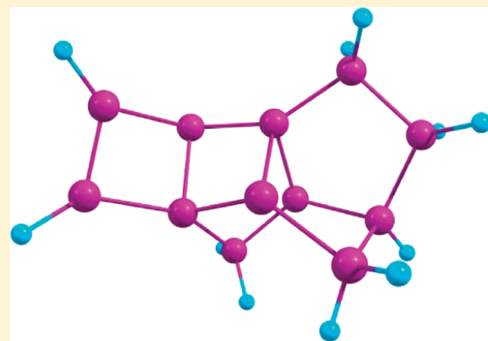
Thermochemical Property Estimation of Hydrogenated Silicon Clusters

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S Supporting Information

ABSTRACT: The thermochemical properties for selected hydrogenated silicon clusters (Si_xH_y , $x = 3\text{--}13$, $y = 0\text{--}18$) were calculated using quantum chemical calculations and statistical thermodynamics. Standard enthalpy of formation at 298 K and standard entropy and constant pressure heat capacity at various temperatures, i.e., 298–6000 K, were calculated for 162 hydrogenated silicon clusters using G3//B3LYP. The hydrogenated silicon clusters contained ten to twenty fused Si–Si bonds, i.e., bonds participating in more than one three- to six-membered ring. The hydrogenated silicon clusters in this study involved different degrees of hydrogenation, i.e., the ratio of hydrogen to silicon atoms varied widely depending on the size of the cluster and/or degree of multifunctionality. A group additivity database composed of atom-centered groups and ring corrections, as well as bond-centered groups, was created to predict thermochemical properties most accurately. For the training set molecules, the average absolute deviation (AAD) comparing the G3//B3LYP values to the values obtained from the revised group additivity database for standard enthalpy of formation and entropy at 298 K and constant pressure heat capacity at 500, 1000, and 1500 K were 3.2%, 1.9%, 0.40%, 0.43%, and 0.53%, respectively. Sensitivity analysis of the revised group additivity parameter database revealed that the group parameters were able to predict the thermochemical properties of molecules that were not used in the training set within an AAD of 3.8% for standard enthalpy of formation at 298 K.



INTRODUCTION

As a cluster of atoms crosses from the microscopic scale to the macroscopic scale, the system begins to behave more like bulk matter instead of being atom-like in nature.¹ The physical and chemical properties change accordingly with the system size, and this quality of atomic clusters is one of the key driving forces of modern cluster science. Clusters of atoms composed of silicon with varying levels of surface passivation by hydrogen atoms have attracted increased attention over the past several decades. Silicon-based clusters are studied in the context of chemical vapor deposition (CVD),² biological imaging,³ combustion enhancement,^{4–6} and interstellar science^{7,8} because of gas-phase nucleation under pyrolytic and plasma conditions, unique size-dependent photoluminescent properties, positive standard enthalpies of formation, and detection in the circumstellar envelopes of stars, respectively. Hydrogenated silicon clusters play important roles in a number of complex reacting and nonreacting systems, and filling the gap in knowledge for the thermochemical properties of larger hydrogenated silicon clusters is needed.

Considerable data exist for the theoretical geometries of the lowest energy structures of fully dehydrogenated silicon clusters and small hydrogenated silicon structures.^{9–21} Small- to medium-sized silicon hydrides have been studied by Katzer, Sax et al.^{19–21} using theoretical investigations that quantify thermochemistry and the effects of anharmonic vibrations on thermochemistry. Moreover, the thermochemistry of larger hydrogenated clusters has been studied by Swihart et al.²² Theoretical studies of strained,

polycyclic silicon hydrides were presented by Zhao and Gimarc²³ and by Nagase and co-workers.^{24–27} To the best of our knowledge, the larger and less-strained molecules considered here have not previously been studied.

Experimental data for the thermochemistry of hydrogenated silicon species only exist for acyclic species composed of one to three silicon atoms.²⁰ Larger cluster sizes have been studied extensively with experiment using spectroscopic methods to probe their photoluminescent behavior but will not be reviewed here. For structure calculations and insights into the reactivity of very large clusters, i.e., sizes greater than 15–30 silicon atoms up to 6400 silicon atoms, semiempirical methods, ab initio molecular dynamics, and/or genetic algorithm with tight binding (GA/TB) approaches have been used.^{9,28–47} These methods are used (1) due to very long supercomputing times using very accurate quantum chemical composite methods such as G3//B3LYP or CBS-QB3 and (2) due to the difficulty and inefficiency in finding the global minimum in structure through manual manipulation. There is interest in larger clusters and their reactivity (e.g., hydrogen dissociation from hydrogenated silicon clusters), and thermochemical data for larger clusters is greatly needed to gain insight into the reaction kinetics through existing kinetic correlations.^{47–49} It is well-established that hydrogenated silicon

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Table 1. G3//B3LYP Triplet–Singlet Splitting Values of Key Hydrogenated Silicon Clusters^a

| molecule | G3//B3LYP electronic energies with zero-point vibrational energies | | |
|----------|--|--------------------|---|
| | spin multiplicity | | triplet–singlet splitting (kcal mol ^{−1}) |
| | singlet (Hartrees) | triplet (Hartrees) | |
| 62 | −867.9446 | −867.9430 | 1.0 |
| 63 | −1158.5421 | −1158.4851 | 35.8 |
| 64 | −1157.3346 | −1157.3034 | 19.6 |
| 65 | −1159.7192 | −1159.6667 | 32.9 |
| 72 | −1449.0958 | −1449.0340 | 38.8 |
| 73 | −1449.0941 | −1449.0513 | 26.9 |
| 77 | −1446.6858 | −1446.6447 | 25.8 |
| 85 | −1738.4557 | −1738.4166 | 24.5 |
| 87 | −1737.2949 | −1737.2323 | 39.3 |
| 88 | −1736.0324 | −1736.0128 | 12.2 |
| 92 | −1737.2618 | −1737.2197 | 26.4 |
| 102 | −2030.2151 | −2030.1769 | 24.0 |
| 103 | −2027.8134 | −2027.7776 | 22.5 |
| 107 | −2317.1797 | −2317.1524 | 17.1 |
| 111 | −2318.3578 | −2318.3278 | 18.8 |
| 112 | −2319.5173 | −2319.4951 | 13.9 |
| 114 | −2319.5308 | −2319.5007 | 18.9 |
| 115 | −2318.3707 | −2318.3451 | 16.0 |

^aThe molecules are indexed according to the notation in the Supporting Information.

nanostructures pass through metastable configurations (or transient chemical species) before reaching a global minimum from molecular dynamics simulations,⁵⁰ but detailed knowledge of the structure and thermochemistry of a wide range of hydrogenated silicon clusters is still needed.

Recently, automated network generation techniques^{51–57} have emerged that allow the kinetics of silicon cluster formation to be described at the mechanistic level.⁵⁸ Rate coefficients must be estimated for every elementary step comprising the mechanistic model, and kinetic correlations are used to make this tractable. A data set such as the one developed in this study, i.e., composed of 162 hydrogenated silicon clusters where Si_xH_y, $x = 3–13$, $y = 0–18$, is vital to better understand the formation of silicon clusters in the gas phase. This data set can be used to regress group additivity values for the prediction of thermochemical properties. These thermochemical properties can then be used in kinetic correlations to model the reaction dynamics of silicon cluster formation under pyrolysis conditions. Current group additivity databases for silicon hydrides do not account for multifunctional polycyclic species in the training set for the regression of group additivity parameters.^{2,59} As reported for hydrocarbon systems composed of polycyclic aromatic species,^{60,61} there are significant deviations in the prediction of the thermochemical properties of more complex multifunctional polycyclic species. By analogy, the accuracy of the current group additivity database for the prediction of silicon hydride thermochemical properties can only be tested using a more complex data set like the one developed in this study. A revised set of group additivity parameters can then be regressed to capture a wider range of silicon hydrides.

Table 2. Comparison of Experimental Vibrational Modes for SiH₂, SiH₄, and Si₂H₆ to Unscaled Harmonic Vibrational Modes Using the B3LYP/6-31G(d) Level of Theory^a

| (a) Vibrational Modes of Si ₂ H ₆ | | | | |
|---|----------------------|------------------------|------------------------|----------------------|
| mode symmetry | calculated frequency | experimental frequency | deviation (exp – calc) | percentage deviation |
| A _{1g} | 2235 | 2152 | −83 | −3.9 |
| A _{1g} | 931 | 909 | −22 | −2.4 |
| A _{1g} | 433 | 434 | 1 | 0.2 |
| A _{1u} | 134 | 131 | −3 | −2.3 |
| A _{2u} | 2225 | 2154 | −71 | −3.3 |
| A _{2u} | 856 | 844 | −12 | −1.4 |
| E _g | 2239 | 2155 | −84 | −3.9 |
| E _g | 943 | 929 | −14 | −1.5 |
| E _g | 638 | 625 | −13 | −2.1 |
| E _u | 2249 | 2179 | −70 | −3.2 |
| E _u | 958 | 940 | −18 | −1.9 |
| E _u | 383 | 379 | −4 | −1.1 |
| av | | | −33 | −2.2 |

| (b) Vibrational Modes of SiH ₂ | | | | |
|---|----------------------|------------------------|------------------------|----------------------|
| mode symmetry | calculated frequency | experimental frequency | deviation (exp – calc) | percentage deviation |
| a ₁ | 2053 | 1996 | −57 | −2.9 |
| A ₁ | 1040 | 999 | −41 | −4.1 |
| B ₂ | 2058 | 1993 | −65 | −3.3 |
| av | | | −54 | −3.4 |

| (c) Vibrational Modes of SiH ₄ | | | | |
|---|----------------------|------------------------|------------------------|----------------------|
| mode symmetry | calculated frequency | experimental frequency | deviation (exp – calc) | percentage deviation |
| A ₁ | 2252 | 2187 | −65 | −3.0 |
| E | 975 | 975 | 0 | 0.0 |
| T ₂ | 2265 | 2191 | −74 | −3.4 |
| T ₂ | 916 | 914 | −2 | −0.2 |
| av | | | −35 | −1.6 |

^aAll values are reported in cm^{−1}.

This paper presents the thermochemical properties of 162 cyclic and polycyclic silicon hydrides, i.e., standard enthalpies of formation, standard entropy values, and constant pressure heat capacities, and specifically examines both multifunctional and monofunctional molecules containing between three and thirteen silicon atoms. The hydrogenated silicon clusters in this study involved different degrees of hydrogenation; i.e., the ratio of hydrogen to silicon atoms varied widely depending on the size of the cluster and/or degree of multifunctionality. Species containing different numbers of fused rings composed of three to six silicon atoms were considered. The composite method of G3//B3LYP⁶² was used to calculate the electronic energy, and then statistical thermodynamics was applied to all the hydrogenated silicon clusters to incorporate temperature effects. Enthalpies of formation at 1 atm and 298 K were calculated using atomization energies and corrected with bond additivity correction parameters. Standard entropies and constant pressure heat capacities at elevated temperatures, i.e., 298–6000 K, were calculated using a temperature-dependent scaling factor for the vibrational frequencies to account

for anharmonic vibrational modes. The existing group additivity database⁵⁹ for the prediction of thermochemical properties of hydrogenated silicon clusters was revised and augmented with new atom-centered groups, ring corrections, and bond-centered groups to accurately capture more complex species. Lastly, sensitivity analysis was performed to test if the regressed group additivity parameters were able to predict the thermochemical properties of molecules that were not included in the training set.

COMPUTATIONAL METHODOLOGY

Quantum Chemical Calculations and Statistical Thermodynamics. Quantum chemical calculations were performed with Gaussian 03.⁶³ All electronic energies for the hydrogenated silicon clusters were calculated using the G3//B3LYP method,⁶² which uses B3LYP geometries and higher-level corrections based on single point energies. The optimized structures for all 162 hydrogenated silicon clusters investigated in this study are depicted in the Supporting Information. The hydrogenated silicon clusters of this study exist in the singlet state; however, an unsaturated silicon hydride such as a silylene can exist in either the singlet or the triplet state.⁶⁴ Using the G3//B3LYP method, triplet–singlet splitting values of key substituted silylenes and polycyclic species were investigated (Table 1). These calculated triplet–singlet splitting values suggest that the singlet potential energy surface is significantly lower in energy than the triplet potential energy surface despite different degrees of triplet state stabilization through divalent center substituent effects. Thus, for all results reported, the electronic wave functions for the hydrogenated silicon clusters were optimized in the singlet state. Geometries and harmonic frequencies of the confirmed local minima on the singlet potential energy surface, i.e., all of the vibrational frequencies were real, for hydrogenated silicon clusters composed of no dangling Si–Si σ bonds were determined at the B3LYP/6-31G(d) level (Table 2). The harmonic frequencies and zero-point energy (ZPE) were linearly scaled by a temperature-dependent scaling factor and a factor of 0.98, respectively, to account for anharmonicity in the normal vibrational modes as a function of temperature as suggested by Scott and Radom.⁶⁵ The Cartesian coordinates and unscaled frequencies for all hydrogenated silicon clusters can be found in the Supporting Information.

Using conventional statistical thermodynamics, partition functions based on the harmonic oscillator and rigid rotor approximations were used to calculate thermodynamic properties as a function of temperature. A closer investigation of the 162 structures in this study reveals no dangling Si–Si σ bonds capable of internal rotation, and thus internal rotation corrections that account for anharmonic movements in potential torsional vibrational modes were not needed. Anharmonic small ring movements (e.g., the pseudorotation of cyclopentasilanes and the ring puckering of cyclotetrasilanes incorporated into the multifunctional polycyclic structures) were not treated.^{19,66} The internal rotations present in the 131 molecules in the work of Wong et al.⁵⁹ were treated with a linear scaling factor. The protocol in our study was implemented because (1) there are reduced anharmonic small ring movements for the more rigid structures in this study, which was verified by the animation of key vibrational modes, and (2) the calculation of a revised partition function to account for anharmonic small ring movements was beyond the scope of this study given the large number and size of the molecules investigated. Enthalpy, H , and entropy, S , are calculated using standard formulas.⁶⁷ This procedure was performed automatically using the *CalcTherm* script developed

Table 3. Comparison of Standard Enthalpy of Formation at 298 K from Atomization Energies and Bond Additivity Correction (BAC) Parameters Calculated from Weizmann-1 (W-1) and G3//B3LYP Methods for Selected Hydrogenated Silicon Species to Available Experimental Data²⁰

| species | experimental ΔH_f^{298} (kcal mol ⁻¹) | deviation | |
|------------------------------------|--|------------------------|------------------------------|
| | | (experiment)- (W-1) | (experiment)- (G3//B3LYP) |
| H ₂ | 0.0 | 0.0 | 0.4 |
| SiH ₄ | 8.2 | 2.1 | 0.8 |
| :SiH ₂ | 65.2 | 2.0 | 1.9 |
| H ₃ SiSiH ₃ | 19.1 | 3.4 | 0.7 |
| :SiHSiH ₃ | 75.1 | 2.8 | 1.4 |
| H ₂ Si=SiH ₂ | 65.7 | 1.6 | 0.7 |
| av abs dev | | 2.0 | 1.0 |

by our group.⁶⁸ The external symmetry numbers for the symmetric hydrogenated silicon clusters examined in this study impact the molecular partition function for rotation and reduce the rotational entropy by an amount equivalent to $R \ln \sigma_{\text{rot}}$ ⁶⁷ where σ_{rot} is the external symmetry of the molecule and R is the ideal gas constant.

To benchmark the G3//B3LYP method for this theoretical study, Weizmann-1 (W-1) calculations⁶⁹ were performed and found to be in reasonable agreement with the G3//B3LYP results and available experimental data for standard enthalpy of formation at 298 K. The performance summary of additional quantum chemical composite methods, i.e., CBS-QB3, CBS-Q, and G2 methods, for silicon hydride chemistry was documented in work by Wong et al.⁵⁹ Wong et al. demonstrated that the G3//B3LYP composite method outperforms the CBS-QB3, CBS-Q, and G2 composite methods on average when estimating available experimental data for the standard enthalpy of formation at 298 K within absolute deviations of 1.2, 2.7, 1.6, and 1.4 kcal mol⁻¹, respectively. Comparison of W-1 and G3//B3LYP standard enthalpies of formation at 298 K to available experimental data is provided in Table 3. The G3//B3LYP composite method agrees with available experimental data within an average absolute deviation of 1.0 kcal mol⁻¹ while the W-1 method captures available experimental data within an average absolute deviation of 2.0 kcal mol⁻¹. The W-1 method was developed to be an affordable and accurate method for the determination of thermochemistry; however, the improved predictions by the G3//B3LYP method can be attributed to the use of a higher level correction based upon a regression of correction parameters from an experimental data set of 299 energies containing enthalpies of formation, ionization potentials, electron affinities, and proton affinities.⁷⁰ In addition, the G3//B3LYP method was a reasonable choice because the multifunctional polycyclic data set is intended to be used in conjunction with an existing G3//B3LYP database developed by our group⁵⁹ for the estimation of silicon hydride thermochemical properties.

The enthalpy of formation of a given molecule Si_xH_y can be calculated from its atomization energies using eq 1:

$$\Delta H_{f,298}^{\circ}(\text{Si}_x\text{H}_y) = [x\Delta H_{f,298}^{\circ}(\text{Si}) + y\Delta H_{f,298}^{\circ}(\text{H})] - \Delta H_{a,298}^{\circ}(\text{Si}_x\text{H}_y) \quad (1)$$

where the enthalpies of formation of atomic silicon and hydrogen are the experimental values obtained from the JANAF tables⁷¹

Table 4. Comparison of Standard Enthalpies of Formation and Standard Entropies at 298 K for Selected Hydrogenated Silicon Clusters to Literature Values^a

| species | species no. from Supporting Information | Swihart et al. ²² | | this study | | deviation (this study) – (literature) | |
|---------------------------------|---|--|--|--|--|--|--|
| | | ΔH_f^{298} (kcal mol ⁻¹) | S^{298} (cal mol ⁻¹ K ⁻¹) | ΔH_f^{298} (kcal mol ⁻¹) | S^{298} (cal mol ⁻¹ K ⁻¹) | ΔH_f^{298} (kcal mol ⁻¹) | S^{298} (cal mol ⁻¹ K ⁻¹) |
| Si ₇ H ₈ | 8 | 122.1 | 100.6 | 122.9 | 101.9 | 0.8 | 1.3 |
| Si ₇ H ₁₀ | 100 | 95.1 | 107.3 | 94.8 | 107.4 | -0.3 | 0.1 |

^aThe thermochemical data presented are for species 8 and 100 depicted in the Supporting Information. This study calculates the standard enthalpy of formation from atomization energies and bond additivity correction (BAC) parameters, while the literature source uses homodesmotic reactions.

Table 5. Summary of Parameters for the Bond Additivity Correction (BAC) of Different Bond Types for Standard Enthalpy of Formation at 298 K Calculated from Atomization Energies and G3//B3LYP

| | Si—H and =Si—H | :Si—H | Si—Si | :Si—Si | Si=Si |
|--------------------------------------|----------------|-------|-------|--------|-------|
| BAC values (kcal mol ⁻¹) | 0.16 | 0.95 | 0.35 | 0.57 | -0.66 |

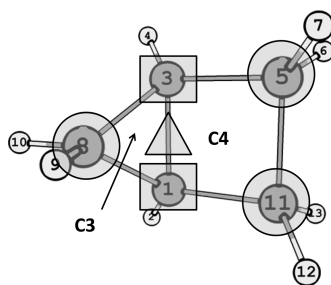


Figure 1. Representative hydrogenated silicon cluster divided into atom-centered and bond-centered groups, as well as ring corrections. The unique atom-centered groups are denoted with circles (SiSi₂H₂) and squares (SiSi₃H). The bond-centered group is denoted with a triangle (3–4). The ring corrections are denoted with C3 and C4.

($\Delta H_{f,298}^{\circ}(\text{Si}) = 107.55 \text{ kcal mol}^{-1}$, $\Delta H_{f,298}^{\circ}(\text{H}) = 52.10 \text{ kcal mol}^{-1}$) and $\Delta H_{a,298}^{\circ}(\text{Si}_x\text{H}_y)$ is the atomization energy defined as the enthalpy change upon decomposition of a molecule into its component atoms, which can be evaluated as eq 2:

$$\Delta H_{a,298}^{\circ}(\text{Si}_x\text{H}_y) = [xH^{298}(\text{Si}) + yH^{298}(\text{H})] - H^{298}(\text{Si}_x\text{H}_y) \quad (2)$$

where $H^{298}(\text{Si})$ and $H^{298}(\text{H})$ are the enthalpies of atomic silicon and hydrogen at 298 K, respectively, and $H^{298}(\text{Si}_x\text{H}_y)$ is the enthalpy of Si_xH_y at the same temperature. These enthalpies can be calculated as the sum of the electronic energies (E_{el}), zero point energies (ZPE), and thermal corrections (E_{vib}^{298} , E_{trans}^{298} , and E_{rot}^{298}) from 0 to 298 K, as follows from canonical molecular partition functions assuming an ideal gas at 1 atm:

$$H^{298} = E_{\text{el}} + \text{ZPE} + E_{\text{vib}}^{298} + E_{\text{trans}}^{298} + E_{\text{rot}}^{298} + \Delta PV \quad (3)$$

All of the quantities on the right-hand side of eq 3 are obtained from quantum chemical calculations, and the enthalpy of formation of Si_xH_y is then calculated.

Table 6. (a) Statistical Analysis for Least Squares Regression of Group Additivity Parameters for Standard Enthalpy of Formation at 298 K from Atomization Energies and Bond Additivity Correction (BAC) parameters and (b) Summary of Errors (Average Absolute Deviation (AAD)) for the Prediction of Standard Enthalpy of Formation at 298 K from Atomization Energies and Bond Additivity Correction (BAC) Parameters

| (a) | | | |
|-------|--------------|----------------------|------------|
| model | R^2 -value | regression F -test | |
| | | F -value | P -value |
| 1 | 0.949 | 162 | <0.001 |
| 2 | 0.998 | 1686 | <0.001 |
| 3 | 0.975 | 249 | <0.001 |
| 4 | 0.998 | 2005 | <0.001 |

| (b) | | | | |
|-------|-------------------------------|-------|-----------------------------------|-----------|
| model | AAD (kcal mol ⁻¹) | % AAD | std dev (kcal mol ⁻¹) | % std dev |
| 1 | 10.0 | 6.3 | 19.1 | 11.2 |
| 2 | 5.1 | 4.0 | 4.6 | 3.4 |
| 3 | 8.3 | 5.3 | 17.6 | 10.3 |
| 4 | 4.2 | 3.2 | 4.0 | 2.9 |

The isodesmic bond additivity correction (BAC) proposed by Petersson et al.⁷² and applied to silicon hydride chemistry by Wong et al.⁵⁹ was used in our calculations of standard enthalpy of formation. This approach uses a set of reference molecules that have experimental data available which then are compared to G3//B3LYP enthalpies of formation from homodesmotic reactions to calculate a set of correction parameters. The inclusion of these correction parameters was shown to lead to values that very closely approximate standard enthalpies of formation based on available experimental data and data calculated using the method of homodesmotic reactions (Table 4).⁵⁹ The BAC parameters used in this study to calculate enthalpies of formation are presented in Table 5 and follow eq 4.

$$\Delta H_{f,298}^{\circ}(\text{BAC}) = \Delta H_{f,298}^{\circ}(\text{calculated}) + \sum_i N_i \text{BAC}_i \quad (4)$$

BAC_{*i*} is the BAC parameter of a certain bond type *i*, and enthalpies of formation estimated from BACs, $\Delta H_{f,298}^{\circ}(\text{BAC})$, can be defined as the enthalpies of formation calculated on the basis of atomization energies, $\Delta H_{f,298}^{\circ}(\text{calculated})$, corrected by

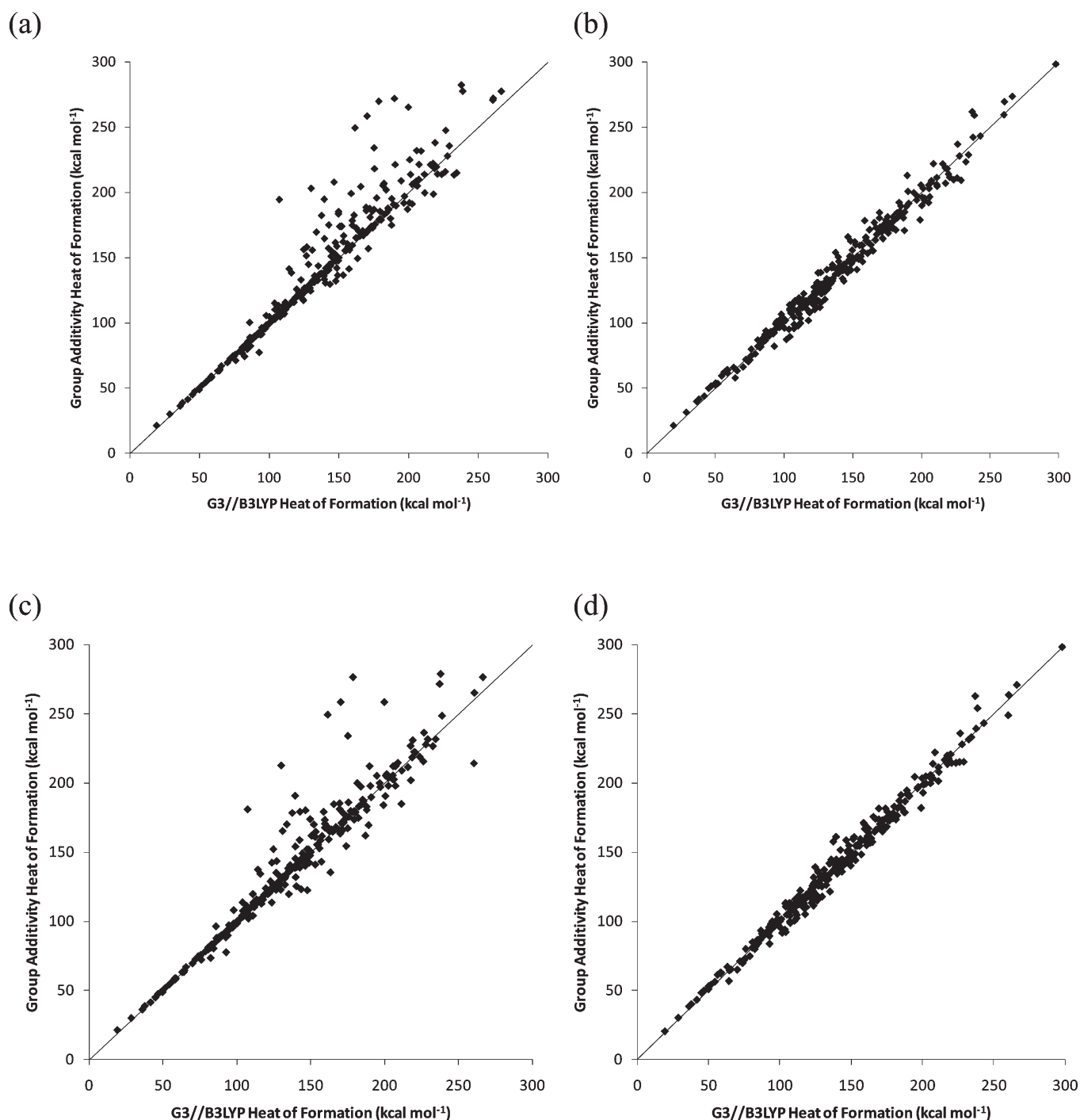


Figure 2. Parity plots of standard enthalpy of formation for the training set of 293 molecules: (a) model 1, (b) model 2, (c) model 3, and (d) model 4.

the summation of the BAC_i parameters multiplied by the number of bonds of that type (N_i). Analogous to the work performed by Wong et al.,⁵⁹ the application of BAC parameters to molecules that cannot be calculated using the method of homodesmotic reactions required approximating bonds containing a triply coordinated silicon center without a double bond, i.e., $:Si-Si$ and $Si-Si$, as $:Si-Si$ bonds. These triply coordinated silicon centers without a double bond in our study always occur in pairs. Moreover, all multifunctional polycyclic hydrogenated silicon clusters in our study have a nondoublet or singlet spin multiplicity for the electronic wave function, which was shown to be more stable

than the triplet spin multiplicity for the electronic wave function (Table 1). This pairing of valence electrons in selected clusters to lower electronic energy motivated the approximation of $Si-Si$ bonds as $:Si-Si$ bonds.

Group Additivity Models and Application to the Thermochemistry of Multifunctional Polycyclic Hydrogenated Silicon Clusters. The performance of four different group additivity (GA) models was compared. The first two models were based on the existing group additivity scheme for the thermochemical properties of silicon hydride clusters that was developed from the thermochemical properties of silicon hydrides containing up to

Table 7. (a) Statistical Analysis for Least Squares Regression of Group Additivity Parameters for Standard Entropy at 298 K and Constant Pressure Heat Capacity at 500, 1000, and 1500 K and (b) Summary of Errors (Average Absolute Deviation (AAD)) for the Prediction of Standard Entropy at 298 K and Constant Pressure Heat Capacity at 500, 1000, and 1500 K

| (a) | | | | |
|----------------|--------------|----------------------|------------|--|
| model | R^2 -value | regression F -test | | |
| | | F -value | P -value | |
| S | 1.000 | 5427 | <0.001 | |
| C_p (500 K) | 1.000 | 105518 | <0.001 | |
| C_p (1000 K) | 1.000 | 156840 | <0.001 | |
| C_p (1500 K) | 1.000 | 175797 | <0.001 | |

| (b) | | | | |
|----------------|--|-------|--|-----------|
| model | AAD | | std dev | |
| | (cal mol ⁻¹ K ⁻¹) | % AAD | (cal mol ⁻¹ K ⁻¹) | % std dev |
| S | 2.1 | 1.9 | 1.7 | 1.8 |
| C_p (500 K) | 0.26 | 0.53 | 0.23 | 0.72 |
| C_p (1000 K) | 0.26 | 0.43 | 0.23 | 0.57 |
| C_p (1500 K) | 0.26 | 0.40 | 0.23 | 0.53 |

seven silicon atoms.⁵⁹ Thermochemical properties were calculated on the basis of the sum of atom-centered groups and ring corrections. Following the group additivity method of Benson,⁷³ the atom-centered groups were differentiated according to the number of Si and H atoms and type of Si atoms to which the central atom was attached. For example, silicon atoms can be part of a double bond (SiA), have a divalent center (SiB), have a double bond and two nonbonded electrons (SiAB), or have a triply coordinated center without a double bond (SiR). Ring corrections were included and dependent on the size of the ring and degree of functionality of the ring. When a molecule contained a single ring, inclusion of a ring correction was straightforward. However, when multiple rings were present for a given silicon hydride, all closed cycles of silicon atoms were assigned a ring correction associated with the ring size and degree of functionality of the ring. The degree of functionality, or multifunctionality, was defined as the number of divalent centers, double bonds, and/or triply coordinated silicon centers without a double bond in the ring. However, all of the molecules in the present study cannot be completely described by the existing atom-centered groups and ring corrections of Wong et al.⁵⁹ due to the presence of triply coordinated silicon centers without a double bond (SiR), which appear in pairs. Therefore, new atom-centered groups and ring corrections were included to account for these silicon centers.

The first two GA models were based on only atom-centered groups and ring corrections and were formulated as: model 1, atom-centered groups and ring corrections of Wong et al.⁵⁹ were fixed at the values reported by Wong et al. and additional atom-centered groups and ring corrections required to describe the molecules of this study were optimized; model 2, all atom-centered groups and ring corrections (those defined by Wong et al.⁵⁹ and additional ones required to describe the molecules of this study) were optimized.

The next two GA models also included bond-centered groups, which were inspired by the group additivity work on polycyclic aromatic hydrocarbons of Yu et al.^{60,61} Bond-centered groups capture the additional ring strain present in polycyclic species that contain fused rings. Thus, bond-centered groups are only implemented for Si–Si bonds that are part of two or more rings. Figure 1 illustrates how atom-centered groups, bond-centered groups, and ring corrections are assigned to a multifunctional polycyclic hydrogenated silicon cluster. In Figure 1, the bond shared by the three- and four-membered rings is described by one bond-centered group, and this bond-centered group is assigned a “3–4” parameter, using the sizes of the rings to which the bond belongs to designate the parameter. The simultaneous use of bond-centered groups and ring corrections is aimed at capturing accurately the thermochemical properties of both cyclic and complex polycyclic species. GA models 3 and 4 were thus defined as: model 3, atom-centered groups and ring corrections of Wong et al.⁵⁹ were fixed at the values reported by Wong et al. and additional atom-centered groups and ring corrections required to describe the molecules of this study and bond-centered groups introduced by us were optimized; model 4, all atom-centered groups and ring corrections (those defined by Wong et al.⁵⁹ and additional ones required to describe the molecules of this study) and bond-centered groups introduced by us were optimized.

To develop the group additivity parameters for the four different GA models, the data set of 162 molecules shown in the Supporting Information and the 131 molecules used in our previous work⁵⁹ was used. The entire training set for this study was thus composed of 293 molecules. The hydrogenated silicon clusters in the training set of 293 molecules had a maximum of thirteen silicon atoms and a minimum of two silicon atoms. With the exception of cycloheptasilane in the work of Wong et al.,⁵⁹ rings larger than six silicon atoms were not examined because (1) larger and less-strained polycyclic systems are computationally more intensive for quantum chemical calculations and (2) crystalline silicon without defects will assume a diamond cubic structure where six-membered rings form a series of hexagonal channels, and larger ring sizes are thermodynamically unfavorable.^{74,75} Moreover, our previous work has predicted a net formation of three-, four-, and five-membered rings in hydrogenated amorphous silicon nanostructures under pyrolysis conditions.⁷⁶ The group additivity parameters for the four different models were obtained using multiple linear regression with the least-squares method for the standard enthalpies of formation of all training set molecules. The overall model was deemed significant if the F -test satisfied the 99% confidence level (i.e., the p -value was below $\alpha = 0.01$). Of the four models, the one that best captured the standard enthalpy of formation values was then extended to entropy and heat capacity values.

Finally, the best group additivity model and its parameters were validated using the sensitivity analysis proposed by Mavrovouniotis.⁷⁷ This approach removes 10% of the molecules randomly (or 29 molecules for our study), and the group additivity parameters are refitted. The new group additivity parameters are then used to predict the thermochemical properties of the removed molecules. The differences between these thermochemical properties and the values predicted from the original group additivity parameters are then calculated to assess the sensitivity of the group additivity parameters.

Table 8. Summary of Group Additivity Parameters^a for the Prediction of Thermochemical Properties Generalized from G3//B3LYP for Model 4 (See Text)^b

| parameter type | parameter | thermochemical properties | | | | |
|----------------|-----------------|---------------------------|-----------|-------|--------|--------|
| | | ΔH_f^{298} | S^{298} | C_p | | |
| | | | | 500 K | 1000 K | 1500 K |
| atom-centered | Si/Si/H3 | 10.26 | 30.17 | 13.72 | 18.43 | 20.44 |
| groups | Si/SiA/H3 | 10.26 | 30.17 | 13.72 | 18.43 | 20.44 |
| | Si/SiB/H3 | 10.26 | 30.17 | 13.72 | 18.43 | 20.44 |
| | Si/Si2/H2 | 9.82 | 18.22 | 11.24 | 14.50 | 15.84 |
| | Si/SiA2/H2 | 9.82 | 18.22 | 11.24 | 14.50 | 15.84 |
| | Si/SiB2/H2 | 9.82 | 18.22 | 11.24 | 14.50 | 15.84 |
| | Si/Si/SiA/H2 | 9.82 | 18.22 | 11.24 | 14.50 | 15.84 |
| | Si/Si/SiB/H2 | 9.82 | 18.22 | 11.24 | 14.50 | 15.84 |
| | Si/SiA/SiB/H2 | 9.82 | 18.22 | 11.24 | 14.50 | 15.84 |
| | Si/Si3/H | 7.76 | 4.56 | 9.21 | 11.00 | 11.67 |
| | Si/SiA3/H | 7.76 | 4.56 | 9.21 | 11.00 | 11.67 |
| | Si/SiB3/H | 7.76 | 4.56 | 9.21 | 11.00 | 11.67 |
| | Si/Si/SiA2/H | 7.76 | 4.56 | 9.21 | 11.00 | 11.67 |
| | Si/Si/SiB2/H | 7.76 | 4.56 | 9.21 | 11.00 | 11.67 |
| | Si/Si/SiA/SiB/H | 7.76 | 4.56 | 9.21 | 11.00 | 11.67 |
| | Si/Si2/SiA/H | 7.76 | 4.56 | 9.21 | 11.00 | 11.67 |
| | Si/Si2/SiB/H | 7.76 | 4.56 | 9.21 | 11.00 | 11.67 |
| | Si/SiA2/SiB/H | 7.76 | 4.56 | 9.21 | 11.00 | 11.67 |
| | Si/SiA/SiB2/H | 7.76 | 4.56 | 9.21 | 11.00 | 11.67 |
| | Si/Si4 | 2.26 | −8.66 | 6.90 | 7.40 | 7.49 |
| | Si/Si3/SiA | 2.26 | −8.66 | 6.90 | 7.40 | 7.49 |
| | Si/Si3/SiB | 2.26 | −8.66 | 6.90 | 7.40 | 7.49 |
| | Si/Si2/SiA2 | 2.26 | −8.66 | 6.90 | 7.40 | 7.49 |
| | Si/Si2/SiA/SiB | 2.26 | −8.66 | 6.90 | 7.40 | 7.49 |
| | Si/Si2/SiB2 | 2.26 | −8.66 | 6.90 | 7.40 | 7.49 |
| | Si/Si/SiA3 | 2.26 | −8.66 | 6.90 | 7.40 | 7.49 |
| | Si/Si/SiA2/SiB | 2.26 | −8.66 | 6.90 | 7.40 | 7.49 |
| | Si/Si/SiA/SiB2 | 2.26 | −8.66 | 6.90 | 7.40 | 7.49 |
| | Si/Si/SiB3 | 2.26 | −8.66 | 6.90 | 7.40 | 7.49 |
| | Si/SiA4 | 2.26 | −8.66 | 6.90 | 7.40 | 7.49 |
| | Si/SiA3/SiB | 2.26 | −8.66 | 6.90 | 7.40 | 7.49 |
| | Si/SiA2/SiB2 | 2.26 | −8.66 | 6.90 | 7.40 | 7.49 |
| | Si/SiA/SiB3 | 2.26 | −8.66 | 6.90 | 7.40 | 7.49 |
| | Si/SiB4 | 2.26 | −8.66 | 6.90 | 7.40 | 7.49 |
| | SiA/SiA/H2 | 32.64 | 28.20 | 11.20 | 13.99 | 15.24 |
| | SiA/SiA/Si/H | 28.26 | 16.25 | 8.52 | 10.11 | 10.76 |
| | SiA/SiA/SiA/H | 28.26 | 16.25 | 8.52 | 10.11 | 10.76 |
| | SiA/SiA/SiB/H | 28.26 | 16.25 | 8.52 | 10.11 | 10.76 |
| | SiA/SiAB/Si/H | 99.36 | 44.12 | 13.10 | 14.63 | 15.27 |
| | SiA/SiAB/SiA/H | 99.36 | 44.12 | 13.10 | 14.63 | 15.27 |
| | SiA/SiAB/SiB/H | 99.36 | 44.12 | 13.10 | 14.63 | 15.27 |
| | SiA/SiA/Si2 | 22.66 | 2.91 | 6.24 | 6.58 | 6.66 |
| | SiA/SiA/Si/SiA | 22.66 | 2.91 | 6.24 | 6.58 | 6.66 |
| | SiA/SiA/Si/SiB | 22.66 | 2.91 | 6.24 | 6.58 | 6.66 |
| | SiA/SiA/SiA2 | 22.66 | 2.91 | 6.24 | 6.58 | 6.66 |
| | SiA/SiA/SiA/SiB | 22.66 | 2.91 | 6.24 | 6.58 | 6.66 |
| | SiA/SiA/SiB2 | 22.66 | 2.91 | 6.24 | 6.58 | 6.66 |
| | SiA/SiAB/Si2 | 91.74 | 30.69 | 10.61 | 11.04 | 11.13 |
| | SiA/SiAB/Si/SiA | 91.74 | 30.69 | 10.61 | 11.04 | 11.13 |

Table 8. Continued

| parameter type | parameter | thermochemical properties | | | | |
|----------------|------------------|---------------------------|-----------|-------|--------|--------|
| | | ΔH_f^{298} | S^{298} | C_p | | |
| | | | | 500 K | 1000 K | 1500 K |
| | SiA/SiAB/Si/SiB | 91.74 | 30.69 | 10.61 | 11.04 | 11.13 |
| | SiA/SiAB/SiA2 | 91.74 | 30.69 | 10.61 | 11.04 | 11.13 |
| | SiA/SiAB/SiA/SiB | 91.74 | 30.69 | 10.61 | 11.04 | 11.13 |
| | SiA/SiAB/SiB2 | 91.74 | 30.69 | 10.61 | 11.04 | 11.13 |
| | SiB/Si/H | 61.82 | 32.82 | 7.87 | 9.15 | 9.69 |
| | SiB/SiA/H | 54.40 | 28.19 | 7.90 | 9.26 | 9.81 |
| | SiB/SiB/H | 55.51 | 31.88 | 7.74 | 8.91 | 9.46 |
| | SiB/Si2 | 60.75 | 18.12 | 5.40 | 5.38 | 5.34 |
| | SiB/Si/SiA | 56.26 | 18.48 | 5.08 | 5.14 | 5.12 |
| | SiB/Si/SiB | 47.81 | 17.34 | 5.21 | 5.41 | 5.46 |
| | SiB/SiA2 | 42.93 | 17.57 | 5.00 | 5.23 | 5.28 |
| | SiB/SiA/SiB | 54.99 | 6.22 | 6.36 | 6.77 | 6.82 |
| | SiB/SiB2 | 36.03 | 10.20 | 5.58 | 5.90 | 5.89 |
| | SiB/SiR/Si | 61.80 | 12.85 | 5.83 | 5.86 | 5.91 |
| | SiB/SiR2 | 55.39 | −14.15 | 8.61 | 9.53 | 9.70 |
| | Si/SiR/Si/H2 | 9.82 | 18.22 | 11.24 | 14.50 | 15.84 |
| | Si/SiR2/H2 | 9.82 | 18.22 | 11.24 | 14.50 | 15.84 |
| | Si/SiA/SiR/H2 | 9.82 | 18.22 | 11.24 | 14.50 | 15.84 |
| | Si/SiR/Si2/H | 7.76 | 4.56 | 9.21 | 11.00 | 11.67 |
| | Si/SiR2/Si/H | 7.76 | 4.56 | 9.21 | 11.00 | 11.67 |
| | Si/SiR2/SiB/H | 7.76 | 4.56 | 9.21 | 11.00 | 11.67 |
| | Si/SiR/SiB/Si/H | 7.76 | 4.56 | 9.21 | 11.00 | 11.67 |
| | Si/SiR/SiA/Si/H | 7.76 | 4.56 | 9.21 | 11.00 | 11.67 |
| | Si/SiR/SiA2/H | 7.76 | 4.56 | 9.21 | 11.00 | 11.67 |
| | Si/SiR/SiA/SiB/H | 7.76 | 4.56 | 9.21 | 11.00 | 11.67 |
| | Si/SiR3/H | 7.76 | 4.56 | 9.21 | 11.00 | 11.67 |
| | Si/SiR/Si3 | 2.26 | −8.66 | 6.90 | 7.40 | 7.49 |
| | Si/SiR2/Si2 | 2.26 | −8.66 | 6.90 | 7.40 | 7.49 |
| | Si/SiR2/SiB2 | 2.26 | −8.66 | 6.90 | 7.40 | 7.49 |
| | Si/SiR2/SiB/Si | 2.26 | −8.66 | 6.90 | 7.40 | 7.49 |
| | Si/SiR/SiA/Si2 | 2.26 | −8.66 | 6.90 | 7.40 | 7.49 |
| | Si/SiR/SiB/Si2 | 2.26 | −8.66 | 6.90 | 7.40 | 7.49 |
| | Si/SiR3/SiB | 2.26 | −8.66 | 6.90 | 7.40 | 7.49 |
| | SiR/Si2/H | 38.73 | 21.52 | 7.97 | 9.37 | 10.00 |
| | SiR/SiB/Si/H | 38.73 | 21.52 | 7.97 | 9.37 | 10.00 |
| | SiR/SiA/Si/H | 38.73 | 21.52 | 7.97 | 9.37 | 10.00 |
| | SiR/Si3 | 44.30 | 12.75 | 5.27 | 5.33 | 5.29 |
| | SiR/Si2/SiB | 44.30 | 12.75 | 5.27 | 5.33 | 5.29 |
| | SiR/Si2/SiA | 44.30 | 12.75 | 5.27 | 5.33 | 5.29 |
| | SiR/Si/SiB2 | 44.30 | 12.75 | 5.27 | 5.33 | 5.29 |
| | SiR/Si/SiA2 | 44.30 | 12.75 | 5.27 | 5.33 | 5.29 |
| | SiR/SiB3 | 44.30 | 12.75 | 5.27 | 5.33 | 5.29 |
| | SiA/SiA/SiR/H | 28.26 | 16.25 | 8.52 | 10.11 | 10.76 |
| | SiA/SiA/SiR/SiA | 22.66 | 2.91 | 6.24 | 6.58 | 6.66 |
| | SiA/SiA/SiR/Si | 22.66 | 2.91 | 6.24 | 6.58 | 6.66 |
| | SiA/SiA/SiR2 | 22.66 | 2.91 | 6.24 | 6.58 | 6.66 |
| ring | C3 | 27.41 | 16.61 | −1.21 | −1.52 | −1.58 |
| corrections | C3B | 11.81 | 16.50 | −1.57 | −1.70 | −1.70 |
| | C3A | 27.76 | 19.00 | −1.52 | −1.85 | −1.93 |
| | C3BB | 16.40 | 17.41 | −1.67 | −1.91 | −1.97 |

Table 8. Continued

| parameter type | parameter | thermochemical properties | | | | |
|----------------------|-----------|---------------------------|-----------|-------|--------|--------|
| | | ΔH_f^{298} | S^{298} | C_p | | |
| | | | | 500 K | 1000 K | 1500 K |
| bond-centered groups | C3AB | 16.40 | 17.41 | −1.67 | −1.91 | −1.97 |
| | C3R | 14.93 | 12.75 | −0.80 | −1.02 | −1.03 |
| | C3AR | −20.34 | −1.71 | −1.17 | −0.66 | −0.66 |
| | C3BR | −17.96 | 23.42 | −2.63 | −2.70 | −2.75 |
| | C3BBB | 41.91 | 37.51 | −3.55 | −3.99 | −3.86 |
| | C4 | 14.93 | 10.60 | −0.87 | −1.07 | −1.11 |
| | C4B | 1.45 | 8.55 | −0.94 | −1.06 | −1.04 |
| | C4A | 14.91 | 12.69 | −1.21 | −1.45 | −1.50 |
| | C4AB | −9.59 | 8.69 | −1.21 | −1.28 | −1.28 |
| | C4AA | 18.71 | 15.02 | −1.51 | −1.80 | −1.90 |
| | C4BB | −0.51 | 9.43 | −1.28 | −1.54 | −1.67 |
| | C4R | 11.60 | 8.62 | −0.61 | −0.77 | −0.80 |
| | C4RR | −0.25 | 3.18 | −0.31 | −0.28 | −0.27 |
| | C4AR | −14.44 | 0.83 | −0.19 | −0.20 | −0.14 |
| | C4BR | −3.14 | 6.66 | −0.68 | −0.72 | −0.72 |
| | C4ABB | −21.86 | 32.61 | −3.81 | −4.51 | −4.60 |
| | C4RRB | −13.36 | 18.79 | −2.01 | −2.43 | −2.41 |
| | C4BBRR | −21.86 | 32.61 | −3.81 | −4.51 | −4.60 |
| | C5 | 1.87 | 3.19 | −0.44 | −0.44 | −0.44 |
| | C5B | −4.23 | 3.68 | −0.54 | −0.57 | −0.54 |
| | C5A | 2.81 | 5.22 | −0.68 | −0.77 | −0.80 |
| | C5BB | −4.59 | 5.02 | −0.62 | −0.70 | −0.72 |
| | C5AB | −4.59 | 5.02 | −0.62 | −0.70 | −0.72 |
| | C5R | −13.32 | −4.99 | −0.01 | 0.29 | 0.28 |
| | C5RR | −3.69 | 0.87 | −0.27 | −0.19 | −0.14 |
| | C5BR | −30.97 | −3.30 | −0.57 | −0.11 | −0.11 |
| | C5AR | 20.86 | 16.69 | −1.01 | −1.59 | −1.65 |
| | C5BRR | −4.59 | 5.02 | −0.62 | −0.70 | −0.72 |
| | C5RRA | −4.59 | 5.02 | −0.62 | −0.70 | −0.72 |
| | C5BBRR | −34.58 | 15.78 | −2.54 | −2.54 | −2.64 |
| | C6 | −2.58 | 0.81 | −0.31 | −0.27 | −0.27 |
| | C6A | −0.98 | 1.79 | −0.45 | −0.39 | −0.40 |
| | C6B | −5.07 | 0.39 | −0.37 | −0.25 | −0.24 |
| | C6BB | −5.07 | 0.39 | −0.37 | −0.25 | −0.24 |
| | C6AA | 10.55 | 6.51 | −0.48 | −0.67 | −0.67 |
| | C6AB | −6.61 | −4.16 | −0.06 | 0.05 | 0.06 |
| | C6R | 7.14 | 6.88 | −0.29 | −0.71 | −0.59 |
| | C6RR | −13.50 | 1.32 | −0.34 | −0.37 | −0.27 |
| | C6BR | 22.26 | 12.39 | −0.50 | −1.11 | −0.91 |
| | C6ARR | −20.64 | −4.62 | 0.02 | 0.19 | 0.24 |
| | C6RRR | −21.74 | −9.11 | 0.71 | 0.98 | 1.14 |
| | C7 | −4.09 | −4.42 | 0.12 | 0.31 | 0.35 |
| | 3−3 | −3.07 | 0.07 | −0.05 | −0.03 | −0.02 |
| | 3−4 | −0.56 | 0.16 | 0.01 | 0.01 | 0.01 |
| | 3−5 | 0.09 | 0.79 | −0.05 | −0.08 | −0.09 |
| | 3−6 | −0.13 | 0.76 | −0.09 | −0.11 | −0.11 |
| | 4−4 | −0.89 | 0.46 | −0.06 | −0.06 | −0.06 |
| | 4−5 | −1.44 | 1.31 | −0.17 | −0.17 | −0.17 |
| | 4−6 | −0.16 | 0.93 | −0.16 | −0.15 | −0.15 |
| | 5−5 | 1.92 | 1.76 | −0.14 | −0.19 | −0.19 |

Table 8. Continued

| parameter type | parameter | thermochemical properties | | | | |
|----------------|-----------|---------------------------|-----------|-------|--------|--------|
| | | ΔH_f^{298} | S^{298} | C_p | | |
| | | | | 500 K | 1000 K | 1500 K |
| | 5–6 | 1.40 | 2.19 | −0.22 | −0.22 | −0.24 |
| | 6–6 | 4.47 | −0.58 | 0.21 | 0.25 | 0.28 |

^aFollowing the group additivity method of Benson, the atom-centered groups were differentiated according to the number of Si and H atoms and type of Si atoms to which the central atom was attached. Silicon atoms can be part of a double bond (SiA), have a divalent center (SiB), have a double bond and two nonbonded electrons (SiAB), or have a triply coordinated center without a double bond (SiR). Individual ring corrections were dependent on the size of the ring and degree of functionality of the ring. The bond-centered groups are denoted by two numbers separated by a hyphen, where the two numbers represent the sizes of the two smallest rings participating in the shared bond. ^bStandard enthalpy of formation at 298 K has units of kcal mol^{−1}. Standard entropy at 298 K and constant pressure heat capacity at elevated temperatures have units of cal mol^{−1} K^{−1}.

RESULTS AND DISCUSSION

Structures. The structures for the 162 hydrogenated silicon clusters that were investigated in the present study were optimized using B3LYP/6-31G(d). The optimized structures for all of the species showed complex polycyclic or cyclic nature and a varying level of surface passivation with hydrogen atoms, as illustrated in the Supporting Information. High-energy sterically strained structural isomers were calculated in this study to capture the diverse range of strain energies possible in hydrogenated silicon clusters.

Comparison of our results to the work of Li et al.⁷⁸ and Swihart et al.²² revealed that the B3LYP/6-31G(d) level of theory is sufficient to capture the geometry of hydrogenated silicon clusters. Geometric data for small- to medium-sized hydrogenated silicon clusters from different levels of theory were directly compared, i.e., for species 8, 13, 63, and 100. The geometric data for bond angles and bond lengths differed by no more than 2° and 0.02 Å, respectively. Primary differences in geometry arose due to the use of p-type polarization functions for hydrogen atoms and diffuse functions with B3LYP, BHLYP, and BPW91 functionals for the Si₄ species by Li et al. BHLYP predicts the most reliable Si–Si bond lengths and B3LYP predicts the most reliable H–Si bond lengths.¹⁵ Primary differences in geometry also arose due to the use of a HF mean field Hamiltonian and a 3-21G(d) split-valence basis set by Swihart et al.²² for the Si₇ species. In contrast, our calculations used a B3LYP hybrid density functional and the 6-31G(d) split-valence basis set for the Si₄ and Si₇ species that contains a combination of HF exchange plus Slater and Becke exchange functionals, as well as a correlation potential, and enhances the effect of the valence (or bonding electrons) in the larger basis set. Moreover, our study did not impose symmetry before geometry optimization.

Frequencies. Experimental spectroscopic data for the vibrational frequencies of silicon hydrides are limited. The unscaled harmonic frequencies for SiH₂, SiH₄, and Si₂H₆ calculated using the B3LYP/6-31G(d) level of theory were compared against available experimental data^{79–83} (Table 2). The unscaled harmonic frequencies for SiH₂, SiH₄, and Si₂H₆ were determined to have average absolute deviations from experimental values of 2.2%, 3.4%, and 1.6%, respectively. The use of a temperature-dependent scaling factor for vibrational frequencies as suggested by Scott and Radom⁶⁵ was then used for more accurate thermochemical property estimation (see Computational Methodology).

Thermochemical Properties. To the best of our knowledge, there is no extensive investigation of thermochemical property estimation or even of frequency calculations for optimized hydrogenated silicon clusters, i.e., greater than or equal to seven silicon atoms, outside of the work of Wong et al.⁵⁹ and Swihart et al.²² The thermochemical properties of all 162 species studied here are reported in the Supporting Information. Swihart et al.²² investigated the structure and thermochemistry of eight complex hydrogenated silicon clusters, and direct comparison of our results with two of these species was possible. These structural isomers are depicted in the Supporting Information as species 8 and 100, respectively. Our results for standard enthalpies of formation from atomization energies with BAC parameters included at 298 K were within +0.8 and −0.3 kcal mol^{−1} of the standard enthalpies of formation at 298 K of Swihart et al.²² from the method of homodesmotic reactions and higher by 1.3 and 0.1 cal mol^{−1} K^{−1} for standard entropy at 298 K for Si₇H₈ and Si₇H₁₀, respectively (Table 4).

Group Additivity Parameters. As detailed above, four group additivity models were explored composed of (1) frozen atom-centered groups and ring corrections of Wong et al.⁵⁹ and additional relaxed atom-centered groups and ring corrections required to describe the molecules of this study, (2) relaxed atom-centered groups and ring corrections of Wong et al.⁵⁹ and relaxed additional atom-centered groups and ring corrections required to describe the molecules of this study, (3) frozen atom-centered groups and ring corrections of Wong et al.⁵⁹ and additional relaxed atom-centered groups, ring corrections, and bond-centered groups required to describe the molecules of this study, and (4) relaxed atom-centered groups and ring corrections of Wong et al.⁵⁹ and additional relaxed atom-centered groups, ring corrections, and bond-centered groups required to describe the molecules of this study. Group additivity parameters were regressed from a training set of the 162 molecules listed in Supporting Information and the 131 molecules investigated by Wong et al.⁵⁹ The matrices used to derive the group additivity parameters were constructed using a sum of the relaxed atom-centered groups, ring corrections, and bond-centered groups, depending on the model. Several of the equations, i.e., the summation of parameters for a thermochemical property, are linearly dependent on others. This number of linearly dependent equations in all cases is much less than 293, i.e., or the total number of equations; however, the linear dependencies must be removed to regress group parameters. Moreover, to generalize the group parameters in the event of missing group parameters, i.e., a

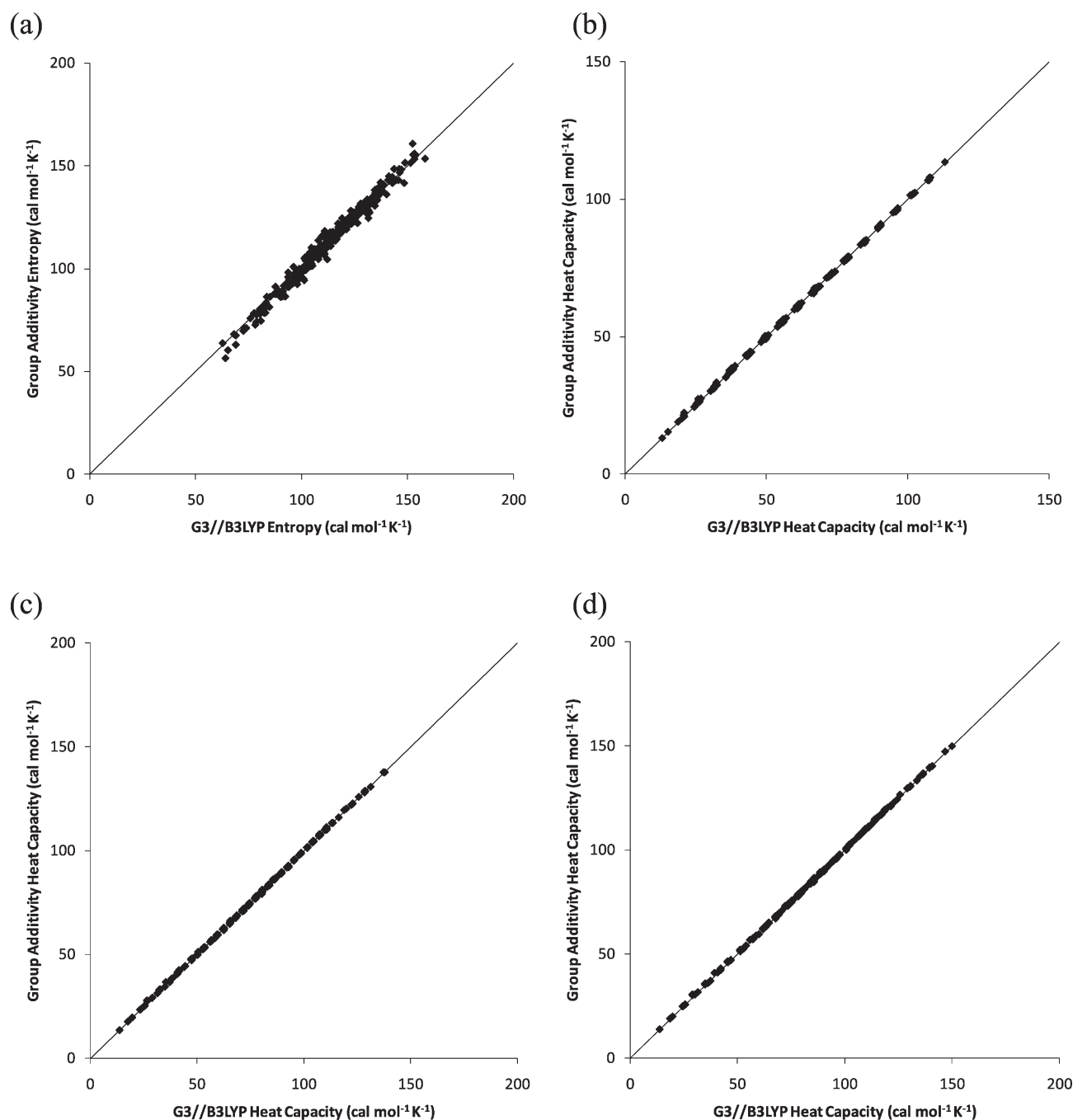


Figure 3. Parity plots of (a) standard entropy and constant pressure heat capacity at (b) 500 K, (c) 1000 K, and (d) 1500 K for the training set of 293 molecules using the group additivity database composed of relaxed atom-centered groups, ring corrections, and bond-centered groups (model 4).

particular group that potentially exists but was not included in the regression of group parameters in this study, groups with the same central silicon atom and number of neighboring silicon atoms were set equal to each other. This assumption was performed for Si, SiA, and SiR central silicon atoms, and the only exception to this assumption was for group parameters composed of SiB as the central silicon atom. For the potential group parameters with SiAB as the central silicon atom, a SiA atom will always be attached; therefore, to avoid linearly dependent SiA and SiAB group parameters, SiAB represents the composite structure :Si=Si and is never treated as a central silicon atom.

The statistics for the four different models and a performance summary of the group additivity parameters are presented in Table 6 for the prediction of standard enthalpy of formation at 298 K from atomization energies and BAC parameters. Parity plots depicting how well the four models capture the training set values of standard enthalpy of formation are shown in Figure 2. The model which included relaxed atom-centered groups, ring corrections, and bond-centered groups predicted the standard enthalpies of formation most accurately with an average of 3.2% error for the entire training set of 293 molecules and a standard deviation of 2.9 for the percentage of error in the prediction of standard enthalpies of formation. For the prediction of standard

Table 9. Performance Summary of the Independent Runs of the Sensitivity Analysis for Model 4 (See Text) for the Prediction of Standard Enthalpy of Formation at 298 K from Atomization Energies and Bond Additivity Correction (BAC) Parameters Using (a) the Refitted Group Additivity Parameters for the Two Independent Runs and (b) the Group Additivity Parameters from the Full Regression Containing 293 Molecules^a

| (a) | | | | |
|-------|----------------------------------|-------|--------------------------------------|-----------|
| model | AAD (kcal mol ⁻¹) | % AAD | std dev (kcal mol ⁻¹) | % std dev |
| run 1 | 9.7 | 6.3 | 10.6 | 5.2 |
| run 2 | 6.8 | 5.0 | 6.4 | 3.8 |

| (b) | | | | |
|-------|----------------------------------|-------|--------------------------------------|-----------|
| model | AAD (kcal mol ⁻¹) | % AAD | std dev (kcal mol ⁻¹) | % std dev |
| run 1 | 5.7 | 4.1 | 5.5 | 3.2 |
| run 2 | 4.3 | 3.4 | 3.5 | 2.7 |

^aAAD is average absolute deviation.

enthalpy of formation, including bond-centered groups increased the goodness of fit (see Figure 2a,b for parity plots of models not containing bond-centered groups, Figure 2c,d for the corresponding parity plots of models containing bond-centered groups, and Table 6 for statistical analysis of least-squares regressions). In addition, as summarized in Table 6, the goodness of fit is decreased in both cases in which the group additivity values of Wong et al.⁵⁹ are frozen. These more simplified models reveal that the existing group additivity parameters do not accurately capture the thermochemical properties of more complex species and pinpoint the more significant structural factors affecting the thermochemical properties. It is interesting to examine how the accuracy of the fits of the properties of the molecules in the original group additivity database studied by Wong et al.⁵⁹ changed when the group additivity parameters of Wong et al.⁵⁹ were relaxed to capture a larger and more complex set of silicon hydrides. The molecules in the original group additivity database for silicon hydride thermochemistry using the parameters developed by Wong et al.⁵⁹ were captured with an average absolute deviation of 0.64 kcal mol⁻¹ for standard heats of formation at 298 K. The new models 2 and 4 (as summarized in Table 6) captured these molecules with an average absolute deviation of 3.9 and 2.8 kcal mol⁻¹, respectively, for standard heats of formation at 298 K, indicating that regression against a larger and more diverse data set did compromise the fit of more simple silicon hydrides; however, the expanded group additivity data set is applicable to a much greater diversity of types of silicon atoms.

On the basis of these analyses, model 4 was selected for further expansion and analysis. Table 7 summarizes the least-squares regressions and performance of group additivity parameters for standard entropy and heat capacity at 500, 1000, and 1500 K. The group additivity parameter model contains 72 unique parameter values (or degrees of freedom), i.e., 22 atom-centered groups, 40 ring corrections, and 10 bond-centered groups. The group additivity values for the full model are summarized in Table 8 for the prediction of standard enthalpy of formation, standard entropy, and constant pressure heat capacity. The temperature range used in the regression of group additivity values was chosen

to allow for the direct comparison of the revised group additivity database to the original group additivity database reported by Wong et al.⁵⁹ Parity plots depicting how well the full model captures the 293 training set values of the thermochemical properties are shown in Figure 2d, Figure 3a, and Figure 3b–d for standard enthalpy of formation at 298 K, standard entropy at 298 K, and constant pressure heat capacity at elevated temperatures, respectively. For the training set molecules, the average absolute deviations comparing the G3//B3LYP values to the values obtained from the revised group additivity database for thermochemical properties are 3.2%, 1.9%, 0.40%, 0.43%, and 0.53%, respectively. The average absolute deviations per silicon atom for the entire training set for the prediction of standard enthalpy of formation, as well as standard entropy and heat capacity at 500, 1000, and 1500 K, were 0.67 kcal mol⁻¹, 0.33 cal mol⁻¹ K⁻¹, 0.04 cal mol⁻¹ K⁻¹, 0.05 cal mol⁻¹ K⁻¹, and 0.06 cal mol⁻¹ K⁻¹, respectively.

Sensitivity Analysis of Group Additivity Parameters. The group additivity parameters were then tested by comparing the ability of the group additivity method to capture the G3//B3LYP values for the molecules removed from the regression in two independent runs. The method of sensitivity analysis proposed by Mavrovouniotis⁷⁷ was implemented. This approach removes 10% of the molecules randomly (or 29 molecules for our study), and the group additivity parameters are refitted. The new group additivity parameters are then used to predict the thermochemical properties of the removed molecules. A performance summary for the prediction of standard enthalpy of formation at 298 K for the removed molecules using the refitted group additivity parameters for the two independent runs and the group additivity parameters from the full regression containing 293 molecules is presented in Table 9. The two runs using the refitted group additivity parameters had average absolute deviation values of 6.3% and 5.0%, respectively, for the validation set of 29 molecules compared to the G3//B3LYP values, which are slightly higher errors than the errors obtained using the group additivity parameters from the full regression containing 293 molecules. Thus, the predictive capability of the revised group additivity database for molecules not included in the training set is very good. This generalization for the prediction of thermochemical properties is necessary because computational and/or experimental investigation of all potential hydrogenated silicon clusters is not feasible.

CONCLUSIONS

Standard enthalpy of formation at 298 K and standard entropy and constant pressure heat capacity at elevated temperatures, i.e., 298–6000 K, were calculated for 162 hydrogenated silicon clusters using G3//B3LYP and statistical thermodynamics. The hydrogenated silicon clusters contained between three and thirteen silicon atoms and polycyclic nature by way of fused three to six-membered rings, as well as different degrees of dehydrogenation or multifunctionality. The existing group additivity database for the prediction of thermochemical properties of hydrogenated silicon clusters composed of atom-centered groups and ring corrections created by Wong et al.⁵⁹ was evaluated for the molecules of this study. The complete training set of molecules used to evaluate group additivity parameters contained 293 hydrogenated silicon clusters, i.e., 131 molecules from Wong et al.⁵⁹ and 162 molecules from this study. The relaxation of existing group parameter values during regression and addition of new atom-centered groups, ring corrections, and bond-centered groups best

captured the more complex species of this study. A group additivity database composed of atom-centered groups and ring corrections, including bond-centered groups, was created to predict thermochemical properties most precisely. Sensitivity analysis of the revised group additivity parameter database revealed that the parameters were able to predict the thermochemical properties of molecules that were not used in the training set.

■ ASSOCIATED CONTENT

S Supporting Information. Geometries and unscaled frequencies calculated for all of the hydrogenated silicon clusters of this study (Table S1). Standard enthalpy of formation at 298 K from atomization energies and bond additivity correction (BAC) parameters and standard entropy and constant pressure heat capacity at selected temperatures for the all of the species in this study (Table S2). Graphics depicting the 162 hydrogenated silicon clusters investigated in this study (Figure S1). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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