J. Phys. Chem. A 1997, 101, 3942−3958

Computational Thermochemistry of Medium-Sized Silicon Hydrides

Gernot Katzer, Margot C. Ernst, Alexander F. Sax,* and Josef Kalcher

Institut für Theoretische Chemie, Karl-Franzens Universität Graz, A-8010 Graz, Austria

Received: October 17, 1996; In Final Form: February 12, 1997⊗

Standard enthalpies $\Delta_f H^{298}$, entropies S^{298}, and Gibbs functions of formation $\Delta_f G^{298}$ for a large number of silicon hydrides containing one to five Si atoms have been calculated. The choice of compounds includes cyclic and acyclic silanes, silyl radicals, silylenes, disilenes, and cyclic diradicals. The thermodynamic functions were calculated using an empirically corrected *ab initio* scheme. The electronic energies were obtained with multiconfiguration reference averaged coupled-pair functional (ACPF) wave functions. Two different basis sets were employed to demonstrate the validity of the correction scheme. The computed data are compared with experimental and theoretical data from other laboratories. Increment rules and substituent effects are presented and various reaction enthalpies are tabulated and discussed. The performance of the correction scheme and potential pitfalls in its general applicability are discussed.

I. Introduction

Various experimental techniques known collectively as chemical vapor deposition (CVD) yield amorphous silicon from the decomposition of silanes. The reaction mechanisms proposed for these processes involve a large number of reaction steps including unimolecular decomposition, abstraction, elimination, and insertion reactions. Several of these individual steps involve small, reactive species that, due to the reactivity, still pose a challenge to experimental techniques but, due to their rather small size, can be treated with quantum theoretical methodology. Despite the efforts of both theoretical[1−7] and experimental[8−20] groups to increase the number of systems for which reliable thermodynamic data are known, there is still need for thermochemical data of silicon hydrides.

Although *ab initio* methods still cannot compete with the best experimental techniques for large or even medium-sized molecules, they are very useful for small molecules or for transient and reactive species for most of which neither calculated nor measured enthalpies are reported in the literature.

Silicon hydrides are a class of compounds for which good thermodynamic data with known or reasonably small error bounds are still sparse. Grev and Schaefer[7] pointed out some fundamental questions concerning the thermochemistry of silicon hydrides, but the method applied by these authors to obtain theoretical enthalpies is applicable only to the smallest systems. Several other investigations[2,4−6] also provide computed enthalpies of formation of fairly high quality for a selection of small molecules, but very little data exist for medium-sized and larger molecules. To be useful in kinetic modeling, for example, computed thermodynamic data should be of consistent quality for all species of interest, which poses a serious problem if both small and large species are to be considered. This is simply because the cost of computational methods increases rapidly with molecular size.

In order to consider data for a wide range of systems, the use of empirical corrections has been advised.[3] It is only through the combined use of *ab initio* quantum chemical methods and empirical corrections that a consistent data base of small and medium-sized systems can be compiled. In this spirit we have continued to explore a method that is suitable for generating accurate thermodynamic properties of small and medium-sized silicon hydrides on the basis of a conceptually compact procedure.

In this paper, we present enthalpies of formation ($\Delta_f H^{298}$) and Gibbs functions of formation ($\Delta_f G^{298}$) of 143 molecular ground state systems, along with a large number of associated low-lying excited states, and compare some of our data with other theoretical and experimental results.

In the tables as well as in the text, acyclic silicon hydrides with no more than three Si atoms will be denoted by a chemical formula, and all other species will be identified by systematic names. In disilenes featuring exocyclic double bonds, the terms *silylidene* and *disilanylidene* are used to denote the substituents $=SiH_2$ and $=SiHSiH_3$, respectively, in analogy to the usage in carbon chemistry. Therefore, the names silylidenecyclotrisilane and (disilanylidene)cyclotrisilane are used for the disilene *cyclo*-$Si_3H_4=SiH_2$ and its homologue *cyclo*-$Si_3H_4=SiHSiH_3$. In figures, structural formulas will be employed.

To calculate these enthalpies, we used high-quality wave functions and moderately sized basis sets in our *ab initio* procedure, supplemented by empirical corrections. The same computational scheme was used for all species of interest to provide consistent data.

II. Computational Methodology

A. Calculation of the Electronic Energies. All calculations were performed with a local pseudopotential for silicon developed in our group.[21,22] Although the use of a pseudopotential is not necessary for the smaller species, it allows us to use correlated multiconfiguration reference wave functions for molecules containing several Si atoms.

From our experience in the field of silicon hydrides with formal multiple bonds or divalent silicon atoms[23] that exhibit a significant diradical character, we know that there are at least two basic requirements for a correct treatment of these species.

(1) The nondynamic correlation should be accounted for by a proper multiconfiguration reference wave function, since it is frequently not only decisive for the quality of geometry parameters but even for the nature of stationary points.[23]

(2) Dynamic correlation corrections can satisfactorily be accounted for by an appropriate *post-self-consistent field (post-SCF)* calculation when all nondynamic correlation effects are already included in the reference wave function. By this, significant improvements in relative energies and singlet triplet

---

⊗ Abstract published in *Advance ACS Abstracts,* May 1, 1997.

S1089-5639(96)03194-5 CCC: $14.00

splittings of systems with multiple bonds or divalent silicon atoms can be observed.

For many systems (silanes, radicals, triplet states of disilenes, silylenes, and diradicals), equilibrium geometries and harmonic frequencies were obtained at the Hartree–Fock level of theory. The singlet states of disilenes, silylenes, and diradicals, however, were optimized with MC-SCF wavefunctions. In either case, we scaled the harmonic frequencies by a factor of 0.90 for the calculation of thermodynamic functions.

Total electronic energies were calculated at the equilibrium geometry using averaged coupled-pair functional (ACPF) wave functions and usually the same kind of reference function that was employed for the geometry optimization. The ACPF procedure was chosen because it allows the use of multiconfiguration reference functions and is nearly size-consistent, thus performing much better than Davidson corrected multireference configuration interaction (MR-CI), which resulted in large residual size-consistency errors for the larger systems.

Disilenes were optimized with CAS(2,2) SCF wave functions (correlating the formal π bond only). The difference in the total ACPF energies, however, when comparing a CAS(2,2) with a CAS(4,4) (σ and π bonds correlated) reference, was roughly 2–3 kJ/mol, in cases of cyclic disilenes even more. Therefore, CAS(4,4) reference wave functions were used throughout for singlet disilenes and a CAS(8,8) reference wave function was employed for tetrasila-1,3-diene ($SiH_2{=}SiH{-}SiH{=}SiH_2$). It should be noted that because of program limitations, it was not possible to calculate ACPF energies with a CAS(4,4) reference for the largest disilenes Si_5H_{10}; therefore, a CAS(2,2) reference had to be used and the resulting enthalpies of formation were corrected by an increment. These increments (ranging from 2.1 to 2.5 kJ/mol) were derived from the differences between ACPF energies with CAS(2,2) and CAS(4,4) reference wave functions for smaller but structurally similar disilenes. A similar remark applies to the triplet state of tetrasila-1,3-diene.

The calculations reported here were performed with two different basis sets. The first is our standard (3s,3p) basis set for silicon and a 3s basis for hydrogen augmented with a set of d-type functions on silicon and a set of p-type functions on hydrogen. Since the (3s,3p) basis set is of valence triple ζ quality this basis is termed TZdp. The second, smaller basis set is obtained from the first one by omitting the p functions on hydrogen and is, therefore, labeled TZd. Details of these basis sets are given in ref 22. The geometry optimizations and harmonic vibrational frequencies at the MC-SCF level were performed with the program system GAMESS.[24] The ACPF[25] calculations were done using MOLPRO 96.[26] Both programs, GAMESS and MOLPRO, were modified to allow the use of our pseudopotential.

B. Calculation of Enthalpies of Atomization and Standard Enthalpies. The enthalpy of atomization, Δ_aH, is the enthalpy change on shattering a molecular system completely into its component atoms. At temperature T, the contributions to Δ_aH^T are

$$\Delta_aH^T = \Delta_aU^T = \Delta(pV) = \Delta_aU^0 + \Delta_aU(T) + \Delta(pV)$$

where $\Delta_aU(T)$ refers to the temperature dependent part of the atomization energy and Δ_aU^0 the temperature-independent part of the internal energy, which comprises the electronic atomization energy ΔE_{el} minus the zero-point vibrational energy H^0_{vib}:

$$\Delta_aU^0 = \Delta E_{el} - H^0_{vib}$$

The temperature-dependent part of the internal energy and the term $\Delta(pV)$ are calculated as detailed in our prior work.[4]

From our calculated enthalpies of atomization in conjunction with the experimental enthalpies of formation of atomic hydrogen ($\Delta_fH^{298}(H) = 218$ kJ/mol) and atomic silicon ($\Delta_fH^{298}(Si_{(g)}) = 450$ kJ/mol),[27] we calculate the enthalpies of formation of the investigated molecules.

$$\Delta_fH^{298}(\text{molecule}) = \sum_{\text{atoms}} \Delta_fH^{298}(\text{atom}) - \Delta_aH^{298}(\text{molecule})$$

Standard entropies S^{298} are the sum of the four contributions

$$S^{298}_{t+r+v+e} = S^{298}_{tr} + S^{298}_{rot} + S^{298}_{vib} + S^{298}_{elec}$$

where the translational contribution S^{298}_{tr} refers to a standard pressure of 1 bar.[27] Together with the experimental standard entropies for elementary hydrogen ($S^{298}(H_2) = 130.68$ J mol^{-1} K^{-1}) and crystalline silicon ($S^{298}(Si_{(s)}) = 18.82$ J mol^{-1} K^{-1}),[27] these standard entropies allow us to construct reaction entropies Δ_rS^{298} for the formation of a compound from the elements and thence to calculate Gibbs functions of formation Δ_fG^{298}:

$$\Delta_rS^{298}(\text{molecule}) = \sum_{\text{elements}} S^{298}(\text{element}) - S^{298}(\text{molecule})$$

$$\Delta_fG^{298} = \Delta_fH^{298} - 298.15\Delta_rS^{298}$$

The enthalpies of formation calculated according to this scheme are *uncorrected* values.

C. Calculation of Enthalpies of Formation and Determination of Enthalpy Corrections. It is well-known that incomplete basis sets and truncations of the electronic wave functions both lead to a systematic underestimation of the theoretical enthalpies of atomization, and thus, the theoretical enthalpies of formation are too large.

The use of multiconfiguration reference wave functions for the calculation of dynamical correlation effects largely eliminates the error associated with the truncated configuration space and strongly improves the theoretical enthalpy values compared with single-reference data. The use of sufficiently large AO basis sets, on the other hand, is prohibitive except for very small systems.

Owing to these technical limitations, it is still necessary to correct empirically the systematic error of theoretical techniques. This can be done by fitting the differences between experimental and theoretical enthalpies to a data model that depends on adjustable parameters. To make such a data model attractive to use, it should contain as few parameters as possible and, moreover, the parameters should be accessible to physical interpretation.

As the prime prerequisite for the success of such an empirical correction scheme, highly systematic errors in the atomization enthalpies are needed. In order to ensure this, we have adopted the philosophy of using wave functions of high quality, which should guarantee that most of the residual error is due to basis set limitations and not due to deficient descriptions of weak bonds or diradical character, spin contamination, etc. by the wave function. If the configuration space for the correlated calculation is chosen to be of comparable quality for all systems, including open shell species and species where nondynamical correlation is important, the same correction scheme can be used for all compounds of interest.

Because atomization of a molecule means breaking all bonds, the atomization enthalpy may be expressed as the sum of all bond enthalpies. An excessive enthalpy of formation is,

TABLE 1: Reference Compounds for the Correction Scheme

molecule	$\Delta_f H^\circ_{298}$ (exp) [kJ/mol]	TZdp [kJ/mol] uncorr	TZdp [kJ/mol] corr	TZd [kJ/mol] uncorr	TZd [kJ/mol] corr
SiH_4	34.3 ± 2.1	57.6	34.4	171.9	35.0
SiH_3	200.4 ± 2.5	220.3	200.0	304.4	198.2
$^1SiH_2$	272.8 ± 2.1	289.8	272.9	349.1	273.7
Si_2H_6	79.9 ± 1.3	125.5	79.9	295.6	80.0
Si_2H_5	234.0 ± 5.0	277.2	234.6	418.0	233.2
Si_3H_8	120.9 ± 4.2	188.6	120.6	414.7	120.5

therefore, equivalent to an underestimation of bond strengths. Direct usage of topological information (number of bonds) is, however, cumbersome because it cannot be derived directly from the stoichiometry, and in some systems (e.g., butterfly Si_2H_2) it is rather uncertain how the number of bonds should be counted.

Since in the systems focused on here the number of Si−H bonds exactly equals the number of H atoms and the number of Si−Si bonds is close to the number of Si atoms, we have decided to build our correction model on stoichiometric information only:

$$\Delta H_{\mathrm{corr}} = an_{\mathrm{Si}} + bn_{\mathrm{H}} + c$$

where n_{Si} is the number of Si atoms and n_{H} the number of hydrogen atoms. The three parameters a, b, and c have to be determined by least-squares fitting.

The next step is the selection of experimental enthalpies of formation to be used in the fitting procedure. For some silicon hydrides, e.g., for $^1SiH_2$ and SiH_3, different enthalpies of formation are found in the literature, called "low" and "high" values, that differ by several kJ/mol. In these cases, one has to select according to internal consistency of the resulting fit. We decided to take the three saturated silanes SiH_4, Si_2H_6, and Si_3H_8 as the core of our reference set to which we added several radical systems and, if possible, varied the experimental values. The lowest χ^2 value was found with $^1SiH_2$, SiH_3, and Si_2H_5 in addition to the three saturated silanes, using the "low" experimental enthalpies for $^1SiH_2$ and SiH_3. Table 1 contains the experimental values along with the corrected and uncorrected computed values and gives references for all experimental values. The values found for the fit parameters were for the TZdp basis 16.5356, 2.9375, and −5.1145 kJ/mol and for the TZd basis 17.0750, 30.7689, and −3.1917 kJ/mol. Not surprisingly, we got a much higher b value with basis TZd, which lacks polarization functions on the hydrogen atoms.

Whenever we used the "high" experimental enthalpies of formation for $^1SiH_2$ and SiH_3, their theoretical values were shifted toward the "low" values by the fit. We note that the differences between our theoretical and the (low) experimental enthalpies of formation of the six reference systems cited above can be fitted to the three-parametric data model with high precision.

Although there are experimental enthalpy values for disilene and silylsilylene reported in the literature, we did not include either of these two systems in the reference set, since any of it destroyed the fit, giving unreasonable χ^2 values. The fitted $\Delta_f H^{298}$ were shifted to values that were at least 10 kJ/mol higher than the recommended 275 kJ/mol for disilene.

To decide whether this large discrepancy between experimental and our fitted enthalpies is an artifact of our chosen method and basis set, we recalculated all systems that were used in the fit procedure with the CCSD[T] method using an even tempered basis. The result was in essence identical with our previous results: $^1SiH_2$ and SiH_3 were shifted toward the low experimental values and inclusion of disilene into the reference set destroyed the fit and shifted the fitted enthalpy toward high values.

On the basis of what we learned from our fit procedure, we are convinced that the experimental $\Delta_f H^{298}$ value of 275 kJ/mol for disilene is incompatible with the respective experimental enthalpies of the six reference systems and that, according to our calculations, the value is much higher.

Another possibility of deriving standard enthalpies of formation of larger systems from both quantum chemical data and experimental enthalpies of formation of smaller homologues is by means of isodesmic or homodesmotic reaction cycles. In this method, which avoids empirical corrections, reaction enthalpies of isodesmic or homodesmotic reactions building the larger molecule from its homologues are computed from *ab initio* results. If experimental heats of formation are known for all but one species, this species' $\Delta_f H^{298}$ can be obtained easily. For example, we calculate for the isodesmic reaction

$$4Si_2H_6 \rightarrow Si_5H_{12} + 3\,SiH_4 \quad \Delta_r H^{298} = 17.1 \text{ kJ/mol}$$

and the homodesmotic reaction

$$3Si_3H_8 \rightarrow Si_5H_{12} + 2\,Si_2H_6 \quad \Delta_r H^{298} = -2.4 \text{ kJ/mol}$$

reaction enthalpies of 17.1 and −2.4 kJ/mol, respectively. Using experimental $\Delta_f H^{298}$ values from Table 1, we can determine $\Delta_f H^{298}$(pentasilane) as 199.2 and 200.5 kJ/mol, respectively; our result using empirical correction is 199.7 kJ/mol. The small difference solely arises from the fact that our corrected enthalpies do not reproduce the experimental values *exactly*; the empirical correction itself does not affect enthalpies of reactions with the same number of product and educt molecules, since, in these cases, the correction terms on both sides cancel each other.

Heats of formation of cyclic silanes found by this method, however, differ by a larger amount from our empirically corrected data because isodesmic (or homodesmotic) reactions building cyclic from acyclic compounds involve a change in the number of molecules, e.g.,

$$4Si_2H_6 \rightarrow cyclo\text{-}Si_4H_8 + 4SiH_4 \quad \Delta_r H^{298} = 44.4 \text{ kJ/mol}$$

$$4Si_3H_8 \rightarrow cyclo\text{-}Si_4H_8 + 4Si_2H_6 \quad \Delta_r H^{298} = 63.4 \text{ kJ/mol}$$

Proceeding as above, we obtain a correction-free $\Delta_f H^{298}$(cyclotetrasilane) of 226.8 and 227.4 kJ/mol, respectively, which is about 4 kJ/mol lower than the result using empirical corrections. Approximately the same results will be found for other monocyclic examples.

D. Errors that Influence Theoretical $\Delta_f H$ Values. In the following sections, we shall show that our procedure for the computation of enthalpies of formation of small and medium-sized silicon hydrides performs well and allows the use of a smaller basis without serious drawbacks in the accuracy. The method relies on the use of an empirical correction. We continued to pursue our goal of developing a computational scheme that requires only a simple, minimal correction of the *ab initio* thermochemical properties. In the present work, we test a structure-independent correction scheme on a large sample of molecular systems.

To elaborate the necessity for the empirical correction step and the associated difficulties, we shall discuss error sources in the computed thermochemical properties, specifically the enthalpies, entropies, and Gibbs functions of formation, within the formalism used in this work.

TABLE 2: Thermodynamic Data for Silicon Hydrides with Up to Three Si Atoms

system	H_v^0 [kJ mol^{-1}]	H_{t+r+v}^{298} [kJ mol^{-1}]	$S_{t+r+v+e}^{298}$ [J mol^{-1} K^{-1}]	$\Delta_f H_{TZpd}^{298}$ [kJ mol^{-1}]	$\Delta_f H_{TZp}^{298}$ [kJ mol^{-1}]	$\Delta_f G^{298}$ [kJ mol^{-1}]
SiH_4	79.8	90.3	204.5	34.4	35.0	57.0
SiH_3	54.6	65.0	216.6	200.0	198.2	199.5
$^1SiH_2$	29.9	39.9	207.2	272.9	273.7	255.7
$^3SiH_2$	31.2	41.3	214.9	355.2	351.2	335.7
SiH	11.9	20.5	192.4	372.6	371.5	340.4
Si	0.0	3.7	168.0	450.0	450.0	405.5
H	0.0	3.7	114.7	218.0	218.0	203.3
H_2			130.7	0.0	0.0	0.0
Si_2H_6	125.8	141.6	283.2	79.9	80.0	123.6
Si_2H_5	102.0	117.4	291.4	234.6	233.2	256.3
$^1SiH_2{=}SiH_2$	79.8	94.0	267.9	281.2	277.6	290.5
$^3SiH_2{=}SiH_2$	78.6	93.3	282.1	396.0	392.3	401.0
$^1SiH\text{-}SiH_3$	79.4	93.9	278.5	318.8	318.9	324.9
$^3SiH\text{-}SiH_3$	81.0	95.5	289.3	373.3	371.0	376.2
$Si\text{-}SiH_3$	61.3	74.3	273.7	411.7	409.6	399.8
$SiH{=}SiH_2$	58.1	71.6	274.8	417.5	413.8	405.2
$HSi{\equiv}SiH$	36.9	49.6	260.9	464.5	459.7	436.9
$Si{=}SiH_2$	38.1	50.8	262.9	455.2	450.8	427.0
$Si(H_2)Si$	39.5	50.3	245.5	411.5	421.5	388.5
Si_3H_8	170.9	193.1	347.0	120.6	120.5	189.8
$SiH_2{-}SiH_2{-}SiH_3$	147.2	169.1	355.8	274.8	273.5	321.9
$SiH_3{-}SiH{-}SiH_3$	148.5	170.2	358.0	268.2	267.3	314.7
$^1SiH_2{=}SiH{-}SiH_3$	127.1	147.4	336.9	312.2	309.4	345.5
$^3SiH_2{=}SiH{-}SiH_3$	125.0	146.1	353.9	419.7	417.4	447.9
cyclotrisilan	128.7	147.3	301.9	281.6	277.6	325.3
$^1SiH\text{-}SiH_2\text{-}SiH_3$	124.2	145.3	344.7	360.3	360.2	391.2
$^3SiH\text{-}SiH_2\text{-}SiH_3$	126.0	147.0	354.4	414.4	412.0	442.5
$^1SiH_3\text{-}Si\text{-}SiH_3$	126.9	148.0	342.4	360.8	359.9	392.5
$^3SiH_3\text{-}Si\text{-}SiH_3$	129.2	150.0	357.2	392.5	391.7	419.7
cyclotrisilanyl	106.5	124.4	318.2	420.2	416.0	439.5
$SiH_2\text{-}SiH\text{-}SiH_2$	102.9	122.7	335.1	443.0	438.4	457.3
^{1}cyclotrisilene	86.5	103.1	298.1	468.5	465.6	474.4
^{3}cyclotrisilene	84.4	101.6	311.5	548.9	544.3	550.8
^{1}cyclotrisilan-1,1-diyl	85.2	102.8	307.4	483.1	478.5	486.2
^{3}cyclotrisilan-1,1-diyl	87.7	104.0	306.5	516.3	513.3	519.7
$SiH_3{-}Si{\equiv}SiH$	87.0	105.0	322.8	486.7	483.3	485.2
$SiH{-}SiH{-}SiH_2$	81.8	100.6	325.2	511.0	508.1	508.8

(1) For molecular geometries, the calculated equilibrium geometry influences the total energy and the vibrational frequencies. The error that is introduced by errors in the optimized geometries is usually not very large, and the systems under investigation in this work are fairly "soft", i.e., the total electronic energy is not very sensitive toward distortions near the minimum geometry. The molecular geometry does not enter our correction scheme. The consequences of inaccuracies in our molecular geometries should be negligible.

(2) The harmonic frequencies obtained by MC-SCF calculations are known to be too high by 10% for the higher (stretching) modes and not particularly reliable for the low-lying frequencies. The harmonic frequencies enter the enthalpies through the zero-point energies and, via heat capacities, through the temperature-dependent part of the internal energy. These contributions are small compared to the electronic energy, and the commonly adopted procedure of scaling the harmonic frequencies usually gives good results. The problem is more pronounced for the entropies, which depend strongly on the low-frequency part of the vibrational spectrum. Therefore, it should be noted that the absolute entropies and Gibbs function values are likely to carry a greater uncertainty than the enthalpies.

(3) The electronic atomization energy is the greatest contribution to the enthalpy of atomization. Consequently, the quality of the uncorrected thermodynamic data depends strongly on the quality of the electronic wave function used for the calculation. All attempts to improve computed thermodynamic data have to start with the reduction of the errors in the total electronic energies.

(4) Experimental values enter the final enthalpies and entropies in two different ways: (i) through the use of experimental quantities in the thermodynamic calculation in which the enthalpy of formation of silicon atoms is uncertain by ±8 kJ/mol and this uncertainty propagates into the calculated enthalpies; (ii) through experimental $\Delta_f H^{298}$ values of the molecules used for the calibration of the correction scheme.

(5) Besides faulty experimental values in the reference compounds, the correction scheme might be biased by invalid underlying assumptions, thus resulting in a correction that performs better for some systems than for others.

In order to provide theoretical error bounds for our computed thermodynamic quantities, each of these sources would have to be accounted for. This is, at the present state of affairs, not feasible.

It is well established[28] that the convergence of the AO basis set in correlated calculations is very slow. In the configuration space, MR-ACPF calculations with a full valence CAS reference are nearly converged but only feasible with a very small basis set and for the smallest molecules. Very little is known about the mixed convergence of basis set and configuration space. Any attempt for an empirical correction relies on the assumption that the residual error is well behaved and can be calibrated with a set of sensible parameters. It appears that this is the case for the basis set truncation error, but not for incompleteness in the configuration space, short of an MR-ACPF on a full valence CAS reference.

As we shall point out in the results section, we get good agreement in enthalpies calculated with the two different basis sets. We take this as a strong indication that most of the error in our uncorrected enthalpies indeed stems from the basis set truncation and is dealt successfully with by our correction scheme.

TABLE 3: Thermodynamic Data for Silicon Hydrides with Four Si Atoms

system	H_{v}^{0} [kJ mol^{-1}]	H_{t+r+v}^{298} [kJ mol^{-1}]	$S_{t+r+v+e}^{298}$ [J mol^{-1} K^{-1}]	$\Delta_f H_{TZpd}^{298}$ [kJ mol^{-1}]	$\Delta_f H_{TZp}^{298}$ [kJ mol^{-1}]	$\Delta_f G^{298}$ [kJ mol^{-1}]
tetrasilane	215.8	244.8	411.7	160.3	160.0	254.7
2-silyltrisilane	215.6	245.1	408.9	156.8	157.0	252.1
tetrasilan-1-yl	192.1	220.6	418.7	312.8	311.1	385.7
tetrasilan-2-yl	193.3	221.8	422.7	306.2	305.3	378.0
2-silyltrisilan-1-yl	191.6	220.7	421.9	312.1	310.8	384.1
2-silyltrisilan-2-yl	194.6	223.6	418.2	294.7	294.8	367.8
silylcyclotrisilane	174.4	199.8	379.0	309.9	306.5	375.2
cyclotetrasilane	175.9	199.7	351.1	231.4	228.5	305.0
^{1}tetrasil-1-ene	172.0	198.9	399.5	353.4	350.6	412.6
^{3}tetrasil-1-ene	169.9	197.7	418.2	457.2	455.0	510.8
^{1}tetrasil-2-ene	174.8	202.0	402.1	343.5	341.5	401.9
^{3}tetrasil-2-ene	171.1	198.9	413.9	450.8	449.3	505.7
^{1}2-silyltrisilene	173.6	200.8	399.7	339.1	337.6	398.3
^{3}2-silyltrisilene	171.1	199.4	422.1	446.1	445.0	498.6
^{1}tetrasilan-1,1-diyl	169.0	196.9	410.2	399.7	399.6	455.7
^{3}tetrasilan-1,1-diyl	170.9	198.6	418.0	454.4	451.9	508.1
^{1}tetrasilan-2,2-diyl	171.9	199.7	410.2	403.4	402.2	459.4
^{3}tetrasilan-2,2-diyl	174.1	201.5	427.7	432.5	431.6	483.2
^{1}2-silyltrisilan-1,1-diyl	170.3	198.2	408.2	385.9	386.4	442.5
^{3}2-silyltrisilan-1,1-diyl	170.8	198.9	416.7	447.4	445.3	501.4
1-silylcyclotrisilan-1-yl	153.6	178.3	383.4	443.0	440.1	487.5
2-silylcyclotrisilan-1-yl	152.2	177.0	381.0	449.5	445.8	494.7
cyclotrisilanylsilyl	150.4	175.4	382.2	465.1	460.2	510.0
cyclotetrasilanyl	153.9	177.1	365.1	372.8	369.5	422.8
^{1}silylidenecyclotrisilane	131.6	155.0	364.0	493.4	489.3	524.2
^{3}silylidenecyclotrisilane	129.9	154.1	380.8	593.3	589.0	619.1
^{1}1-silylcyclotrisilene	133.3	157.0	375.6	489.1	486.8	516.5
^{3}1-silylcyclotrisilene	131.4	155.4	381.5	576.1	572.6	601.7
^{1}3-silylcyclotrisilene	131.1	154.9	368.7	506.7	503.6	536.1
^{3}3-silylcyclotrisilene	130.2	154.2	380.4	580.3	576.1	606.2
^{1}cyclotetrasilene	134.3	156.0	340.6	400.0	397.1	437.8
^{3}cyclotetrasilane	131.7	154.2	358.6	519.9	515.8	552.3
^{5}tetrasila-1,3-diene	124.0	150.4	404.0	756.3	751.8	775.1
^{1}tetrasila-1,3-diene	128.3	153.3	382.3	536.1	529.1	561.5
^{3}tetrasila-1,3-diene	125.8	151.7	398.5	624.3	618.8	644.8
^{1}cyclotrisilanylsilylene	129.6	153.3	368.6	518.9	516.1	548.4
^{3}cyclotrisilanylsilylene	128.6	153.4	395.5	601.9	596.2	623.3
^{1}2-silylcyclotrisilan-1,1-diyl	131.5	155.8	375.6	507.3	503.5	534.7
^{3}2-silylcyclotrisilan-1,1-diyl	133.1	156.5	376.3	549.0	546.1	576.2
^{1}cyclotetrasilan-1,1-diyl	132.9	155.4	354.3	455.1	451.8	488.8
^{3}cyclotetrasilan-1,1-diyl	135.3	157.0	355.1	486.8	483.5	520.3
cis-^{1}cyclotetrasilan-1,3-diyl	134.6	156.1	338.5	389.0	384.7	427.4
trans-^{1}cyclotetrasilan-1,3-diyl	136.0	157.3	338.1	442.9	440.7	481.4
cis-^{3}cyclotetrasilan-1,3-diyl	131.4	154.0	357.0	518.8	515.0	551.7
trans-^{3}cyclotetrasilan-1,3-diyl	131.7	154.3	361.7	511.6	508.1	543.1
$SiH_3{-}Si{\equiv}Si{-}SiH_3$	133.2	159.1	415.4	506.1	503.9	521.5

In this paper, the focus is mainly on saturated silanes and structures derived therefrom by removal of only few hydrogen atoms. The bridged structure types that are typical for low-hydrogen compounds[29,30] were not considered; the only exception is butterfly Si_2H_2, which is included for comparison with its isomers. In trying to extend our scheme to this class of compounds, we are faced with two principal problems. (1) We have found that the best electronic energies that can be computed at a reasonable cost are obtained when using MC-SCF wave functions that correlate all formal multiple Si−Si bonds and Si lone pairs as reference for the *post-SCF* treatment. This becomes tricky to do for silicon hydrides that possess many bridging H atoms or otherwise exotic structures, as well as rather expensive with low-hydrogen compounds. (2) In the absence of experimental $\Delta_f H^{298}$ data for such molecules, correction by a least-squares fit to experimental results cannot be done. Alternatively, benchmark calculations could be used, but at the present state these are prohibited by the size of even the smallest low-hydrogen silicon hydrides.

III. Results and Discussion

This work contains thermodynamic data of 143 small and medium-sized (one to five Si atoms) silicon hydride compounds; more than half of them (silylenes, disilenes, and diradicals) have a low-lying triplet state, which was also investigated. Many species with one or two Si atoms are included for comparison with published data. The data presented for the species containing three to five Si atoms are largely new.

The bulk of the molecules described here belong to well-known compound classes, such as cyclic and acyclic silanes, silylenes, disilenes, and silyl radicals. Furthermore, we have included several cyclic diradicals (cyclotetrasilan-1,3-diyl, 1-silylcyclotetrasilan-1,3-diyl, and 2-silylcyclotetrasilan-1,3-diyl with a four-membered ring, cyclopentasilan-1,3-diyl with a five-membered ring, and the bicyclic structures bicyclo[1.1.1]-pentasilan-1,3-diyl and bicyclo[2.1.0]pentasilan-1,3-diyl). These diradicals are remarkably stable; some of them have been subject of a study on bond stretch isomerism[31] in the past.

For all of the investigated systems, we have only considered the lower-lying isomer whenever a pair of structurally similar, nearly isoenergetic choices was found. Several of the investigated systems possess isomers that differ only by a rotation about a single bond or some other minor change in the geometries. The cyclic diradicals possess two sets of isomers that differ in the relative orientation of the H or silyl substituents at the radical sites, which may differ energetically by more than

TABLE 4: Thermodynamic Data for Silicon Hydrides Si_5H_{12}, Si_4H_{11}, Si_5H_{10}, and Si_5H_9

system	H_v^0 [kJ mol^{-1}]	H_{t+r+v}^{298} [kJ mol^{-1}]	$S_{t+r+v+e}^{298}$ [J mol^{-1} K^{-1}]	$\Delta_f H_{TZpd}^{298}$ [kJ mol^{-1}]	$\Delta_f H_{TZp}^{298}$ [kJ mol^{-1}]	$\Delta_f G^{298}$ [kJ mol^{-1}]
pentasilane	260.6	296.4	476.0	199.7	199.3	319.6
2-silyltetrasilane	260.5	296.6	485.9	196.3	196.2	313.3
2,2-disilyltrisilane	260.1	297.3	464.8	188.2	189.2	311.5
pentasilan-1-yl	237.0	272.2	482.4	352.1	350.2	450.6
pentasilan-2-yl	238.1	273.4	486.1	345.7	344.6	443.1
pentasilan-3-yl	238.1	273.3	487.1	345.8	344.8	442.9
3-silyltetrasilan-1-yl	236.8	272.4	481.7	348.8	347.4	447.6
3-silyltetrasilan-2-yl	238.1	273.7	484.1	340.1	339.4	438.1
2-silyltetrasilan-2-yl	239.5	275.2	489.5	331.8	331.9	428.2
2-silyltetrasilan-1-yl	236.8	272.4	481.0	349.3	347.8	448.2
2,2-disilyltrisilan-1-yl	236.4	273.1	485.8	341.4	341.0	439.0
1,1-disilylcyclotrisilane	220.0	252.7	435.3	334.2	332.2	427.3
1,2-disilylcyclotrisilane	219.9	252.3	435.8	337.5	334.7	430.5
disilanylcyclotrisilane	219.1	251.3	443.6	349.5	345.8	440.1
silylcyclotetrasilane	221.2	252.1	423.8	264.5	261.9	361.0
cyclopentasilane	222.4	252.3	425.1	221.4	217.4	317.5
^{1}pentasil-1-ene	216.1	250.0	465.6	392.4	389.2	476.5
^{3}pentasil-1-ene	214.6	249.2	481.3	496.4	494.0	575.8
^{1}pentasil-2-ene	217.3	251.5	467.5	381.8	379.5	465.3
^{3}pentasil-2-ene	215.9	250.4	482.9	488.7	487.0	567.6
^{1}3-silyltetrasil-1-ene	216.2	250.4	463.5	385.9	383.2	470.6
^{3}3-silyltetrasil-1-ene	214.6	249.5	479.4	490.8	488.8	570.8
^{1}2-silyltetrasil-2-ene	218.8	253.3	468.5	367.9	367.1	451.0
^{3}2-silyltetrasil-2-ene	217.1	252.1	485.6	474.9	474.4	553.0
^{1}2-silyltetrasil-1-ene	220.5	254.4	461.8	379.3	377.9	464.5
^{3}2-silyltetrasil-1-ene	216.0	250.9	482.1	483.3	481.9	562.4
^{1}pentasilan-1,1-diyl	216.4	250.8	471.4	441.5	441.2	523.8
^{3}pentasilan-1,1-diyl	215.7	250.2	482.6	493.9	491.2	572.8
^{1}pentasilan-2,2-diyl	218.9	253.0	482.8	444.4	443.1	523.4
^{3}pentasilan-2,2-diyl	218.9	253.0	491.2	472.1	471.2	548.6
^{1}pentasilan-3,3-diyl	218.8	253.3	466.0	445.7	444.3	529.7
^{3}pentasilan-3,3-diyl	218.9	253.0	487.6	472.1	471.2	549.6
^{1}3-silyltetrasilan-1,1-diyl	216.3	250.9	464.9	438.4	438.3	522.7
^{3}3-silyltetrasilan-1,1-diyl	215.7	250.4	478.5	489.6	487.2	569.8
^{1}3-silyltetrasilan-2,2-diyl	219.8	254.5	476.0	431.8	431.7	512.8
^{3}3-silyltetrasilan-2,2-diyl	218.9	253.4	486.2	464.9	464.3	542.8
^{1}2-silyltetrasilan-1,1-diyl	217.1	251.5	466.2	433.2	433.7	517.1
^{3}2-silyltetrasilan-1,1-diyl	215.6	250.4	480.6	487.9	485.6	567.5
^{1}2,2-disilyltrisilan-1,1-diyl	216.9	252.5	471.6	420.5	422.2	502.8
^{3}2,2-disilyltrisilan-1,1-diyl	215.3	251.1	483.0	478.9	477.6	557.7
(1-silylcyclotrisilan-1-yl)silyl	196.1	228.4	444.4	487.5	484.0	558.4
2,2-disilylcyclotrisilan-1-yl	197.9	229.8	443.0	474.6	472.2	545.9
(2-silylcyclotrisilan-1-yl)silyl	195.8	227.9	444.7	492.8	488.6	563.6
1,2-disilylcyclotrisilan-1-yl	199.0	230.8	445.5	471.4	469.0	542.0
2,3-disilylcyclotrisilan-1-yl	197.4	229.3	443.9	479.7	476.4	550.8
2-cyclotrisilanyldisilan-1-yl	195.5	227.2	443.9	505.8	501.1	576.8
1-cyclotrisilanyldisilan-1-yl	196.6	228.4	450.1	492.1	487.8	561.3
1-disilanylcyclotrisilan-1-yl	198.5	230.0	446.5	479.9	476.9	550.2
2-disilanylcyclotrisilan-1-yl	196.9	228.4	445.0	488.6	484.6	559.3
cyclotetrasilanylsilyl	197.3	227.7	427.2	421.7	417.8	497.7
1-silylcyclotetrasilan-1-yl	200.3	230.7	434.4	398.4	396.1	472.3
2-silylcyclotetrasilan-1-yl	199.0	229.2	427.2	404.6	401.8	480.6
3-silylcyclotetrasilan-1-yl	198.9	229.2	427.7	405.4	402.5	481.2
cyclopentasilanyl	200.1	229.4	421.7	365.6	361.1	443.2

50 kJ/mol. These structures are referred to as *cis*- and *trans*-isomers of the diradical.

In the following sections we present the results and discuss the performance of the computational scheme. The focus is on general trends and irregularities that can be extracted from the data rather than the discussion of individual systems.

A. Enthalpies of Formation. Tables 2−5 contain enthalpies of formation ($\Delta_f H^{298}$, listed for both basis sets) and Gibbs enthalpies of formation ($\Delta_f G^{298}$) as well as zero-point energies (H_{vib}^0), absolute entropies ($S_{t+r+v+e}^{298}$), and nonelectronic contributions to the absolute enthalpies (H_{t+r+v}^{298}) at 298 K for all systems under investigation. Owing to the large number of compounds, electronic energies, geometry data, and vibrational frequencies have been omitted but may be requested from the authors. All enthalpies and entropies are reported to 0.1 kJ/mol and 0.1 J mol^{-1} K^{-1}, respectively, to avoid accumulation of roundoff errors when reaction enthalpies are computed. The thermodynamic data provided in these tables allow computation of the enthalpies, Gibbs functions, and equilibrium constants at 298 K for all reactions that can be constructed from the tabulated species.

Unless otherwise stated, the discussion of the $\Delta_f H^{298}$ values is based on the TZdp energies, although the $\Delta_f H^{298}$ values are rather similar for both basis sets used in this study. The largest difference is about 6 kJ/mol, and the mean difference amounts to 2.6 kJ/mol. This show that the correction scheme that we use allows us to calculate acceptable theoretical $\Delta_f H^{298}$; estimates also with the smaller basis set can be used for larger molecules. Additionally, the good agreement between the two sets of data computed with the different basis sets strongly

TABLE 5: Thermodynamic Data for Silicon Hydrides Si_5H_8, Si_5H_7, and Si_5H_6

system	H^0_v [kJ mol^{-1}]	$H^{298}_\mathrm{t+r+v}$ [kJ mol^{-1}]	$S^{298}_\mathrm{t+r+v+e}$ [J mol^{-1} K^{-1}]	$\Delta_\mathrm{f}H^{298}_\mathrm{TZpd}$ [kJ mol^{-1}]	$\Delta_\mathrm{f}H^{298}_\mathrm{TZp}$ [kJ mol^{-1}]	$\Delta_\mathrm{f}G^{298}$ [kJ mol^{-1}]
bicyclo[1.1.1]pentasilane	183.2	208.9	358.4	346.1	343.8	423.1
bicyclo[2.1.0]pentasilane	182.4	209.3	386.3	401.9	397.6	470.6
^{1}3,3-disilylcyclotrisilene	175.9	207.2	427.8	541.0	538.3	597.3
^{3}3,3-disilylcyclotrisilene	175.9	207.2	436.9	606.6	603.6	660.3
^{1}1-silyl-2-silylidenecyclotrisilane	176.8	207.3	426.0	524.9	520.9	581.8
^{3}1-silyl-2-silylidenecyclotrisilane	175.2	206.4	442.8	621.6	617.7	673.5
^{1}1,2-disilylcyclotrisilene	180.1	211.1	443.0	509.0	507.3	560.8
^{3}1,2-disilylcyclotrisilene	178.1	209.1	439.6	601.3	598.8	654.1
^{1}1,3-disilylcyclotrisilene	178.1	209.0	440.0	527.2	524.5	579.9
^{3}1,3-disilylcyclotrisilene	176.9	208.0	444.2	605.7	602.6	657.2
^{1}cyclotrisilanyldisilene	174.7	205.0	426.7	540.6	534.5	597.3
^{3}cyclotrisilanyldisilene	173.0	204.1	444.3	643.0	637.4	694.4
^{1}(disilanylidene)cyclotrisilane	177.4	207.8	429.1	526.6	522.8	582.6
^{3}(disilanylidene)cyclotrisilane	175.9	206.8	445.6	621.3	617.6	672.3
^{1}1-disilanylcyclotrisilene	178.2	208.4	439.0	526.8	524.3	579.8
^{3}1-disilanylcyclotrisilene	176.3	207.0	445.0	613.1	609.5	664.4
^{1}3-disilanylcyclotrisilene	177.3	207.8	429.9	546.7	543.1	602.4
^{3}3-disilanylcyclotrisilene	174.9	205.7	445.3	619.1	614.6	670.2
^{1}silylidenecyclotetrasilane	178.9	207.6	409.2	446.0	441.8	507.9
^{3}silylidenecyclotetrasilane	176.7	206.4	429.1	549.0	545.1	604.9
^{1}1-silylcyclotetrasilene	180.2	209.3	416.5	425.0	422.7	484.8
^{3}1-silylcyclotetrasilene	178.1	207.7	429.7	546.5	543.4	602.3
^{1}3-silylcyclotetrasilene	178.8	207.7	409.7	435.4	434.2	497.2
^{3}3-silylcyclotetrasilene	176.8	206.4	427.3	551.2	547.5	607.7
^{1}cyclopentasilene	180.4	208.1	393.2	395.2	390.3	461.9
^{3}cyclopentasilene	178.0	206.6	414.5	507.8	503.0	568.1
^{1}(1-silylcyclotrisilan-1-yl)silylene	177.0	207.8	429.5	546.7	545.4	602.5
^{3}(1-silylcyclotrisilan-1-yl)silylene	174.4	206.2	448.0	626.6	622.1	676.9
^{1}2,2-disilylcyclotrisilan-1,1-diyl	179.7	210.9	436.9	529.4	527.5	583.1
^{3}2,2-disilylcyclotrisilan-1,1-diyl	178.5	209.3	440.3	577.3	575.2	629.9
^{1}(2-silylcyclotrisilan-1-yl)silylene	176.8	207.4	429.9	548.1	546.0	603.8
^{3}(2-silylcyclotrisilan-1-yl)silylene	175.8	207.4	453.2	631.3	626.3	680.1
^{1}2,3-disilylcyclotrisilan-1,1-diyl	179.4	210.3	430.3	533.5	530.6	589.1
^{3}2,3-disilylcyclotrisilan-1,1-diyl	178.4	209.0	434.3	580.8	578.2	635.3
^{1}2-cyclotrisilanyldisilan-1,1-diyl	174.4	205.1	431.0	589.1	585.6	644.5
^{3}2-cyclotrisilanyldisilan-1,1-diyl	173.9	205.1	451.4	643.9	638.1	693.3
^{1}1-cyclotrisilanyldisilan-1,1-diyl	178.1	208.7	431.2	564.4	560.7	619.7
^{3}1-cyclotrisilanyldisilan-1,1-diyl	177.1	207.9	454.1	618.4	614.2	667.0
^{1}2-disilanylcyclotrisilan-1,1-diyl	177.8	208.7	439.6	548.7	544.8	601.5
^{3}2-disilanylcyclotrisilan-1,1-diyl	177.9	208.0	438.0	587.7	584.5	641.0
^{1}cyclotetrasilanylsilylene	177.9	206.9	411.0	488.3	486.8	549.6
^{3}cyclotetrasilanylsilylene	176.0	205.8	429.1	555.4	550.6	611.4
^{1}2-silylcyclotetrasilan-1,1-diyl	179.9	209.4	416.3	486.3	483.6	546.1
^{3}2-silylcyclotetrasilan-1,1-diyl	180.1	209.0	423.9	520.4	517.4	577.9
^{1}3-silylcyclotetrasilan-1,1-diyl	179.7	209.1	414.2	489.5	486.7	549.9
^{3}3-silylcyclotetrasilan-1,1-diyl	180.4	209.2	422.8	518.0	515.3	575.8
^{1}cyclopentasilan-1,1-diyl	180.4	208.9	400.8	449.9	445.5	514.3
^{3}cyclopentasilan-1,1-diyl	181.6	209.2	403.3	482.2	478.5	545.8
cis-^{1}1-silylcyclotetrasilan-1,3-diyl	182.5	211.2	406.8	423.3	420.6	485.9
trans-^{1}1-silylcyclotetrasilan-1,3-diyl	181.8	210.4	405.7	479.1	477.7	542.1
cis-^{3}1-silylcyclotetrasilan-1,3-diyl	178.0	207.7	431.5	542.8	540.2	598.1
trans-^{3}1-silylcyclotetrasilan-1,3-diyl	178.2	207.9	433.6	536.6	534.2	591.3
cis-^{1}2-silylcyclotetrasilan-1,3-diyl	181.3	210.0	407.8	422.6	418.9	484.9
trans-^{1}2-silylcyclotetrasilan-1,3-diyl	180.8	209.4	407.6	478.2	476.3	540.5
cis-^{3}2-silylcyclotetrasilan-1,3-diyl	176.7	206.3	424.5	548.4	545.1	605.8
trans-^{3}2-silylcyclotetrasilan-1,3-diyl	178.2	207.9	429.4	546.7	543.6	602.6
cis-^{1}cyclopentasilan-1,3-diyl	180.4	208.7	405.4	456.1	451.6	519.2
trans-^{1}cyclopentasilan-1,3-diyl	179.9	208.3	396.5	498.8	495.0	564.5
cis-^{3}cyclopentasilan-1,3-diyl	177.5	206.3	440.0	507.6	502.9	560.3
trans-^{3}cyclopentasilan-1,3-diyl	177.7	206.5	416.5	505.0	500.3	564.8
bicyclo[1.1.1]pentasilan-1-yl	162.1	187.2	367.4	480.5	477.7	535.4
bicyclo[1.1.1]pentasilan-2-yl	160.9	186.0	375.9	494.2	491.2	546.5
bicyclo[2.1.0]pentasilan-5-yl	160.2	186.3	388.2	547.0	542.6	595.7
bicyclo[2.1.0]pentasilan-1-yl	161.7	187.8	389.2	529.5	525.2	577.9
bicyclo[2.1.0]pentasilan-2-yl	159.6	186.0	389.4	544.7	539.7	593.0
^{1}bicyclo[2.1.0]pentasil-2-ene	137.9	163.7	379.9	590.0	584.8	621.7
^{3}bicyclo[2.1.0]pentasil-2-ene	137.5	163.2	388.1	686.2	680.9	715.4
^{1}bicyclo[1.1.1]pentasilan-2,2-diyl	140.5	165.1	364.3	534.0	531.3	570.4
^{3}bicyclo[1.1.1]pentasilan-2,2-diyl	141.2	165.3	367.9	634.2	630.8	669.4
^{1}bicyclo[2.1.0]pentasilan-5,5-diyl	140.4	165.8	381.9	563.3	559.0	594.4
^{3}bicyclo[2.1.0]pentasilan-5,5-diyl	140.1	165.4	386.7	649.0	644.4	678.7
^{1}bicyclo[2.1.0]pentasilan-2,2-diyl	139.2	164.8	379.6	593.5	589.0	625.3
^{3}bicyclo[2.1.0]pentasilan-2,2-diyl	140.4	165.5	384.6	662.1	657.5	692.4
^{1}bicyclo[1.1.1]pentasilan-1,3-diyl	142.2	166.6	352.6	434.2	430.2	474.0
^{3}bicyclo[1.1.1]pentasilan-1,3-diyl	141.9	166.3	362.0	685.1	682.2	722.1

TABLE 5: (Continued)

system	H_{v}^{0} [kJ mol^{-1}]	$H_{\mathrm{t+r+v}}^{298}$ [kJ mol^{-1}]	$S_{\mathrm{t+r+v+e}}^{298}$ [J mol^{-1} K^{-1}]	$\Delta_f H_{\mathrm{TZpd}}^{298}$ [kJ mol^{-1}]	$\Delta_f H_{\mathrm{TZp}}^{298}$ [kJ mol^{-1}]	$\Delta_f G^{298}$ [kJ mol^{-1}]
cis-ax-^{1}bicyclo[1.1.1]pentasilan-2,4-diyl	139.9	164.1	357.9	509.7	505.2	548.0
cis-eq-^{1}bicyclo[1.1.1]pentasilan-2,4-diyl	139.0	163.3	359.7	633.7	629.7	671.4
trans-^{1}bicyclo[1.1.1]pentasilan-2,4-diyl	138.1	162.8	367.5	639.5	636.4	674.9
cis-ax-^{3}bicyclo[1.1.1]pentasilan-2,4-diyl	138.6	163.2	371.1	675.9	672.0	710.2
cis-eq-^{3}bicyclo[1.1.1]pentasilan-2,4-diyl	138.5	163.0	370.5	643.2	639.5	677.7
trans-^{3}bicyclo[1.1.1]pentasilan-2,4-diyl	138.7	163.1	375.5	640.3	636.5	673.3
cis-^{1}bicyclo[2.1.0]pentasilan-1,3-diyl	141.3	166.1	371.9	575.0	571.5	609.1
trans-^{1}bicyclo[2.1.0]pentasilan-1,3-diyl	139.7	165.3	379.1	557.0	552.1	588.9
cis-^{3}bicyclo[2.1.0]pentasilan-1,3-diyl	138.1	163.7	388.3	665.3	660.6	694.5
trans-^{3}bicyclo[2.1.0]pentasilan-1,3-diyl	137.7	163.5	391.2	681.0	676.2	709.3

TABLE 6: Comparison of Our Calculated Enthalpies of Formation with Experimental as Well as Theoretical Values

molecule[d]	$\Delta_f H_{298}^{0}$ (exp) [kJ mol^{-1}]	ref	this work	other theory
SiH_4*	34.3 ± 3.1	8	34.4	34.3,[a] 28.2[b]
SiH_3*	200.4 ± 2.5	16		198.4[a]
	202.9 ± 6.7	11	200.0	193.7/199.9[b]
$^1SiH_2$*	272.8 ± 2.1	18	272.9	290.6[a]
	274.1 ± 4.2	17		266.7/272.7[b]
$^3SiH_2$	362.6 ± 3.0	10	355.2	355.1/361.3[b]
SiH	376.6 ± 7.1	12	372.6	380.8,[a] 368.8/374.9[b]
Si_2H_6*	79.7 ± 1.3	8	79.9	80.0[a]
Si_2H_5*	234.0 ± 5.0	20	234.6	231.8,[a] 223.4[c]
$^1SiH{-}SiH_3$	314.0 ± 8.0	15	318.8	313.4,[a] 300.0[c]
	309.9/320.1	12		
$^1SiH_2{=}SiH_2$	275.0 ± 4.0	15	281.2	263.2,[a] 269.9[c]
Si_3H_8*	120.9 ± 4.2	9	120.6	118.7[a]

[a] Reference 2. [b] Reference 7, lower/upper limit. [c] Reference 5. [d] Reference molecules are labeled with an asterisk.

supports the assumption that the residual error in the uncorrected enthalpies can be successfully gotten rid of by our correction scheme.

In the following paragraphs, we shall attempt to discuss our results in the context of other comparable work. A fairly exhaustive discussion of related papers until 1989 can be found in ref 4. Schlegel[32] reviewed the literature until 1992, and the work by Grev and Schaefer[7] also contains a number of references pertinent to very small systems. Besides the JANAF tables, we frequently consulted the experimental studies by Berkowitz, Green, Cho, and Ruščić,[13] Ruščić and Berkowitz,[14,15] and Boo and Armentrout,[11,12] and Moffat et al.[19] as well as the theoretical studies by Ho, Coltrin, Binkley, and Melius[1−3] and by Curtiss and co-workers.[5]

Table 6 compiles some $\Delta_f H^{298}$ values from a small selection of different experimental and theoretical work for comparison. Enthalpies that were reported at 0 K in the original work have been converted to 298 K using the conversions of ref 11.

Since our theoretical enthalpies of formation were calculated by using experimental values of selected reference compounds, it is not surprising that the agreement between experiment and theory for these molecules is excellent.

The comparison with other theoretical values is rather satisfactory, keeping in mind the different methodologies these values were derived with. Ho and Melius[2] used a bond energy correction scheme based solely on the energies obtained at different levels of Møller−Plesset perturbation theory without any reference to experimental heats of formation. Curtiss et al.[5] used the G2 method energies, which are corrected for basis set incompleteness and missing correlation energy contributions, and Grev and Schaefer[7] obtained their energies, which were corrected for contraction errors, with different basis sets and coupled cluster methods. Finally, these authors added experimental spin−orbit energy contributions to the respective enthalpies of formation. It is, therefore, not surprising that respective theoretical enthalpies may differ. All these methods, however, cannot be used for the large systems that are the central topic of this work.

Grev and Schaefer pointed out that the experimental enthalpies of formation of Si and SiH_4 are incompatible; the sources of this discrepancy are, however, not yet clear. Since our data depend on both these experimental values, they may be systematically biased; but note that our computed reaction enthalpies do not depend on the experimental $\Delta_f H^{298}$ of silicon atoms.

Therefore, we should like to point out that our goal was not to add an additional set of highly accurat enthalpies for very small systems but to test and demonstrate the accuracy attainable for species containing three to five Si atoms in comparison with their smaller analogues.

For the larger systems there are no experimental and almost no theoretical values in the literature apart from those that were obtained by increment extrapolation[33] from calculations on smaller species. The good agreement between the two basis sets (considering that the correction is as high as 100 kJ/mol (TZdp) and 380 kJ/mol (TZd) for Si_5H_{10}, for example) serves as an indication of the reliability of the data.

The large number of systems and corresponding data presented here allow us to study various aspects of thermochemical interest such as increment rules, trends in bond dissociation energies, and substituent effects. The following observations can be extracted from our data.

(1) Branched-chain silanes are more stable than their straight-chain analogues. This is a small energetic effect. Silanes containing a tertiary Si center are very slightly (3 kJ/mol) stabilized relative to the straight-chain isomers, e.g., tetrasilane and 2-silyltrisilane (Table 3) or pentasilane and 2-silyltetrasilane (Table 4). Silanes with a quarternary Si center are stabilized by an additional 8 kJ/mol (2,2-disilyltrisilane vs 2-silyltetrasilane in Table 4). This effect can also be seen in the $\Delta_f H^{298}$ values of silyl radicals and silylenes; isomers containing tertiary and quarternary Si centers are stabilized roughly by the same amounts relative to straight-chain isomers as is the case for silanes.

(2) Small rings are energetically expensive. This strong effect becomes evident whenever isomers with different ring sizes exist. It may be most conveniently demonstrated using the cyclic Si_5H_{10} isomers in Table 4. The three-membered ring species are at least 60 kJ/mol less stable than the four-membered ring, which in turn is more than 40 kJ/mol less favored than the five-membered ring. The much smaller energetic differences among the three-membered rings may be attributed to the different number of tertiary and quarternary Si atoms that are members of the ring (see the point above).

(3) Silyl centers are stabilized by silyl substitution. Evidence for this can be found by direct comparison of the $\Delta_f H^{298}$ values of isomers. The silyl radicals 3-silyltetrasilan-1-yl, 3-silyltet-

rasilan-2-yl, and 2-silyltetrasilan-2-yl (Table 4) exemplify the proposed trend for silyl radicals. The series consists of three isomers, including one of each type: primary, secondary, and tertiary silyl radical with no additional side chains. The secondary radical is stabilized by 9 kJ/mol, the tertiary one by an additional 8 kJ/mol. The stabilizing effect of silyl substituents on a silyl center can also be seen in Si−H bond dissociation enthalpies (see the corresponding section).

(4) Triplet silylenes are also stabilized by silyl substitution at the divalent Si atom, while the substitution has a weak destabilizing effect on singlet silylenes. The isomer groups tetrasilan-1,1-diyl and tetrasilan-2,2-diyl (Table 3) as well as pentasilan-1,1-diyl, pentasilan-2,2-diyl, and pentasilan-3,3-diyl (Table 4) are almost isoenergetic in their singlet states, yet the small destabilization of about 2 kJ/mol is systematic and found for most pairs of primary and secondary silylenes. In their triplet states, secondary silylenes are seen to be stabilized by 20 kJ/mol relative to the primary ones. More evidence for these effects is found in the increment analysis and the H_2 elimination reaction enthalpies, as will be seen below.

(5) Singlet silylenes are stabilized by tertiary and quarternary Si centers in a position α to the divalent Si atom. This effect is particularly strong if the Si center in the α position belongs to a three-membered ring. Consider the two silylenes 3-silyltetrasilan-1,1-diyl and 3-silyltetrasilan-2,2-diyl (Table 4). The extra stabilization of nearly 8 kJ/mol favoring the secondary silylene can be attributed to the side chain in a position α to the divalent Si atom. Since the triplet is unaffected by the presence or absence of the side chain, the singlet state's extra stabilization is also reflected by the increased singlet−triplet splitting. Similar observations can be made with 2-silyltrisilan-1,1-diyl (Table 3), 2-silyltetrasilan-1,1-diyl, or 2,2-disilyltrisilan-1,1-diyl (both in Table 4). It is worth noting that a three-membered ring as a substituent in the α position has a much stronger stabilizing effect than a simple branching point. In the system cyclotrisilanylsilylene (Table 3), we studied the torsion potential of the rotation that the silylene group describes with respect to the three-membered ring. We found the potential to be nearly flat on the triplet surface and to display a preference of approximately 30 kJ/mol for the synplanar equilibrium geometry on the singlet surface. Resonance mixing of the lone-pair orbital on the divalent Si and a bonding MO of the three-membered ring accounts for the extra stabilization that is provided by this particular arrangement. More information on these trends can be derived from singlet−triplet splittings and H_2 elimination enthalpies, where reactions yielding related silylenes with and without substituents in the α position can be studied (*vide infra*).

(6) Cyclic silylenes (where the divalent Si atom is member of a ring) are stabilized, singlet and triplet alike. Since all cyclic silylenes with the exception of cyclotrisilan-1,1-diyl display a tertiary or quarternary Si atom in the position α to the divalent Si atom, this effect is in part obscured by the former and is more easily detected by studying H_2 elimination enthalpies. Comparing the enthalpies of formation for the three isomers 2-cyclotrisilanyldisilan-1,1-diyl, 1-cyclotrisilanyldisilan-1,1-diyl, and 2-disilanylcyclotrisilan-1,1-diyl, we should expect 1-cyclotrisilanyldisilan-1,1-diyl to be the most stable compound because it is stabilized according to the discussion above. Table 5 indeed shows that 1-cyclotrisilanyldisilan-1,1-diyl is preferred by about 25 kJ/mol to 2-cyclotrisilanyldisilan-1,1-diyl, yet the cyclic silylene 2-disilanylcyclotrisilan-1,1-diyl is even 16 kJ/mol more stable. Thence, it can be inferred that the stabilization of silylenes by a cyclic environment of the divalent Si atom exceeds the stabilization due to the three-membered rings in the position α to the divalent Si atom. Of the two secondary triplet silylenes 1-cyclotrisilanyldisilan-1,1-diyl and 2-disilanylcyclotrisilan-1,1-diyl, the latter is about 30 kJ/mol more stable. Thus, we can infer that the stabilization of silylenes in three-membered rings affects the singlet as well as the triplet states.

(7) Disilenes are stabilized by silyl substitution at the double bond. This is suggested by the difference of 11 kJ/mol in the respective $\Delta_f H^{298}$ values of tetrasil-1-ene and tetrasil-2-ene (Table 3). The progression is essentially the same for singlet and triplet states. Similar observations can be made for the pentasilenes Si_5H_{10} in Table 4. Additional support for these conclusions comes from the H_2 elimination enthalpies and Si−Si bond dissociation enthalpies of disilenes with varying degrees of substitution, as will be demonstrated in the appropriate sections.

(8) The formal double bond inside a three-membered ring is not favored. This trend can be studied in detail only by considering H_2 elimination enthalpies of silanes (*vide infra*). Table 5, however, allows us to compare cyclotrisilanyldisilene with 1-disilanylcyclotrisilene. Though the latter is more highly substituted, it is less stable than the former. The destabilization amounts to about 15 kJ/mol.

(9) The *cis* forms of the cyclic diradicals are remarkably stable compared with their silylene and disilene isomers. For example, the cyclic Si_4H_6 system in Table 3 exhibits the following $\Delta_f H^{298}$ values for the isomeric silylene, disilene, and diradical: cyclotetrasilan-1,1-diyl, 455 kJ/mol; cyclotetrasilene, 400 kJ/mol; cyclotetrasilan-1,3-diyl, 389 kJ/mol. The diradical turns out to be the most stable Si_4H_6 isomer found in this study. Increasing the ring size, however, decreases the stability of this type of diradical drastically. Table 5 lists the silyl substituted four-membered ring diradicals 1-silylcyclotetrasilan-1,3-diyl and 2-silylcyclotetrasilan-1,3-diyl and the five-membered ring species cyclopentasilan-1,3-diyl. Although the trivalent Si atoms display different degrees of substitution, the former two are nearly isoenergetic. The latter is significantly higher in energy, which is all the more remarkable because in most other substance classes larger rings are preferred to smaller ones. The stabilization of diradicals vs silylenes is even more pronounced in some bicyclic species. The bicyclic diradical bicyclo[1.1.1]pentasilan-1,3-diyl is about 100 kJ/mol more stable than the bicyclic silylene bicyclo[1.1.1]pentasilan-2,2-diyl (both to be found in Table 5). More information about the stabilities of 1,3 diradicals may be obtained from the section on H_2 elimination reactions.

B. Increment Rules. The total sample of data is now large enough for the straight-chain silanes, primary silyl radicals, and primary silylenes to analyze the homologous series and to revisit increment rules.

In Figure 1, our theoretical $\Delta_f H^{298}$ values for the Si_nH_{2n+2}, Si_nH_{2n+1}, and Si_nH_{2n} straight-chain systems are plotted as functions of the number n of silicon atoms. Two conclusions can be derived from examining the data. (1) There is good correlation for $n \geq 2$, indicating that the increase in the enthalpy of formation of these homologous series is linear in the number of additional SiH_2 groups. The standard deviation for all regression lines, based on the values for $n = 2-5$, is 1.1 kJ/mol. The slopes are 39.8, 38.9, 40.6, and 40.0 kJ/mol for the silanes, radicals, and singlet and triplet silylenes, respectively. (2) The members of the series with one Si atom are not on the regression lines. The relative stabilities of singlet and triplet silylene are known[4] to be affected by silyl substitution. This holds to a lesser extent also for silanes and radicals. The first members of the series deviate from the best fit line by −6 kJ/mol (monosilane), +4 kJ/mol (silyl), −5 kJ/mol (singlet

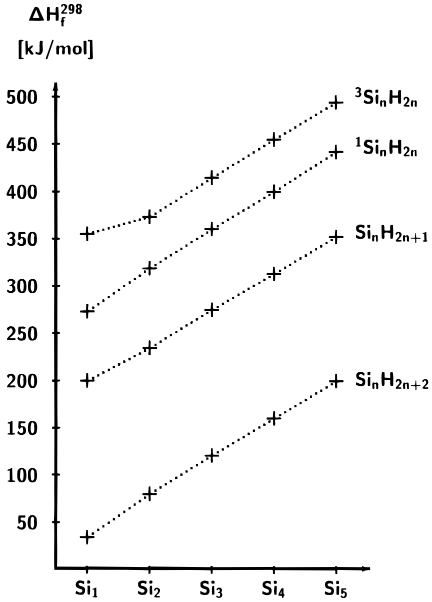


Figure 1. Enthalpies of formation for straight-chain systems.

silylene), and +22 kJ/mol (triplet silylene), always a statistically significant deviation. Consequently, extrapolated heats of formation for larger silicon hydrides species must not be calculated using the monosilane derivatives. The increments of approximately 40 kJ/mol found here agree quite well with the ones proposed in previous work.[4]

The same analysis can be performed for a few other homologous series. We find the same increment of approximately 40 kJ/mol per SiH_2 group for secondary radicals and secondary silylenes as well. Interesting, the increment between SiH and $SiSiH_3$ (39 kJ/mol) seems to indicate that there is neither a stabilizing nor a destabilizing effect of silyl groups on silylidynes.

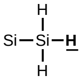
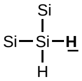
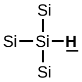
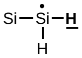
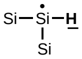
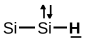
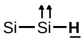
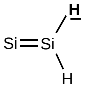
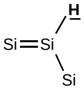
The available data allows us to develop a more general increment scheme by which we are able to reproduce our calculated enthalpies of formation for all 68 acyclic silanes, silyl radicals, silylenes, and disilenes (singlet and triplet states) with an average root-mean-square error of about 1.6 kJ/mol. This scheme consists of 16 parameters (enthalpies of formation for Si_2 species and increments; see Table 7), which were determined such that silanes are reproduced best at the cost of accuracy for the triplet species. The worst case is triplet disilene (7.2 kJ/mol too low), but only three other species are wrong by more than 3 kJ/mol.

From the discussion above, it is clear that the enthalpies of all species with one Si atom must be excluded from the increment scheme. Since the enthalpies of formation for all species with two Si atoms were included in data from which the increments were calculated by a least-squares fitting, their $\Delta_f H^{298}$ values, used as base values for the increment scheme, differ slightly from our calculated enthalpies.

Table 7 gives both the increments and rules on how to obtain estimated enthalpies of formation for any acyclic silane, radical, silylene or disilene. Starting from the corresponding Si_2 structure, increments for the substitution of H by SiH_3 are to be summed up. An additional correction is necessary for singlet silylenes with a side chain in position α to the divalent Si atom. The correction is to be applied only once even in case of two side chains (2,2-disilyltrisilan-1,1-diyl). Still with this correction, branched singlet silylenes are reproduced less accurately than other species.

C. Reaction Enthalpies. From our theoretical enthalpies of formation we can compute and analyze many reaction enthalpies. These reaction enthalpies reveal a number of interesting trends concerning the stability of individual bonds and the thermodynamics of elementary reactions that may be relevant in the CVD of silanes.

TABLE 7: Incremental Extrapolation Scheme for the Prediction of the Heats of Formation of Acyclic Silicon Hydrides

Base Values for Si_2 Species [kJ/mol]			
$SiH_3{-}SiH_3$	80.5	$SiH_3{-}SiH_2$	234.0
$^1SiH_3{-}SiH$	320.7	$^3SiH_3{-}SiH$	373.2
$^1SiH_2{=}SiH_2$	282.1	$^3SiH_2{=}SiH_2$	388.8
Increments for Substitution of H by SiH_3			
 $\mathrm{Si{-}\overset{H}{\underset{H}{Si}}{-}\underline{H}}$	+40.0	 $\mathrm{Si{-}\overset{Si}{\underset{H}{Si}}{-}\underline{H}}$	+35.8
 $\mathrm{Si{-}\overset{Si}{\underset{Si}{Si}}{-}\underline{H}}$	+31.6		
 $\mathrm{Si{-}\overset{\bullet}{\underset{H}{Si}}{-}\underline{H}}$	+31.8	 $\mathrm{Si{-}\overset{\bullet}{\underset{Si}{Si}}{-}\underline{H}}$	+27.7
 $\mathrm{Si{-}\overset{\uparrow\downarrow}{Si}{-}\underline{H}}$	+42.9[a]	 $\mathrm{Si{-}\overset{\uparrow\uparrow}{Si}{-}\underline{H}}$	+18.5
 $\mathrm{Si{=}Si(\underline{H})(H)}$	+30.2	 $\mathrm{Si{=}Si(\underline{H})(Si)}$	+26.0

[a] For singlet silylenes with a side chain in position α to the divalent Si atom, subtract 7.1 kJ/mol

We shall focus on the following reaction types: elimination of H_2 from silanes or cyclosilanes, yielding silylenes, disilenes, and cyclic diradicals; cleavage of Si−H bonds in silanes and silyl radicals; dissociation of Si−Si bond in silanes, disilenes, disilynes, and silyl radicals. To save space, no tables with reaction enthalpies are given in this paper, since these can be derived from the tabulated $\Delta_f H^{298}$ values rather easily. Full tables and other supporting material can be requested from the authors and are also made available on the WEB page http://bkfug.kfunigraz.ac.at/~katzer/work.html.

H_2 Elimination. Eliminations of H_2 from silanes may occur in the 1,1 position, in the 1,2 position, and in the 1,3 position. 1,1 elimination yields silylenes (an important elementary reaction in CVD); elimination in the 1,2 position results in disilene formation. Elimination in the 1,3 position of acyclic silanes results in ring closure, yielding cyclic silanes. 1,3 elimination from four-membered rings yields cyclic diradicals; formation of bicyclic silanes cannot occur, since the resulting bicyclic skeletons of the [1.1.0]-type do not correspond to equilibrium structures.[31]

1,1 elimination of H_2 results in the formation of singlet silylenes. The corresponding calculated enthalpies cover a range from 161 to 246 kJ/mol. Although 1,1 eliminations are more endothermic than the 1,2 and 1,3 eliminations discussed below, they are of chief importance in CVD processes because of comparatively low activation energies and, therefore, of high importance for the modeling of CVD processes.

Primary and secondary acyclic silylenes (without side chains or rings in α position) are formed at an expense of 238−246 kJ/mol. Primary and secondary acyclic silylenes with side chains in the α position require 229−236 kJ/mol, with a four-membered ring in the α position 223 kJ/mol, and with a three-membered ring in the α position 209−215 kJ/mol. Silylenes whose divalent Si atom is part of a three-membered ring are formed even more easily (195−201 kJ/mol), whereas the four-membered ring silylenes exhibit a much higher elimination enthalpy of 222−228 kJ/mol. Some examples illustrating these

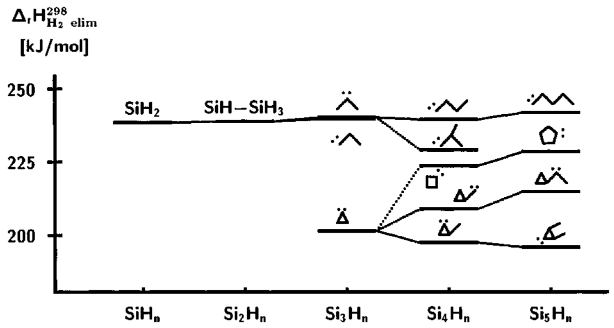


Figure 2. 1,1 H_2 elimination enthalpies from cyclic and acyclic silanes.

trends are given in Figure 2. The bicyclic silylenes are formed at the lowest expense (161−192 kJ/mol).

These reactions enthalpies corroborate the finding that three-membered rings in the α position strongly stabilize silylenes and that tertiary and quaternary Si centers in the α position have some stabilizing effect as well (compared with a straight silyl chain on the divalent center, where the α Si can be primary or secondary).

Cyclic silylenes are stabilized even more. Note that, apart from the simplest case of cyclotrisilan-1,1-diyl, all three-membered ring silylenes benefit from both the ring itself and from the side chain(s), which act like an α-substituent. Four-membered rings turn out to be less stabilizing than three-membered rings.

The following examples illustrate the above-mentioned trend. A primary silylene with a three-membered ring in the *β* position (2-cyclotrisilanyldisilan-1,1-diyl) is formed at the expense of 240 kJ/mol from the parent silane, which falls exactly into the range found for straight chain silylenes. Silylenes with the three-ring in the α position, e.g., the primary (2-silylcyclotrisilan-1-yl)-silylene or the secondary 1-cyclotrisilanyldisilan-1,1-diyl, require only 211 and 215 kJ/mol, respectively. The difference of about 30 kJ/mol to straight chain silylenes corresponds to the stabilization of the lone pair by the three-membered ring in the α position, as mentioned in section III.A.

The formation of cyclopentasilan-1,1-diyl requires 229 kJ/mol, the three four-membered ring silylenes (cyclotetrasilan-1,1-diyl, 2-silylcyclotetrasilan-1,1-diyl, and 3-silylcyclotetrasilan-1,1-diyl) require 222−225 kJ/mol, and the three-membered ring silylenes range from 195 to 202 kJ/mol. These values fall below the ones that are found for the formation of acyclic secondary silylenes (244−250 kJ/mol) and show the stabilization of cyclic silylenes relative to acyclic ones.

1,1 elimination from bicyclic silanes is even less endothermic than elimination from monocyclic silanes. All the resulting silylenes gain an extra stabilization from the ring itself (especially bicyclo[2.1.0]pentasilan-5,5-diyl whose divalent Si atom is part of a three-membered ring), and they also benefit from the bridge-heads adjacent to the divalent Si atoms (especially bicyclo[2.1.0]pentasilan-5,5-diyl and bicyclo[1.1.1]-pentasilan-2,2-diyl with two bridge-heads in the α,α′ positions). Thence, the elimination enthalpies to these silylenes are the lowest 1,1 elimination enthalpies from silanes found in this study (161−192 kJ/mol).

Only two examples of disilenes undergoing 1,1 elimination can be constructed from our data. An energy of 174 kJ/mol is required to remove H_2 from disilene, which is 65 kJ/mol lower than the elimination enthalpy found for disilane, and shows that the Si−H bond involving a trivalent Si atom is weaker than Si−H bonds in silanes. Similarly, Si−H bonds adjacent to the formal double bond are weakened by about 40 kJ/mol, as shown by the 1,1 elimination enthalpy from trisilene to SiH−SiH−SiH_2 (199 kJ/mol).

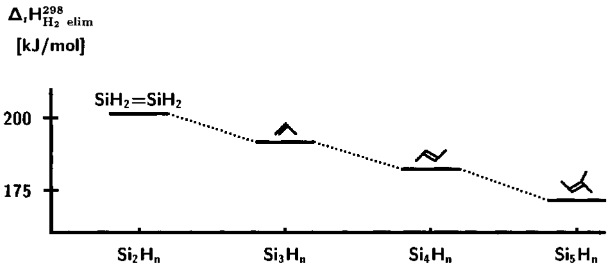


Figure 3. 1,2 H_2 elimination enthalpies from acyclic silanes.

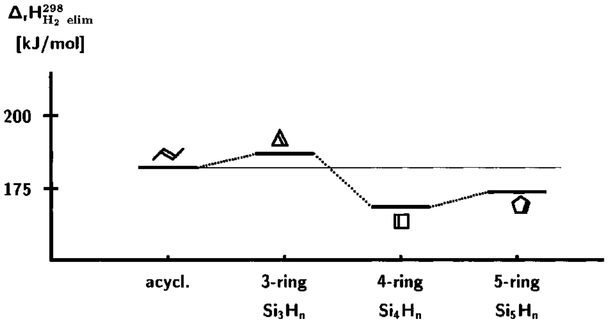


Figure 4. 1,2 H_2 elimination enthalpies from cyclic silanes with different ring sizes (in comparison with the 1,2 elimination enthalpy from tetrasilane).

The reaction enthalpies for the 1,2 elimination of H_2 from silanes span a total range from 159 to 201 kJ/mol. This class of reactions also exhibits interesting trends, since the propensity for the formation of acyclic disilenes clearly depends upon the number of substituents on the double bond; the formation of disilene, with no silyl substituent, requires 201 kJ/mol. The disilenes with one substituent require 190−193 kJ/mol, those with two substituents 182−183 kJ/mol, and the only example with three substituents is formed at an expense of 172 kJ/mol (Figure 3). The decrease in the H_2 elimination enthalpy with increasing number of substituents suggests a stabilizing effect from the silyl substituents on the double bond, where the degree of stabilization appears to depend only on the total number of substituents, and not on their position and size. This effect is also reflected in the corresponding Si═Si bond dissociation enthalpies and will be discussed there as well.

1,2 elimination from cyclic silanes reveals interesting stabilization trends for cyclic disilenes (Figure 4). Comparing the elimination enthalpies for the reactions forming the disilenes tetrasil-2-ene, cyclotrisilene, cyclotetrasilene, and cyclopentasilene (182, 187, 169, and 174 kJ/mol, respectively), we learn that the production of three-membered ring disilenes is slightly disfavored, but four- and (to a lesser degree) five-membered ring disilenes are more stable than their open-chain analogues. The stabilizing effect of the four-membered ring amounts to about 13 kJ/mol.

From the series of reaction enthalpies 187, 197, and 207 kJ/mol for the elimination reactions leading to cyclotrisilene, 3-silylcyclotrisilene, and 3,3-disilylcyclotrisilene, it may be learned that substitution at the tetravalent Si atom in an unsaturated three-membered ring decreases the stability of the respective disilene considerably (Figure 5). Although these disilenes differ neither in the number of substituents at the formal double bond nor in the ring size, the H_2 elimination reaction enthalpies increase by 10 kJ/mol per substituent at the *tetravalent* Si atom. This trend is less pronounced in four-membered rings.

In bicyclic silanes, 1,2 elimination leads to disilenes only if no bridge-head atoms are involved in the resultant double bond; otherwise, valence isomers are formed (bicyclic 1,2 diradicals,

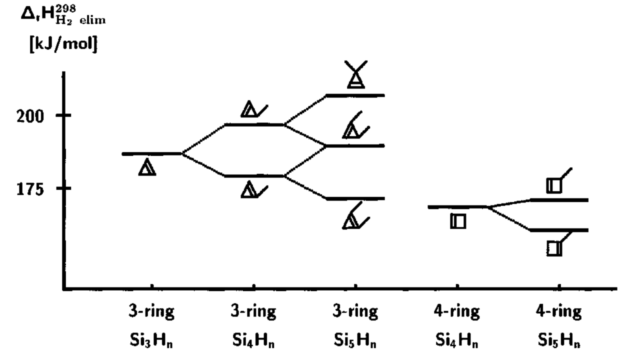


Figure 5. 1,2 H_2 elimination enthalpies from three-membered and four-membered ring cyclosilanes.

monocyclic disilenes with an additional silylene function or the like). Therefore, the only example of a bicyclic disilene is bicyclo[2.1.0]pentasil-2-ene, whose singlet state features a C_s structure. Probably owing to less conformational freedom in the bicyclic Si backbone, the compound is formed at a rather high expense (183 kJ/mol).

A few 1,2 elimination reactions from disilenes may also be discussed. The formation of the “conjugated” tetrasila-1,3-diene from tetrasil-1-ene via 1,2 elimination is achieved by 187 kJ/mol. This is not much different from the elimination enthalpies of open-chain silanes to disilenes discussed above, indicating that there is only small stabilizing interaction between the two formal double bonds.

By H_2 elimination from the two trivalent Si atoms in a disilene, one arrives at disilynes: disilyne $HSi\equiv SiH$ is formed at the expense of 183 kJ/mol. Silyl substitution facilitates this reaction by about 10 kJ/mol per silyl substituent, indicating a strong stabilization of the formal triple bond by the SiH_3 groups.

As a general rule, hydrogen elimination is most endothermic in saturated silanes. As soon as one or two hydrogen atoms have been removed from a silane, further elimination becomes thermodynamically more easy. For example, 1,2 elimination from trisilane costs 192 kJ/mol, but from trisilan-1-yl ($SiH_2-SiH_2-SiH_3$) and trisilan-1,1-ylen ($SiH-SiH_2-SiH_3$), the elimination enthalpies are significantly lower; the allyl analogue radical $SiH_2-SiH-SiH_2$ (C_s minimum structure) is formed at the expense of 168 kJ/mol, and formation of the unsaturated silylene $SiH-SiH-SiH_2$ costs only 151 kJ/mol, indicating a stabilizing interaction between the unsaturated (tri- or divalent) center and the formal double bond. This is further corroborated by comparing 1,1 elimination enthalpies from trisilane (formation of the saturated silylene $SiH-SiH_2-SiH_3$, 240 kJ/mol) and from trisilene (whence again the unsaturated silylene $SiH-SiH-SiH_2$ is obtained, 199 kJ/mol).

The 1,3 elimination of H_2 from silanes results in formation of either cyclic diradicals (from four- or five-membered rings or bicyclic silanes) or in cyclization to three-membered ring compounds.

Formation of the more stable *cis* form of the four-membered ring diradicals requires only 158−159 kJ/mol. The effect of substitution at the radical sites is negligible. These diradicals are bond stretch isomers of the (nonexistent) bicyclo[1.1.0]-tetrasilane. The transannular distance between the two radical sites (2.85−2.90 Å) is considerably shorter than the transannular distance in cyclotetrasilane (3.60 Å), indicating a weak bonding interaction between these atoms. The *trans* forms (211−215 kJ/mol) of the four-membered ring diradicals are about 55 kJ/mol less favored than the *cis* forms. Their transannular Si−Si distances are slightly longer (2.87−2.97 Å) than in the respective *cis*-isomers.

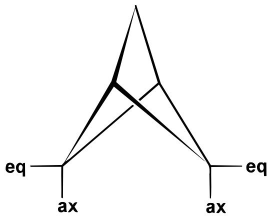


Figure 6. Equatorial and axial hydrogen positions in bicyclo[1.1.1]-pentasilane.

In the case of five-membered rings, both the bicyclo[2.1.0]-pentasilane and the diradical are found to exist. Furthermore, the formation of the diradical (*cis* form 235 kJ/mol, *trans* form 277 kJ/mol) is much less favorable than that of the bicyclus (180 kJ/mol). In the diradical, the transannular Si−Si distance between the two trivalent Si atoms is considerably larger than in the four-membered rings (3.26 and 3.24 Å for *cis* and *trans* forms, respectively, compared with 2.39 Å (MC-SCF geometry) in the diradical’s bond stretch isomer bicyclo[2.1.0]pentasilane).

By 1,3 elimination from the bicyclic silane bicyclo[1.1.1]-pentasilane, bicyclic diradicals are obtained. According to whether the elimination takes place at the bridge Si atoms or at the bridge-head Si atoms, two topologically different diradicals are formed: the secondary bicyclo[1.1.1]pentasilan-2,4-diyl and the tertiary bicyclo[1.1.1]pentasilan-1,3-diyl. Owing to less conformational freedom in the rigid silicon structure, the stabilities of these bicyclic diradicals follow a pattern different from that of their monocyclic analogues.

The secondary diradical exists in several different geometric isomers, which differ in the orientation of the H atoms with respect to the C_2 axis through the SiH_2 group (see Figure 6). Whereas in monocyclic diradicals all the singlet states show *axial* and all the triplet states *equatorial* geometry at the trivalent Si atoms, the bicyclic diradical features distinct *cis-ax-* and *cis-eq*-isomers for both multiplicities. In the *trans*-isomer, one H atom is in the equatorial and the other in the axial position.

Formation of the *cis-axial*-isomer is achieved by 164 kJ/mol, falling in line with the monocyclic diradicals (the distance between the trivalent Si atoms is 2.90 Å). The other isomers show a considerably higher transannular Si−Si distance (3.26 Å for the *cis-equatorial* and 3.33 Å for the *trans* structures) and are, therefore, much less stable. The respective elimination enthalpies from the parent bicyclo[1.1.1]pentasilane are 288 and 294 kJ/mol.

In the tertiary diradical bicyclo[1.1.1]pentasilan-1,3-diyl (silicon analogue of propellane), on the other hand, the distance between the radical sites is lower than in any other diradical discussed here (2.74 Å; in the parent silane the two bridge-head Si atoms are separated by 2.89 Å), and consequently, it is formed at very low expense. The elimination enthalpy amounts to only 88 kJ/mol, which is the lowest value found for all H_2 eliminations considered in this work (see Figure 7).

1,3 elimination from bicyclo[2.1.0]pentasilane yields the four-membered ring diradical bicyclo[2.1.0]pentasilan-1,3-diyl. Owing to steric reasons, the *trans*-isomer is preferred to the *cis* form and the respective elimination enthalpies are 155 and 173 kJ/mol.

The 1,3 elimination of H_2 from acyclic silanes yields cyclic compounds. The enthalpies of these reactions range from 161 to 138 kJ/mol. The lower values are found when tertiary or quarternary Si atoms are formed in the reaction products. It is noted that ring closure and formation of four-membered ring diradicals are energetically nearly equivalent. 1,4 eliminations are less endothermic (65−82 kJ/mol) because, as noted before, four-membered rings are preferred by 60−80 kJ/mol over three-membered rings.

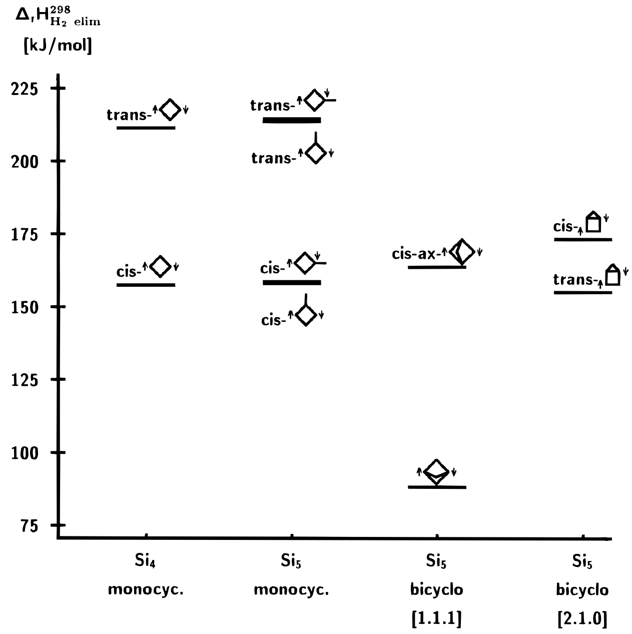


Figure 7. 1,3 H_2 elimination enthalpies from cyclic and bicyclic silanes.

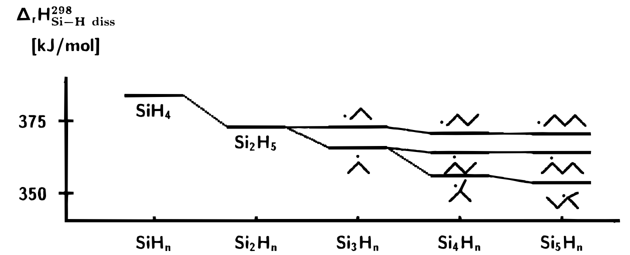


Figure 8. Si−H bond dissociation enthalpies in acyclic silanes.

Si−H Dissociation. In this section, we shall mainly concentrate on Si−H bonds in silanes and silyl radicals. Throughout this work, the term “bond strength” will be used synonymously with “bond dissociation enthalpy”.

Si−H bond dissociation in silanes is endothermic by 346−384 kJ/mol, and the Si−H bonds in silanes are the strongest of all those investigated in this work. The wide range of Si−H bond strengths indicates that the individual bonds are sensitive to the molecular environment.

The dissociation enthalpies are coarsely grouped according to primary, secondary, and tertiary Si−H bonds, as can readily be grasped from Figure 8. Si−H bonds are weakened by successive substitution of the parent monosilane by approximately 9 kJ/mol per additional substituent, whereby the size and structure of the substituent are not decisive. The formation of SiH_3 costs 384 kJ/mol, primary silyl radicals require 370−373 kJ/mol, secondary ones require 362−366 kJ/mol, and tertiary ones require 353−356 kJ/mol. From these dissociation enthalpies as well as from the $\Delta_f H^{298}$ values of isomer pairs discussed before, the stabilization of silyl centers through silyl substitution is evident.

Additionally, secondary and tertiary cyclic radicals are slighly stabilized with respect to acyclic ones, and this effect diminishes, as expected, with increasing ring size. For example, the formation of secondary ring radicals from the cyclosilane parents requires 357−360 kJ/mol whereas the secondary acyclic radicals cover the range 365−369 kJ/mol.

Regarding the Si−H bond dissociation in radicals, it is convenient to distinguish between Si^{rad}−H bonds involving the radical center (by dissociation, silylenes are formed), Si^{α}−H bonds (yielding disilenes by dissociation) and Si^{β}−H bonds, whose cleavage leads to formation of 1,3 diradicals. It will be seen that there are different, although overlapping, enthalpy ranges for the respective types.

Dissociation enthalpies for Si−H bonds at radical Si centers range from 234 to 318 kJ/mol, indicating substituent effects on the stabilities of reactants and products. From the trends noted in the H_2 elimination and Si−H dissociation in silanes, we know already that a high degree of substitution stabilizes a radical center and that silylenes are stabilized by side chains and rings in the α position. The reaction enthalpies with acyclic reactants span the range 292−318 kJ/mol, and the reactions yielding either cyclic silylenes or silylenes with cyclic substituents in the α position occur at lower enthalpies, starting at 273 kJ/mol.

The acyclic cases can readily be divided into primary radicals forming primary silylenes and into secondary radicals forming secondary silylenes. The former usually displays reaction enthalpies between 302 and 305 kJ/mol. If the reaction product (silylene) has a tertiary or quarternary Si atom, however, significantly decreased dissociation enthalpy values from 291 to 302 kJ/mol are found. The secondary acyclic silylens are formed from the parent radicals at an expense of 310−318 kJ/mol, with the lower value of 310 kJ/mol for 3-silyltetrasilan-2,2-diyl, the only example of a secondary acyclic silylene with a tertiary Si atom in the α position. Thus, the stabilizing effect of highly substituted Si centers in a position α to a silylene center again becomes evident. The enthalpy difference between the formation of primary and secondary silylenes that is observed for this class of reaction lies in the different reactant and product stabilities—secondary radicals are more stable than the primary ones, whereas the trend is the inverse for silylenes. Both these influences strengthen the Si−H bond in higher substituted radicals.

In cyclic radicals, the stabilization of the radical is outweighed by the stabilization of the silylene. Therefore, we observe generally lower bond strengths than in the acyclic series. This is especially worth noting for three-membered rings, where nearly always the dissociation is further facilitated by side chains stabilizing the resulting silylene. Therefore, the lowest value found in the cyclic series is 272 kJ/mol (2,3-disilylcyclotrisilan-1,1-diyl). Bicyclic silylenes (234−267 kJ/mol) are formed even less endothermically, owing to both the influence of the ring size and the tertiary bridge-head atoms. The lowest value of 234 kJ/mol is observed with the three-membered ring bicyclic silylene bicyclo[2.1.0]pentasilane-5,5-diyl.

The dissociation enthalpies for the Si−H bond in the position α to a radical site range from 238 to 284 kJ/mol. The reaction enthalpy in the acyclic series depends mainly on the degree of substitution of the α Si atom and not on the degree of substitution of the radical Si atom because any silyl group at the latter site stabilizes both the educt (radical) and the product (disilene) by the same amount. In an SiH_3 group next to a radical Si center, we find Si−H dissociation enthalpies of 262−266 kJ/mol. Introduction of silyl substituents decreases the Si−H dissociation enthalpies by about 9 kJ/mol per substituent.

Since cyclic environments exert a strong influence on the stability of disilenes, a larger variation of bond strengths is found with cyclic radicals. Si−H bond dissociation that lead to formation of Si=Si double bonds in three-membered rings are about 10 kJ/mol more costly than in analogous open-chain compounds. As discussed before, three-membered ring disilenes are further destabilized by substitution of the tetravalent Si atom in the ring. Therefore, formation of 3,3-disilylcyclotrisilene from 2,2-disilylcyclotrisilan-1-yl is the most endothermic reaction in this class (284 kJ/mol). On the other side, four-membered ring disilenes are energetically preferred by about

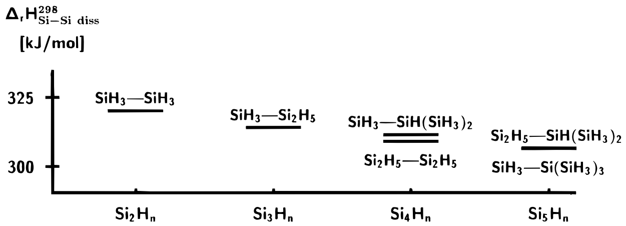


Figure 9. Si−Si bond dissociation enthalpies in acyclic silanes.

10 kJ/mol to acyclic analogues. In agreement with the substitution influence pattern established in the previous paragraph, we find the lowest reaction enthalpy when a tertiary Si−H bond is broken in the radical 2-silylcyclotetrasilan-1-yl (238 kJ/mol).

The dissociation of an Si−H bond in the position β to a radical site causes ring closure in acyclic silyl radicals. From a four-membered ring cyclic radical, the formation of a 1,3 diradical is observed. Only the latter case is discussed here.

Bond cleavage leading to the *cis*-isomer of the diradical costs 172−311 kJ/mol. The extremely low Si−H bond dissociation enthalpy of 172 kJ/mol is observed for the formation of the tertiary bicyclic diradical bicyclo[1.1.1]pentasilane-1,3-diyl and is the lowest Si−H bond strength reported in this study, thereby emphasizing the energetic preference for the said tertiary bicyclic diradical. On the other hand, the 311 kJ/mol needed to form the five-membered ring diradical reflects its low stability. The much smaller energetic variation among the other species can be understood by considering the influence of the substitution on the educt radical.

As mentioned before in the discussion of H_2 elimination enthalpies, unsaturated compounds display weaker Si−H bonds than saturated silanes. Successive Si−H dissociation from trisilane via trisilan-1-yl to the corresponding silylene costs 372 and 303 kJ/mol. The presence of an Si═Si double bond in trisilene reduces these bond dissociation enthalpies to 349 and 286 kJ/mol, respectively, destabilizing the Si—H bonds by about 20 kJ/mol.

Si−Si Bond Dissociation. It has already been mentioned that the bond dissociation enthalpy of Si═Si double bonds and Si≡Si triple bonds are influenced by substitution. For Si—Si single bonds this effect is not as pronounced.

Si−Si single bonds in saturated silanes are less affected by substitution than Si−H bonds. The strongest single bond is that in disilane (320 kJ/mol); breaking of a $H_3Si-SiH_2R$ bond requires 314−316 kJ/mol. The dissociation enthalpies of R^1H_2-$Si-SiH_2R^2$ as well as $H_3Si-SiHR^1R^2$ bonds range from 308 to 312 kJ/mol. $R^1H_2Si-SiHR^2R^3$ and $H_3Si-SiHR^1R^2R^3$ bonds, finally, are broken at the expense of 305−309 kJ/mol (Figure 9). Nevertheless, the weakest and the strongest bonds differ by no more than 15 kJ/mol. It may be noted that there is no significant difference between acyclic systems and the side chains in cyclic silanes.

Radicals display different types of Si−Si bonds. In this work, we discuss bond dissociation enthalpies for bonds between the radical site and its neighbor ($Si^{rad}-Si^{\alpha}$), between the first and the second neighbor of the radical site ($Si^{\alpha}-Si^{\beta}$), and between the second and the third neighbor of the radical site ($Si^{\beta}-Si^{\gamma}$). Besides a radical, the respective products of these dissociation reactions are a silylene, a disilene, and a cyclic diradical. Although all these Si−Si bonds in silyl radicals are weaker than those in silanes, we find the $Si^{rad}-Si^{\alpha}$ to be the strongest and the $Si^{\beta}-Si^{\gamma}$ to be the weakest.

Si−Si single bonds between the trivalent Si atom and its neighbor are at least 40 kJ/mol weaker than in saturated silanes, and also the variation of the bond strength by more than 50 kJ/mol is much larger. These large differences in the bond strengths are due to the interplay of the relative stabilization of reactants and products. When the dissociation of $H_{3-n}R_nSi-\dot{Si}R_mH_{2-m}$ (m and n being the degree of substitution of the trivalent Si atom and its neighbor, respectively) is discussed, all three species, namely, educt radical, product radical, and product silylene, must be taken into account. A high m stabilizes the product radical and destabilizes the product silylene, thus strengthening the bond, whereas n has no strong influence on the educt but weakens the bond by stabilizing the product radical. Our data indicate that the effect of both m and n on the bond dissociation enthalpies is rather linear and independent of each other. The respective bond increments are about +15 and −4 kJ/mol.

If the product radical is cyclic, the bond is slightly destabilized (about 2 kJ/mol according to the small stabilization of cyclic radicals), but in case of a cyclic product silylene we find a strong decrease in the bond dissociation enthalpies due to the strong stabilization of three-membered ring silylenes (up to 36 kJ/mol in 1,2-disilylcyclotrisilan-1-yl vs 2-silyltetrasilan-2-yl).

Breaking Si−Si bonds in radicals between Si atoms in positions α and β to the radical center yields disilenes and radicals. These Si−Si single bonds are among the weakest of all investigated in this study, ranging from 195 to 227 kJ/mol. In agreement with the results discussed before, the formation of three-membered ring disilenes appears at the higher end of this range, whereas open-chain disilenes are formed at the lower cost. The formation of the four-membered ring disilene cyclotetrasilene from the radical 2-silylcyclotetrasilan-1-yl corresponds to the least endothermic reaction in this reaction class.

For the cleavage of the Si−Si bond between β and γ atoms in radicals, only one example can be given. Rather surprisingly, the dissociation of 3-silylcyclotetrasilan-1-yl in SiH_3 and cyclotetrasilan-1,3-diyl is the least endothermic of all Si−Si bond dissociation reactions considered in this work if the *cis*-isomer of the diradical is formed: 184 kJ/mol.

The dissociation enthalpies of Si−Si bonds involving the divalent Si atom in silylenes show a pattern similar to that in radicals. Substitution at the divalent Si atom and at its neighbor independently influence the Si−Si bond strength. The least substituted representative, silylsilylene $SiH-SiH_3$, is dissociated by 254 kJ/mol, thus lying intermediate in the total range from 242 to 274 kJ/mol. Although introducing a substituent at the divalent site lowers the bond dissociation enthalpy uniformly by 3−6 kJ/mol, the α Si atom shows a much more interesting trend, as can be learned from the series $SiH-SiH_{3-n}(SiH_3)_n$ ($SiH-SiH_3$, $SiH-SiH_2-SiH_3$, 2-silyltrisilan-1,1-diyl, and 2,2-disilyltrisilan-1,1-diyl), where we find the respective bond dissociation enthalpies to be 254, 247, 255, and 247 kJ/mol. The reason for this behavior is the strong stabilization of silylenes by side chains at the α Si atom, which overcompensates for the stabilization of the product radical $SiH_{3-n}(SiH_3)_n$. As discussed before, three-membered ring substituents show an even stronger effect on silylene stability: the Si−Si bond dissociation enthalpies of the respective silylenes range from 267 to 274 kJ/mol.

It is interesting to consider the successive silyl dissociation from neopentasilane (2,2-disilyltrisilane) and to compare the results with the stepwise Si−H dissociation of monosilane. Figure 10 visualizes the results of this comparison. Concerning the Si−H bonds in monosilane (386, 289, 318, and 300 kJ/mol), the first and third dissociation enthalpies are larger than the second and fourth. The Si−Si bond enthalpies in $Si(SiH_3)_4$ (2,2-disilyltrisilane), on the other hand, decrease monotonically (306, 266, 251, and 243 kJ/mol). The difference between these two seemingly homologous systems may be explained by

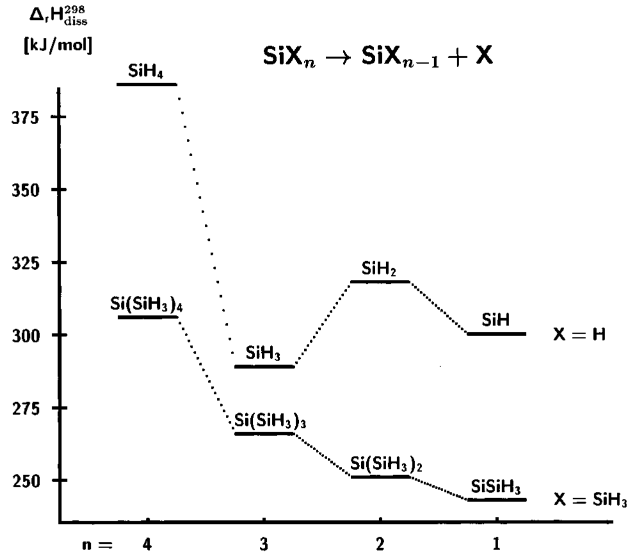


Figure 10. Stepwise dissociation of SiH_4 and $Si(SiH_3)_4$.

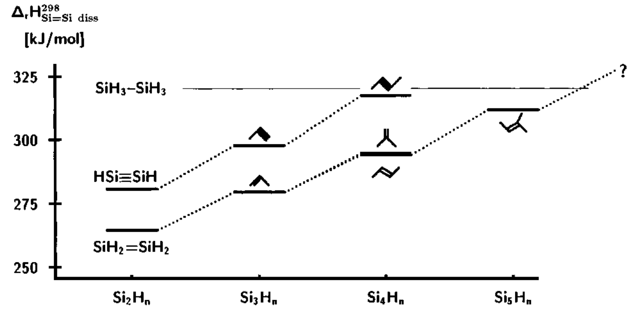


Figure 11. Bond dissociation enthalpies of multiple bonds in disilenes and disilynes.

substitution effects. Since, by substitution, radicals gain stability and silanes and silylenes lose, substitution decreases the first and increases the second Si−Si dissociation enthalpy, thus counteracting the strong oscillations observed in the Si−H case. The third Si−Si dissociation enthalpy is again decreased by the stabilization of the silylene, the silylidyne being not much affected by substitution.

This dissociation behavior may also be compared to the stepwise dissociation of various carbon analogues, CX_4, as can be computed from the well-known[27] enthalpies of formation of CX_n species. Tetrachloromethane (C−Cl bond dissociation enthalpies being 297, 280, 385, and 336 kJ/mol) and tetrafluoromethane (541, 367, 486, and 570 kJ/mol) both resemble silane in that their second dissociation step, involving the formation of the carbene, is the least endothermic in the series. Furthermore, all three systems have in common a central atom that is more electropositive than the ligand and the divalent species SiH_2, CCl_2, and CF_2 that all have singlet ground states.

In methane (439, 459, 426, and 341 kJ/mol), on the other hand, the second C−H bond dissociation leading to triplet carbene is the most endothermic. Comparison with the stepwise dissociation of Si−Si bonds in $Si(SiH_3)_4$ shows that the second Si−Si dissociation enthalpy is very high (although not the highest one), which can be attributed to the low-lying triplet state of $Si(SiH_3)_2$.

The stabilizing effect of silyl substituents on disilenes mentioned already in sections III.A and III.C is even more evident from the dissociation enthalpies of the double bond in disilenes (see also Figure 11): The Si═Si bond strength increases linearly from 265 kJ/mol in disilene by 15 kJ/mol per substituent. The only exception to this rule is 3-silyltetrasil-1-ene, whose Si═Si dissociation enthalpy is about 6 kJ/mol lower than expected, because the product silylene profits from a branching point in α position to the divalent Si atom.

Tetrasila-1,3-diene, the silicon analogue of butadiene, shows the lowest Si═Si bond dissociation enthalpy reported in this study: 248 kJ/mol, which is 32 kJ/mol less than in tetrasil-1-ene. The extra stabilization of the reaction product SiH−SiH−SiH_2, discussed previously in the section on H_2 eliminations, probably accounts for this surprisingly small bond strength.

No Si═Si bond dissociation enthalpies are given for cyclic disilenes because the dissociation products of these dissociation reactions have not been studied. However, Si═Si bond strengths can be given for disilenes with cyclic substituents or disilenes with an exocyclic Si═Si bond. These systems show a behavior different from their acyclic analogues. Their Si═Si bond dissociation enthalpies throughout are considerably lower than the value found for disilene. Exocyclic double bonds from three-membered rings are about 30 kJ/mol weaker than in analogue, acyclic disilenes, and even more so if the ring is silyl-substituted (e.g., 1-silyl-2-silylidenecyclotrisilane 255 kJ/mol). The weakest bond is displayed by cyclotrisilanyldisilene (251 kJ/mol), which is the only example of a double bond substituted with a cyclotrisilanyl group. In all these cases, the weakening of the Si═Si bond can be attributed to the stabilization of the product silylene.

Si−Si single bonds neighboring double bonds in disilenes are not much affected by the double bond. They are only slightly (maximum of 10 kJ/mol) weaker than single bonds in silanes. It may be noted that the single bond in tetrasila-1,3-diene (300 kJ/mol) equals the central Si−Si bond in tetrasil-1-ene (299 kJ/mol), thus indicating that a second Si═Si bond does not affect the Si−Si single bond further. The second next Si−Si angle bond is more strongly influenced by the double bond. Dissociation of tetrasil-1-ene in the "allylic" SiH_2−SiH−SiH_2 and SiH_3 costs 290 kJ/mol, which is 25 kJ/mol less than the analogous Si−Si bond in tetrasilane.

Silicon hydrides with a formal triple bond are referred to as disilynes. Si≡Si bond dissociation enthalpies display a similar trend as the disilene. Although the Si≡Si bond in the *trans-bent*-isomer of Si_2H_2 is rather weak (281 kJ/mol, thus ranging in the upper double bond region), silyl substitution increases the bond strength by about 19 kJ/mol per substituent.

Comparing our results for the Si−Si bond strength of silanes, disilenes, and disilynes, we find that silanes are affected least by substitution (about −4.5 kJ/mol per substituent), whereas formal multiple bonds in disilenes and disilynes are much more sensitive to silyl substituents (+15 and +19 kJ/mol, respectively). It is worth noting that, although unsubstituted multiple bonds are considerably weaker than single bonds (265 and 281 kJ/mol for disilene and disilyne vs 320 kJ/mol for disilane), the double substituted triple bond (317 kJ/mol) is nearly as strong as the Si−Si bond in disilane, and the extrapolated bond dissociation enthalpy for the tetrasubstituted double bond in tetrasilyldisilene (2,3-disilyltetrasil-2-ene) $(SiH_3)_2Si{=}Si(SiH_3)_2$ (327 kJ/mol) is higher than any Si−Si bonds reported in this work—a rather unexpected result (cf. Figure 11). Multiple bonds in silicon hydrides were assumed to always be weaker than single bonds, based on the rather weak bonds in the parent compounds disilene and disilyne.

Silicon hydride chemistry is frequently, especially by organic chemists, thought of as "exotic" because the Si═Si double bond (in disilene) is considerably weaker than the single bond (in disilane). In carbon chemistry,[27] the double bond in ethene (720 kJ) is nearly twice as strong as the single bond in ethane (376 kJ/mol). If, however, the hydrogen atoms are substituted by substituents that are more electronegative than carbon, thus matching the relative electronegativities in silicon hydrides, double bonds are drastically destabilized with respect to the single bond (C_2Cl_6/C_2Cl_4 293/489 kJ/mol), and in the case of the fluorinated species, the "double" bond becomes significantly weaker than the "single" bond (C_2F_6/C_2F_4 403/295 kJ/mol).

D. Singlet−Triplet Splittings. Singlet−triplet splittings will be reported for silylenes, disilenes, and diradicals.

With respect to silylenes, the well-known influence of substituents on both the singlet and triplet states causes the singlet−triplet (ST) splitting to decrease with the degree of substitution. Therefore, SiH_2 has the highest ST splitting of all open-chain silylenes (82 kJ/mol); primary silylenes exhibit about 50−55 kJ/mol and secondary silylenes about 26−32 kJ/mol. Interestingly, cyclic silylenes display nearly the same ST splittings as open-chain secondary silylenes. Since it has been shown before (by analyzing 1,1 H_2 elimination enthalpies) that their singlet states are strongly stabilized, it appears that the ring environment has an equal effect on both singlet and triplet states.

As discussed before, the singlet states of silylenes with side chains or three-membered rings in the position α to the divalent Si atom are energetically favored. The triplet states, however, are not influenced. Therefore, the ST splitting increases. In the acyclic series, the effect remains rather small. The highest ST splitting found for a primary silylene is 61 kJ/mol (2-silyltrisilan-1,1-diyl), for a secondary 33 kJ/mol (2-silyltetrasilan-2,2-diyl). Three-membered ring substituents may increase the ST splitting strongly, up to 83 kJ/mol (primary, cyclotrisilanylsilylene) and 54 kJ/mol (secondary, 1-cyclotrisilanyldisilan-1,1-diyl). Bicyclic silylenes display much higher ST splittings, up to 100 kJ/mol (bicyclo[1.1.1]pentasilan-2,2-diyl).

Our singlet−triplet splitting of unsubstituted SiH_2 (82 or 81 kJ/mol at the purely electronic level) is about 6 kJ/mol lower than the most accurate values found in the literature.[7,34,35] It may be concluded that by basis set incompleteness (especially, lack of f functions) all our ST splittings for silylenes are systematically biased. We expect the error to be the same size for different silylenes.

Less variation is found in the ST splittings of disilenes, which range from 66 to 121 kJ/mol. Acyclic disilenes (104−107 kJ/mol) show no systematic variation with the structure, although all of them are significantly lower than disilene (115 kJ/mol). Three-membered ring disilenes (66−92 kJ/mol) show decreased and four-membered ring disilenes (116−121 kJ/mol) increased ST splittings, which fits well the previously noted destabilization of the three-membered ring disilenes and stabilization of four-membered ring disilenes.

The ground state of tetrasila-1,3-diene (nearly isoenergetic *cis*- and *trans*-isomers) is separated from the lowest triplet state by 93 kJ/mol. In the triplet minimum structure, one of the formal double bonds features typical singlet disilene-like bond length and dihedral angles, while the other is strongly reminiscent of triplet disilene. Since the singlet−triplet splitting is only marginally lower than that of typical disilenes, it seems reasonable to assume two approximately independent double bonds without strong interaction. Further support for this view comes from the singlet−quintet splitting of 222 kJ/mol, which is nearly twice as high as the singlet−triplet splitting of typical substituted acyclic disilenes.

In monocyclic diradicals, the *cis* form is preferred on the singlet surface and the *trans* form is slightly preferred on the triplet surface. Therefore, *cis*- and *trans*-isomers differ drastically in their ST splitting. For four-membered rings, the difference amounts to about 55 kJ/mol. The ST splitting of this class of compounds decreases with increasing ring size, but there is no strong influence of substitution.

Bicyclic diradicals, however, show a different behavior, which in bicyclo[1.1.1]pentasilan-2,4-diyl is caused by the conformational rigidity of the system, fixing the H atoms at the radical sites in either axial or equatorial position. Moreover, in the system bicyclo[1.1.1]pentasilan-1,3-diyl the singlet benefits from the short distance (2.74 Å) of the two radical sites. Thence, bicyclo[1.1.1]pentasilan-1,3-diyl shows the highest ST splitting of 251 kJ/mol reported in this work. The bicyclic diradical bicyclo[2.1.0]pentasilan-1,3-diyl favors the *trans* form in the singlet state, and its ST splitting is therefore at variance with those of their monocyclic analogues.

E. General Remarks. The presented analysis of our data is not exhaustive, but we hope to have pointed out some results of general interest. The data presented here allow the study of several additional types of reactions, such as displacement and insertion reactions. These are probably of less general interest than the trends that can be seen in the dissociation reactions, and owing to the large number of systems presented here, a selection had to be made. The tabulated thermodynamic data allow the reader to calculate reaction enthalpies, Gibbs functions, and equilibrium constants for several hundred reactions that may occur in the gas phase kinetics of the CVD of silane.

Acknowledgment. Part of this work was contained in G.K.'s master thesis at the Karl-Franzens Universität Graz, which has been made possible through project funding from the Austrian FWF, Grant Number P8884-TEC. We also thank the authors of MOLPRO for their permission to incorporate our pseudopotential into the program.

References and Notes

(1) Ho, P.; Coltrin, M. E.; Binkley, J. S.; Melius, C. F. *J. Phys. Chem.* **1986**, *90*, 3399.

(2) Ho, P.; Melius, C. F. *J. Phys. Chem.* **1990**, *94*, 5120.

(3) Ho, P.; Coltrin, M. E.; Binkley, J. S.; Melius, C. F. *J. Phys. Chem.* **1990**, *89*, 4647.

(4) Sax, A. F.; Kalcher, J. *J. Phys. Chem.* **1991**, *95*, 1769.

(5) Curtiss, L. A.; Raghavachari, K.; Deutsch, P. W.; Pople, J. A. *J. Chem. Phys.* **1991**, *95*, 2433.

(6) Leroy, G.; Sana, M.; Wilante, C.; Temsamani, D. R. *J. Mol. Struct.: THEOCHEM* **1992**, *259*, 369.

(7) Grev, R. S.; Schaefer, H. F., III *J. Chem. Phys.* **1992**, *97*, 8389.

(8) Gunn, S. R.; Green, L. G. *J. Phys. Chem.* **1961**, *65*, 779.

(9) Gunn, S. R.; Green, L. G. *J. Phys. Chem.* **1964**, *68*, 946.

(10) Berkowitz, J.; Green, J. P. *J. Chem. Phys.* **1987**, *86*, 1235.

(11) Boo, B. H.; Armentrout, P. B. *J. Am. Chem. Soc.* **1987**, *109*, 3549.

(12) Boo, B. H.; Elkind, J. L.; Armentrout, P. B. *J. Am. Chem. Soc.* **1990**, *112*, 2083.

(13) Berkowitz, J.; Greene, J. P.; Cho, H.; Ruščić, B. *J. Chem. Phys.* **1987**, *86*, 1235.

(14) Ruščić, B.; Berkowitz, J. *J. Chem. Phys.* **1991**, *95*, 2407.

(15) Ruščić, B.; Berkowitz, J. *J. Chem. Phys.* **1991**, *95*, 2416.

(16) Seetula, J. A.; Feng, Y.; Gutman, D.; Seakins, P. W.; Pilling, M. J. *J. Phys. Chem.* **1991**, *95*, 1658.

(17) Moffat, H. K.; Jensen, K. F.; Carr, R. W. *J. Phys. Chem.* **1991**, *95*, 145.

(18) Walsh, R. In *Energetics in Organometallic Chemistry*; Martinho-Simoes, J. A., Ed.; Kluwer: Dordrecht, 1992.

(19) Moffat, H. K.; Jensen, K. F.; Carr, R. W. *J. Chem. Phys.* **1992**, *96*, 7695.

(20) Goumri, A.; W-Yuan, J.; Ding, L.; Marshall, P. *Chem. Phys. Lett.* **1993**, *204*, 296.

(21) Janoschek, R.; Sax, A.; Halevi, E. *Isr. J. Chem.* **1983**, *23*, 58.

(22) Sax, A. F.; Kalcher, J. *J. Comput. Chem.* **1985**, *6*, 469.

(23) Sax, A. F.; Kalcher, J. *J. Mol. Struct.: THEOCHEM* **1990**, *208*, 123.

(24) Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Jensen, J. H.; Koseki, S.; Gordon, M. S.; Nguyen, K. A.; Windus, T. L.; Elbert, S. T. *QCPE Bull.* **1990**, *10*, 52.

(25) Werner, H.-J.; Knowles, P. J. *Theor. Chim. Acta* **1990**, *78*, 175.

(26) MOLPRO is a package of *ab initio* programs written by Werner, H.-J. and Knowles, P. J., with contributions from the following: Almlöf,

J.; Amos, R. D.; Deegan, M. J. O.; Elbert, S. T.; Hampel, C.; Meyer, W.; Peterson, K.; Pitzer, R.; Stone, A. J.; Taylor, P. R.

(27) JANAF Thermochemical Tables. *J. Phys. Chem. Ref. Data Suppl. 1* **1985**, *14*.

(28) Taylor, P. R. In *Lecture Notes in Chemistry 58*; Roos, B. O., Ed.; Springer: Berlin 1922; p 325.

(29) Grev, R. S.; Schaefer, H. F., III *J. Chem. Phys.* **1992**, *97*, 7990.

(30) Ernst, M. C.; Sax, A. F.; Kalcher, J.; Katzer, G. *J. Mol. Struct.: THEOCHEM* **1995**, *121*, 334.

(31) Schleyer, P. v. R.; Sax, A. F.; Kalcher, J.; Janoschek, R. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 364.

(32) Gordon, M. S.; Francisco, J. S.; Schlegel, H. B. *Adv. Silicon Chem.* **1993**, *2*, 137.

(33) Walsh, R. *Acc. Chem. Res.* **1981**, *14*, 246.

(34) Balasubramanian, K.; Lean, A. D. *J. Chem. Phys.* **1986**, *85*, 5117.

(35) Bauschlicher, C. W.; Langhoff, S. R.; Taylor, P. R. *J. Chem. Phys.* **1987**, *87*, 387.