Diammoniosilane: Computational Prediction of the Thermodynamic Properties of a Potential Chemical Hydrogen Storage System

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Atomization energies at 0 K and heats of formation at 0 and 298 K are predicted for diammoniosilane, $H_4Si(NH_3)_2$, and its dehydrogenated derivates at the CCSD(T) and G3(MP2) levels. To achieve near chemical accuracy (±1 kcal/mol), three corrections were added to the complete basis set binding energies based on frozen core coupled cluster theory energies: a correction for core-valence effects, a correction for scalar relativistic effects, and a correction for first-order atomic spin−orbit effects. Vibrational zero-point energies were computed at the CCSD(T) or MP2 levels. The edge inversion barrier of silane is predicted to be 88.9 kcal/mol at 298 K at the CCSD(T) level and a substantial amount, −63.6 kcal/mol, is recovered upon complexation with 2 NH_3 molecules, so that the diammoniosilane complex is only 25.6 kcal/mol at 298 K above the separated reactants $SiH_4 + 2NH_3$. The complex is a metastable species characterized by all real frequencies at the MP2/aV(T+*d*)Z level. We predict the heat of reaction for the sequential dehydrogenation of diammoniosilane to yield $H_3Si(NH_2)(NH_3)$ and $H_2Si(NH_2)_2$ to be exothermic by 33.6 and 12.2 kcal/mol at 298 K at the CCSD(T) level, respectively. The cumulative dehydrogenation reaction yielding two molecules of hydrogen at 298 K is −45.8 kcal/mol at the CCSD(T) level. The sequential release of H_2 from $H_2Si(NH_2)_2$ consequently yielding $HN{=}SiH(NH_2)$ and $HN{=}Si{=}NH$ are predicted to be largely endothermic reactions at 45.3 and 55.7 kcal/mol at the CCSD(T) level at 298 K. If the endothermic reaction for the third step and the exothermic reactions for the release of the first two H_2 were coupled effectively, loss of three H_2 molecules from $H_4Si(NH_3)_2$ would be almost thermoneutral at 0 K.

Introduction

There is substantial interest in the discovery of potential molecules for chemical hydrogen storage systems in which dehydrogenation (hydrogen release) from these molecules is near thermoneutral. Near thermoneutral reactions facilitate both H_2 release and regeneration of the spent fuel. There is substantial interest in the use of amine complexes such as ammonia borane for use as chemical hydrogen storage systems.[1−9] Another possibility for an amine complex would be to add NH_3 to SiH_4 to make a square planar SiH_4 with NH_3 molecules coordinating in the two apical positions. This is equivalent to stabilization of the edge inversion transition state for SiH_4 by two amines.[10,11] We would expect that such a stabilized transition state is possible as the H atoms are electronegative with respect to Si, which is the case needed for edge inversion. Diammoniosilane if it could be made would have an excellent weight percent storage for hydrogen at 26 wt % if 8 molecules of H_2 are produced as compared to the amine boranes having 19% if 3 molecules of H_2 are produced.[1]

There has also been considerable interest in understanding the chemistry of the edge inversion process, i.e., the formation of square planar AX_4 structures from tetrahedral AX_4 structures. For example, the isoelectronic species BH_4^-, CH_4, and NH_4^+ as well as AlH_4^-, SiH_4, and PH_4^+ have been studied,[12] as have the Group IVA fluorides,[10] four-coordinate Group IV centers,[13] and the Group IVA hydrides.[14] Edge inversion was first described and observed for tricoordinate pnictogen compounds.[15−19] The possible effects that certain classes of substituents or solvents would have on stabilizing the edge inversion barrier have been described for PF_3O and PO_3OH.[11] Low-level calculations on $SiF_4(NH_3)_2$ have been reported.[20] Yoshizawa and Suzuki[14] reported on the configurational inversion of tetrahedral molecules and predicted the activation energy for the inversion of silane to be 88.6 kcal/mol at the B3LYP/6-311G** level and 91.7 kcal/mol at the CAS(8,8)/6-311G** level. Earlier studies by Schleyer et al. report a silane inversion barrier of 114.1 kcal/mol at the HF/STO-3G* level.[12]

Modern computational chemistry methods implemented on high-performance computer architectures can now provide reliable predictions of thermodynamic properties to within about 1 kcal/mol for most compounds that are not dominated by multireference character.[21] We use the approach that we have been developing with collaborators at Pacific Northwest Laboratory and Washington State University for the prediction of accurate molecular thermochemistry[22] to determine the atomization energies and the heats of formation of these compounds. Our approach is based on calculating the total atomization energy of a molecule and using this value with known heats of formation of the atoms to calculate the heat of formation at 0 K. The approach starts with coupled cluster theory with single and double excitations and includes a perturbative triples correction (CCSD(T)),[23−25] combined with the correlation-consistent basis sets[26] extrapolated to the complete basis set limit to treat the correlation energy of the valence electrons. This is followed by a number of smaller additive corrections including core−valence interactions and relativistic effects, both scalar and spin−orbit. The zero-point energy can be obtained from experiment, theory, or a combination of the two. Corrections to 298 K can then be calculated by using standard thermodynamic and statistical mechanics expressions in the rigid

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rotor−harmonic oscillator approximation[27] and appropriate corrections for the heat of formation of the atoms.[28] We now report reliable calculations on the interaction of two NH_3 molecules with silane and the various dehydrogenation energies.

Computational Methods

The standard aug-cc-pV*n*Z basis sets were used for H and N. It has recently been found that tight *d* functions are necessary for calculating accurate atomization energies for second row elements,[29] so we also included additional tight *d* functions in our calculations. Basis sets containing extra tight *d* functions are denoted aug-cc-pV($n+d$)Z. We use aug-cc-pV($n+d$)Z to represent the combination of aug-cc-pV($n+d$)Z (on the second row atom Si) and aug-cc-pV*n*Z (on H and N) basis sets and abbreviate this as aV($n+d$)Z. Only the spherical component subset (e.g., 5-term *d* functions, 7-term *f* functions, etc.) of the Cartesian polarization functions were used. All CCSD(T) calculations were performed with the MOLPRO-2002[30] program system on an SGI Altix computer, the Cray XD-1, or the dense memory Linux cluster at the Alabama Supercomputer Center or the Dell Linux cluster at The University of Alabama. For the open-shell atomic calculations, we used the restricted method for the starting Hartree−Fock wavefunction and then relaxed the spin restriction in the coupled cluster portion of the calculation. This method is conventionally labeled R/UCCSD(T). Our CBS estimates use a mixed exponential/Gaussian function of the form[31]

$$E(n) = E_{\mathrm{CBS}} + B\mathrm{e}^{-(n-1)} + C\mathrm{e}^{-(n-1)^2} \qquad (1)$$

where $n = 2$ (aV(D+d)Z), 3 (aV(T+d)Z), 4 (aV(Q+d)Z). To achieve thermochemical properties within ±1 kcal/mol of experiment, it is necessary to account for core−valence correlation energy effects. Core−valence (CV) calculations were carried out with the weighted core−valence basis set cc-pwCVTZ.[32] We need to account for relativistic effects in atoms and molecules. The first correction lowers the sum of the atomic energies (decreasing TAE) by replacing energies that correspond to an average over the available spin multiplets with energies for the lowest multiplets as most electronic structure codes produce only spin multiplet averaged wavefunctions. The atomic spin−orbit correction for Si is $\Delta E_{\mathrm{SO}}(\mathrm{Si}) = 0.43$ kcal/mol taken from the tables of Moore.[33] A second relativistic correction to the atomization energy accounts for molecular scalar relativistic effects, ΔE_{SR}. We evaluated ΔE_{SR} by using expectation values for the two dominant terms in the Breit−Pauli Hamiltonian, the so-called mass−velocity and one-electron Darwin (MVD) corrections from configuration interaction singles and doubles (CISD) calculations. The quantity ΔE_{SR} was obtained from the CISD wavefunction with a VTZ basis set at the CCSD(T)/aV(T+d)Z or MP2/aV(T+d)Z geometry. The CISD(MVD) approach generally yields ΔE_{SR} values in good agreement (±0.3 kcal/mol) with more accurate values from, for example, Douglass−Kroll−Hess calculations, for most molecules.

For all of the molecules, numerical geometry optimizations were performed with a convergence threshold on the gradient of approximately $10^{-4}E_{\mathrm{h}}$/bohr or smaller. For the smaller molecules, specifically SiH_4, $HNSiH_2$, and HNSiNH, geometries were optimized at the CCSD(T) level with the aV(D+d)Z and aV(T+d)Z basis sets. The geometries obtained with the aV(T+d)Z basis set were then used in single-point CCSD(T)/aV(Q+d)Z calculations. The zero-point energies (ΔE_{ZPE}) were calculated at the CCSD(T) level with the aV(T+d)Z basis set. For the larger molecules, geometry optimizations were performed at the MP2/aV(T+d)Z level, and the geometry obtained was then further used in single-point CCSD(T) calculation with the aV(D+d)Z, aV(T+d)Z, and aV(Q+d)Z basis sets. The zero-point energies (ΔE_{ZPE}) were calculated at the MP2 level with the aV(T+d)Z basis set. To calculate the zero-point correction, the calculated harmonic N−H and Si−H stretching frequencies were scaled by factors of 0.974 and 0.977, respectively, obtained by taking the average of the theoretical MP2/aV(T+d)Z values and the experimental values[34] for the N−H and Si−H stretches for NH_3 and SiH_4 and dividing the average by the theoretical value.

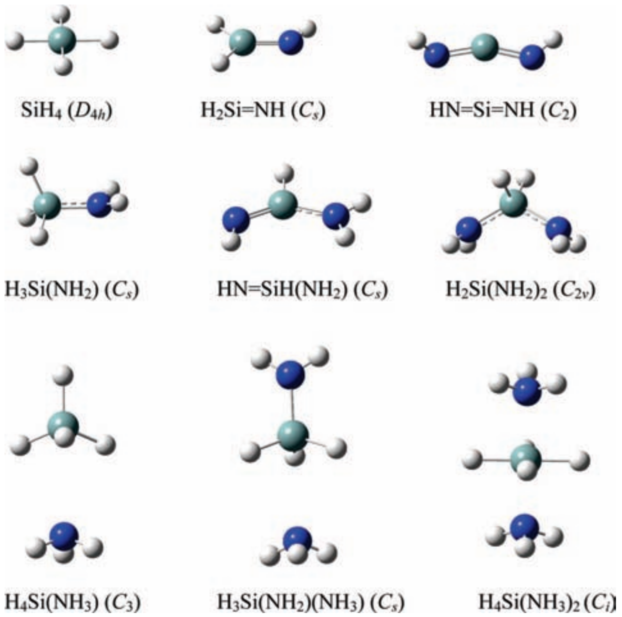

Figure 1. Optimized molecular structures for SiH_4, $H_2Si{=}NH$, $HN{=}Si{=}NH$, $H_3Si(NH_2)$, $HN{=}SiH(NH_2)$, $H_2Si(NH_2)_2$, $H_4Si(NH_3)$, $H_3Si(NH_2)(NH_3)$, and $H_4Si(NH_3)_2$.

By combining our computed $\sum D_0$ values given by the following expression

$$\sum D_0 = \Delta E_{\mathrm{elec}}(\mathrm{CBS}) - \Delta E_{\mathrm{ZPE}} + \Delta E_{\mathrm{CV}} + \Delta E_{\mathrm{SR}} + \Delta E_{\mathrm{SO}} \qquad (2)$$

with the known heats of formation at 0 K for the elements, we can derive ΔH_{f}^0 values for the molecules under study. The heats of formation of H and N are well-established as $\Delta H_{\mathrm{f}}^0(\mathrm{H}) = 51.63$ kcal/mol and $\Delta H_{\mathrm{f}}^0(\mathrm{N}) = 112.53$ kcal/mol.[35] The value for Si is not as well-established and we use $\Delta H_{\mathrm{f}}^0(\mathrm{Si}) = 107.4 \pm 0.6$ kcal/mol from the work of Feller and Dixon on small Si-containing molecules.[36] This value is within the error bars of the NIST value of $\Delta H_{\mathrm{f}}^0(\mathrm{Si}) = 106.6 \pm 1.9$ kcal/mol.[35] Heats of formation at 298 K were obtained by following the procedures outlined by Curtiss et al.[28]

We have also calculated heats of formation and dehydrogenation energies employing a cheaper computational approach based on calculations performed at the G3(MP2) level of theory.[37] We wish to test the effectiveness of this method for use with larger molecules in the future.

Results and Discussion

The calculated geometries for the molecules are given as Supporting Information (Table SI-1), where they are compared with the available experimental values. The optimized molecular structures are depicted in Figure 1. The total CCSD(T) energies and calculated harmonic frequencies for the molecules are also given in Tables SI-2 and SI-3 (Supporting Information), respectively.

Geometries and Frequencies. The structure of diammoniosilane has C_i symmetry with ammonia groups in the apical positions above and below the square planar approximately D_{4h} SiH_4 molecule giving a pseudooctahedral structure at the Si. The lone pairs on the N atoms form dative bonds with the LUMO on Si, which is an empty p orbital of a_{2u} symmetry, similar to the dative bond of ammonia borane, H_3B-NH_3.[1] The Si−N bond distance at the MP2/aV(T+*d*)Z level is 0.29 Å longer than the Si−N single bond distance in $H_2Si-(NH_2)_2$ at the same level. The Si−H distance of diammoniasilane is only 0.026 Å longer than the Si−H distance in SiH_4 (D_{4h}) at the MP2/aV(T+*d*)Z level, showing little perturbation of the Si−H bond distance upon binding of the two ammonia units. Similarly, there is only a small perturbation on the N−H bond distance upon complexation compared to NH_3 with that of the complex calculated to be 0.002 Å longer at the MP2/aV(T+*d*)Z level. The average ∠HNH angle of the ammonia units of the complex is calculated to be 109.0° at the MP2/aV(T+*d*)Z level, only 2.2° larger than the ∠HNH angle of the ammonia at the same level.

Diammoniosilane is characterized by all real harmonic frequencies at the MP2/aV(T+*d*)Z level. There are two very low modes in the diammoniosilane complex of 12 cm^{-1} (a_g mode) and 33 cm^{-1} (a_u mode) corresponding to torsions about the Si−N bonds. The next two largest modes at 197 (a_u mode) and 204 cm^{-1} (a_g mode) correspond to wagging of the NH_3 subunits. The following two higher modes at 355 (a_g mode) and 466 cm^{-1} (a_u mode) correspond to the symmetric and antisymmetric Si−N stretches, respectively, showing the stability of the complex. In addition, there is only a small perturbation in the N−H and Si−H stretching frequencies of $H_4Si(NH_3)_2$ when compared to that of NH_3 (C_{3v}) and SiH_4 (D_{4h}). The symmetric and antisymmetric N−H stretches of the diammoniosilane complex are ~25 cm^{-1} less than the equivalent stretches in ammonia at the MP2/aV(T+*d*)Z level. Similarly, the symmetric and antisymmetric Si−H stretches of the diammonio complex are 114 and 166 cm^{-1} less, respectively, compared to the equivalent stretches in SiH_4 (D_{4h}) at the MP2/aV(T+*d*)Z level.

The first dehydrogenated product of diammoniosilane is the complex $H_3Si(NH_2)(NH_3)$ (C_s). The $Si-NH_2$ bond distance is 0.013 Å longer than the Si−N bond distance in $H_3Si(NH_2)$ at the MP2/aV(T+*d*)Z level, showing minimal effect of the $-NH_3$ group. The $Si-NH_3$ bond distance at the MP2/aV(T+*d*)Z level is 1.00 Å longer than the equivalent bond distance in $H_4Si(NH_3)_2$ but only 0.16 Å shorter than the equivalent bond distance in $H_4Si(NH_3)$. Thus this structure can be considered to be a weak complex of NH_3 with $SiH_3(NH_2)$, bound by only 1.0 kcal/mol at 0 K and 0.7 kcal/mol at 298 K at the CCSD(T) level. The $Si-NH_3$ stretching frequency is calculated to be 88 cm^{-1}, much lower than the equivalent stretching frequency found for the diammoniosilane complex, but similar to that found in $H_4Si(NH_3)$. The structure of $H_3Si(NH_2)$ has C_s symmetry. The Si−H bond distances are calculated to be within 0.009 Å of that found in SiH_4 at the MP2/aV(T+*d*)Z level, showing only a small substituent effect of the NH_2 group on the Si−H bond distance. The N−H bond distance shows a small decrease of 0.008 Å compared to that of ammonia.

The second dehydrogenated product of diammoniosilane is $H_2Si(NH_2)_2$ of C_{2v} symmetry with normal tetrahedral bonding at the Si. The Si−N bond distance is 0.002 Å shorter than that in $H_3Si(NH_2)$. The Si−H and N−H bond distances are essentially the same as those found in $H_3Si(NH_2)$ with the largest difference predicted to be 0.001 Å found for the comparable Si−H bond. The Si−N symmetric stretching frequency is ~60 cm^{-1} less than that found in $H_3Si(NH_2)$. The N−H and Si−H symmetric and antisymmetric stretches are within 6 cm^{-1} of those found in $H_3Si(NH_2)$.

The third and fourth dehydrogenated products are $HN{=}SiH(NH_2)$ and $HN{=}Si{=}NH$, respectively. The structure of $HN{=}Si{=}NH$ has C_2 symmetry with the two $Si{=}N-H$ planes twisted by 83°. The $Si{=}NH$ bond distances are 0.013 and 0.021 Å shorter than that in $H_2Si{=}NH$, respectively, at the MP2/aV(T+*d*)Z level. The $Si-NH_2$ bond distance of $HN{=}SiH(NH_2)$ is calculated to be 0.033 Å shorter than the equivalent bond distance in $H_3Si(NH_2)$ at the MP2/aV(T+*d*)Z level. The structure of $H_2Si{=}NH$ is of C_s symmetry. The $Si{=}N$ bond distance shows a decrease of 0.117 Å compared to that of H_3Si-NH_2, consistent with the formation of a double bond.

Starting from a geometry derived from the diammoniosilane complex for $H_4Si(NH_3)$ leads to the formation of a very weak complex with C_3 symmetry. The complex is best described as the lone pair on the ammonia molecule loosely interacting with a tetrahedral SiH_4 along the C_3 axis pointing at the Si. The Si−N bond distance at the MP2/aV(T+*d*)Z level is 1.16 Å longer than the Si−N bond distance in the diammonio complex. The N−H and Si−H bond distances are only minimally perturbed compared to the equivalent distances in NH_3 (C_{3v}) and SiH_4 (T_d), respectively, with the largest difference calculated to be 0.005 Å for the Si−H bond distance. The $H_4Si(NH_3)$ complex is characterized by all real frequencies at the MP2/aV(T+*d*)Z level. The low Si−N stretching frequency is calculated to be at 86 cm^{-1}, within 2 cm^{-1} of the equivalent frequency in $H_3Si(NH_2)(NH_3)$ and about one fourth that in $H_4Si(NH_3)_2$.

The transition state for the edge inversion process of silane is characterized by one imaginary frequency at 2463.4i cm^{-1} of B_{2u} symmetry and connects to one of the E modes of the T_d structure. As expected, the Si−H bond distance of the square planar D_{4h} structure of 1.532 Å is longer by 0.049 Å than that of the T_d structure of 1.483 Å[22e] at the CCSD(T)/aV(T+*d*)Z level.

Energies and Heats of Formation. The energetic components for predicting the total molecular dissociation energies are given in Table 1. The electronic states and symmetry labels for the molecules under study are included in Table 1. We first describe some general trends in the atomization energy components. The core−valence corrections for the molecules are all positive except for that of SiH_4 (D_{4h}). The corrections are also small with values ranging from −0.90 [SiH_4 (D_{4h})] to 1.06 [$H_2Si(NH_2)_2$] kcal/mol. The scalar relativistic corrections are all small and negative, ranging from −0.65 [SiH_4 (D_{4h})] to −1.57 [$H_4Si(NH_3)_2$] kcal/mol. We estimate that the error bars for the calculated heats of formation are ±1.0 kcal/mol considering errors in the energy extrapolation, frequencies, and other electronic energy components. An estimate of the potential for significant multireference character in the wavefunction can be obtained from the T_1 diagnostic[38] for the CCSD calculation. The values for the T_1 diagnostics are small (<0.03) showing that the wavefunction is dominated by a single configuration. The T_1 values are given in Table SI-4 (Supporting Information).

The calculated heats of formation are given in Table 2 and are compared with experimental values[35,39] where available. The agreement for silane is excellent as expected from previous work.[36] We first discuss the stability of diammoniosilane. Silane has T_d symmetry, and the edge inversion barrier passing through a transition state of D_{4h} symmetry is 89.0 kcal/mol at 0 K and

TABLE 1: CCSD(T) Atomization and Reaction Energies (kcal/mol)[a]

molecule	ΔE(CBS)[b]	ΔE_{ZPE}[c]	ΔE_{CV}[d]	ΔE_{SR}[e]	ΔE_{SO}[f]	$\sum D_0$ (0K)[g]
SiH_4 ($^1A_{1g}$-D_{4h})	235.08	17.70	−0.90	−0.65	−0.43	215.41
$H_2Si{=}NH$ ($^1A'$-C_s)	352.55	17.98	0.24	−0.71	−0.43	333.66
$HN{=}Si{=}NH$ (^1A-C_2)	385.66	16.06	0.85	−0.93	−0.43	369.08
$H_3Si(NH_2)$ ($^1A'$-C_s)	518.64	31.48	0.35	−0.95	−0.43	486.14
$H_4Si(NH_3)$ (^1A-C_3)	625.10	42.17	0.27	−0.84	−0.43	581.92
$HN{=}SiH(NH_2)$ ($^1A'$-C_s)	556.66	30.04	1.03	−1.16	−0.43	526.05
$H_2Si(NH_2)_2$ ($^1A_1$-C_{2v})	716.90	42.83	1.06	−1.36	−0.43	673.35
$H_3Si(NH_2)(NH_3)$ ($^1A'$-C_s)	818.68	53.81	0.91	−1.25	−0.43	764.11
$H_4Si(NH_3)_2$ (^1A_g-C_i)	901.04	68.68	0.70	−1.57	−0.43	831.05

[a] The atomic asymptotes were calculated with the R/UCCSD(T) method. [b] Extrapolated by using eq 1 with aV(D+*d*)Z, aV(T+*d*)Z, and aV(Q+*d*)Z. [c] The zero-point energies were taken as 0.5 the sum of the CCSD(T)/aV(T+*d*)Z or MP2/aV(T+*d*)Z scaled frequencies. [d] Core-valence corrections were obtained with the cc-pwCVTZ (N, Si) basis sets at the optimized CCSD(T)/aV(T+*d*)Z or MP2/aV(T+*d*)Z geometries. [e] The scalar relativistic correction is based on a CISD(FC)/VTZ MVD calculation and is expressed relative to the CISD result without the MVD correction, i.e., including the existing relativistic effects resulting from the use of a relativistic effective core potential. [f] Correction due to the incorrect treatment of the atomic asymptotes as an average of spin multiplets. Values are based on C. Moore's tables, ref 33. [g] The theoretical value of ΔD_0(0K) was computed with the CBS estimates.

TABLE 2: Calculated CCSD(T) Heats of Formation (kcal/mol)

	CCSD(T)		G3(MP2)	
molecule	0 K	298 K	0 K	298 K
NH_3 (C_{3v})[a]	−9.6 ± 0.5[b]	−11.3 ± 0.5[b]	−8.3	−10.0
SiH_4 (T_d)[c]	9.5 ± 0.6[d]	7.2 ± 0.6[d]	10.3	8.0
SiH_4 (D_{4h})	98.5	96.1	99.8	97.4
$H_2Si{=}NH$ (C_s)	41.2	39.1	41.5	39.4
$HN{=}Si{=}NH$ (C_2)	66.6	65.2	65.3	64.1
$H_3Si(NH_2)$ (C_s)	−8.1	−11.7	−6.0	−9.6
$H_4Si(NH_3)$ (C_3)	−0.6	−4.4	0.9	−2.8
$HN{=}SiH(NH_2)$ (C_s)	12.9	9.5	14.4	11.1
$H_2Si(NH_2)_2$ (C_{2v})	−31.1	−35.8	−28.3	−32.9
$H_3Si(NH_2)(NH_3)$ (C_s)	−18.6	−23.6	−16.1	−20.9
$H_4Si(NH_3)_2$ (C_i)	17.7	10.0	21.7	13.0

[a] Experimental $\Delta H_f(NH_3) = -9.30 \pm 0.10$ kcal/mol at 0 K and -10.97 ± 0.10 kcal/mol at 298 K.[35] [b] Reference 1. [c] Experimental $\Delta H_f(SiH_4,T_d) = 9.5 \pm 0.5$ kcal/mol at 0 K.[39] [d] Reference 22e.

TABLE 3: Dehydrogenation and NH_3 Stabilization Reactions at 0 and 298 K (kcal/mol)

	CCSD(T)		G3(MP2)	
reaction	0 K	298 K	0 K	298 K
$H_4Si(NH_3)_2 \rightarrow H_3Si(NH_2)(NH_3) + H_2$	−36.3	−33.6	−38.9	−35.0
$H_3Si(NH_2)(NH_3) \rightarrow H_2Si(NH_2)_2 + H_2$	−12.5	−12.2	−13.5	−13.1
$H_4Si(NH_3)_2 \rightarrow H_2Si(NH_2)_2 + 2H_2$	−48.8	−45.8	−52.4	−48.2
$H_2Si(NH_2)_2 \rightarrow HN{=}SiH(NH_2) + H_2$	44.0	45.3	41.6	42.9
$HN{=}SiH(NH_2) \rightarrow HN{=}Si{=}NH + H_2$	53.7	55.7	49.8	51.9
$H_3Si(NH_2) \rightarrow H_2Si{=}NH + H_2$	49.2	50.7	46.3	47.8
$H_4Si(NH_3)_2 \rightarrow SiH_4$ (T_d) $+ 2NH_3$	−27.4	−25.4	−28.0	−25.0
$H_4Si(NH_3)_2 \rightarrow SiH_4$ (D_{4h}) $+ 2NH_3$	61.6	63.6	61.4	64.4
$H_4Si(NH_3)_2 \rightarrow H_4Si(NH_3) + NH_3$	−27.9	−25.6	−29.1	−25.8
$H_4Si(NH_3) \rightarrow SiH_4$ (T_d) $+ NH_3$	0.5	0.3	1.1	0.8
$H_3Si(NH_2)(NH_3) \rightarrow H_3Si(NH_2) + NH_3$	1.0	0.7	1.7	1.3

88.9 kcal/mol at 298 K at the CCSD(T) level. The corresponding value of the G3(MP2) inversion reaction is 89.5 kcal/mol at 0 K and 89.4 kcal/mol at 298 K, showing good agreement of the G3(MP2) value with the more accurate CCSD(T) value. Although the inversion barrier in SiH_4 is low compared to the edge inversion process of CH_4 predicted to be 109 kcal/mol at the B3LYP/6-311G** level,[14] it is comparable to the Si−H bond dissociation energy (BDE) of 90 kcal/mol at 0 K.[40]

Complexation with two NH_3 molecules recovers a substantial amount of the inversion barrier (63.6 kcal/mol at 298 K at the CCSD(T) level), so that the diammoniosilane complex is only 25.4 kcal/mol above the separated reactants $SiH_4 + 2NH_3$ at the CCSD(T) level at 298 K. The complex is a metastable species characterized by all real frequencies at the MP2/aV(T+*d*)Z level so it is a true intermediate.

The complexation energy of the first ammonia group to silane is only −0.5 kcal/mol at 0 K and −0.3 kcal/mol at 298 K relative to the separated reactants $SiH_4 + NH_3$ at the CCSD(T) level. At the G3(MP2) level, the complexation energy for $H_4Si(NH_3)$ is predicted to be −1.1 kcal/mol at 0 K and −0.8 kcal/mol at 298 K. It is only upon introduction of the second ammonia group that a substantial amount of stabilization occurs and the inversion barrier is recovered. The possibility of the stabilizing effect of electronegative groups such as OH, NH_2, and F on the planar-tetrahedral energy difference in SiH_4 and other isoelectronic molecules has been discussed by Dixon and Arduengo[10] and by Schleyer et al.[12]

We can predict the heat of reaction for the dehydrogenation of diammoniosilane from the calculated heats of formation. The results for the various dehydrogenation reactions of diammoniosilane and its derivatives are presented in Table 3 at the CCSD(T) level and at the G3(MP2) level for comparison. The G3(MP2) result is typically within ±4 kcal/mol of the more accurate CCSD(T) value. The overall dehydrogenation of diammoniosilane yielding two molecules of H_2 is predicted to be substantially exothermic at −45.8 kcal/mol at 298 K at the CCSD(T) level. The first loss of hydrogen from diammoniosilane to produce $H_3Si(NH_2)(NH_3)$ is exothermic by −33.6 kcal/mol at 298 K at the CCSD(T) level. The sequential dehydrogenation reaction of $H_3Si(NH_2)(NH_3)$ to produce $H_2Si(NH_2)_2$ is about a third less exothermic than the initial dehydrogenation reaction of diammoniosilane and is predicted to be −12.2 kcal/mol at 298 K at the CCSD(T) level. Further loss of H_2 to form $HN{=}SiH(NH_2)$ and then $HN{=}Si{=}NH$ results in dehydrogenation reactions that are substantially endothermic at 45.3 and 55.7 kcal/mol at the CCSD(T) level at 298 K. These dehydrogenation reactions are quite endothermic and it is unlikely that one will be able to remove hydrogen from these species. If one can couple the endothermic and exothermic reactions effectively, one can remove three H_2 molecules from $H_4Si(NH_3)_2$.

An additional dehydrogenation reaction that must be considered is loss of hydrogen from $H_3Si(NH_2)$, the deammoniated product of $H_3Si(NH_2)(NH_3)$. The product of the first dehydrogenation reaction of diammoniosilane is $H_3Si(NH_2)(NH_3)$, and there is the possibility of the loss of ammonia from this complex with the reaction calculated to be near thermoneutral at 1.0 kcal/mol at 0 K and 0.7 kcal/mol at 298 K at the CCSD(T) level. The loss of H_2 from $H_3Si(NH_2)$ to yield $H_2Si{=}NH$ is predicted to be substantially endothermic at 50.7 kcal/mol at 298 K at the CCSD(T) level. Therefore, it will be unlikely that H_2 will be removed from the deammoniated product.

In our studies on the electronic structures of carbenes[41] (and of others for silylenes[42]), we found that experimental and calculated nuclear magnetic chemical shifts were extremely useful in characterizing bonding in terms of the chemical shift anisotropy. To aid the search for the hexacoordinate silicon species, we also calculated the NMR chemical shifts for SiH_4 (T_d), SiH_4 (D_{4h}), and $SiH_4(NH_3)_2$ at the density functional theory (DFT) level with the B3LYP gradient corrected hybrid exchange−correlation functional[43] and the Ahlrichs polarized triple-ζ basis set[44] in the GIAO (gauge invariant atomic orbital) formalism.[45] The chemical shifts are given with respect to

TABLE 4: Calculated Si NMR Chemical Shifts for SiH_4 (T_d), SiH_4 (D_{4h}), and $H_4Si(NH_3)_2$ (C_i) at the B3LYP/Ahrichs-VTZ+P Level (ppm)[a]

molecule	δ
SiH_4 (T_d)	−107.9
SiH_4 (D_{4h})	323.4
$H_4Si(NH_3)_2$ (C_i)	−234.1

[a] Calculated with respect to tetramethylsilane.

tetramethylsilane following our previous work on Si chemical shifts.[46] The calculated shifts are given in Table 4. The chemical shift for SiH_4 (T_d) of −107.4 ppm is in the range of other tetrahedrally coordinated silanes and matches well the experimentally determined gas phase values of −106.8 ppm[47] and −104.3 ppm.[48] A planar SiH_4 arrangement exhibits a very substantial downfield shift at the silicon somewhat reminiscent of the chemical shifts of carbenes and silylenes.[41] The addition of two amines to produce an octahedral coordination environment at silicon leads to a substantial upfield shift that is generally expected for increased coordination numbers at main group centers.[49]

Conclusions

We have predicted the heats of formation of diammoniosilane and its dehydrogenated derivates at the CCSD(T) level plus additional corrections. The edge inversion barrier of silane is calculated to 88.9 kcal/mol at the CCSD(T) level and 89.4 kcal/mol at the G3(MP2) level at 298 K. A substantial amount of this edge inversion barrier (−63.6 kcal/mol at 298 K at the CCSD(T) level) is recovered upon complexation with two NH_3 molecules, so that the diammoniosilane complex is only 25.6 kcal/mol at 298 K above the separated reactants $SiH_4 + 2NH_3$. The complex is a metastable species characterized by all real frequencies at the MP2/aV(T+*d*)Z level so it is a true intermediate.

The dehydrogenation pathway of diammoniosilane yielding two molecules of H_2 and $H_2Si(NH_2)_2$ is exothermic at 298 K by −45.8 kcal/mol at the CCSD(T) and −48.2 kcal/mol at the G3(MP2) level. The sequential release of H_2 consequently yielding $HN{=}SiH(NH_2)$ and $HN{=}Si{=}NH$ is predicted to be largely endothermic reactions at 45.3 and 55.7 kcal/mol at the CCSD(T) level at 298 K and 42.9 and 51.9 kcal/mol at the G3(MP2) level, respectively. Coupling the exothermic first two dehydrogenation steps with the endothermic third step yields three H_2 molecules and $HN{=}SiH(NH_2)$ in an almost thermoneutral process at 298 K. The loss of H_2 from $H_3Si(NH_2)$, the deammoniated product of $H_3Si(NH_2)(NH_3)$, is predicted to be largely endothermic at 50.7 and 47.8 kcal/mol at the CCSD(T) and G3(MP2) levels at 298 K, respectively.

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Supporting Information Available: Calculated geometry parameters, total CCSD(T) energies as a function of basis set, calculated MP2 frequencies (cm^{-1}), and T_1 diagnostics. This material is available free of charge via the Internet at http://pubs.acs.org.

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