Heats of Formation and Bond Dissociation Energies of the Halosilanes, Methylhalosilanes, and Halomethylsilanes

Daniel J. Grant and David A. Dixon*

Department of Chemistry, The University of Alabama, Shelby Hall, Box 870336, Tuscaloosa, Alabama 35487-0336

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Atomization energies at 0 K and heats of formation at 0 and 298 K are predicted for SiH_3X, SiH_2XCH_3, and SiH_3CH_2X with X = F, Cl, Br, and I from coupled cluster theory (CCSD(T)) calculations with effective core potential correlation-consistent basis sets for Br and I. 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) level of theory and the C−H and Si−H stretches scaled to experiment. The C−H, Si−H, Si−C, C−X, and Si−X (X = F, Cl, Br, and I) bond dissociation energies (BDEs) in the halosilanes, halomethysilanes, and methylhalosilanes were predicted. Except for methyliodosilane, methyl substitution leads to an increase in Si−X BDE when compared to the Si−X BDE in the halosilanes. Except for methyliodosilane, halide substitution leads to an increase in the Si−C BDE in comparison to the Si−C BDE in methylsilane of 86.9 kcal/mol at 0 K. Unlike the methylhalosilanes, the halomethylsilanes all show a decrease in the Si−C BDE when compared to the Si−C BDE in methylsilane. The trends correlate with the electronegativity of the substituent.

Introduction

There is substantial interest in the energetics of silanes for use in technological applications such as precursors for chemical vapor deposition processes or for regeneration schemes for chemical hydrogen storage systems. There is a limited quantity of experimental thermodynamic data available for the halosilanes, methylhalosilanes, and halomethylsilanes in terms of their heats of formation and bond dissociation energies (BDEs). Although the heats of formation of the silyl radical, the halosilanes, the methyl radical, and the halomethylradicals are known experimentally,[1,2] there have been no experiments measuring the heats of formation for the methylhalosilanes, the halomethylsilanes, or the various radicals involved in several of the bond breaking processes studied. Except for silane, the halosilanes, and methysilane, there are limited experimental BDE data available for the molecules under study.[3] Accurate thermodynamic data are essential in the design of the regeneration process for chemical hydrogen storage systems. In addition, the heats of formation of simple model compounds are needed accurately for use in isodesmic reaction schemes to treat larger molecules.

Because it is difficult to measure BDEs, high-level theoretical calculations of these processes offer a unique opportunity to obtain accurate self-consistent values. Modern computational chemistry methods implemented on high performance computer architectures can now provide reliable predictions of chemical bond energies to within about 1 kcal/mol for most reactants and products that are not dominated by multireference character.[4] We can use the approach that we have been developing with collaborators at Washington State University for the prediction of accurate molecular thermochemistry[5] to determine BDEs in these silane compounds. Our approach is based on calculating the total atomization energy (TAE) 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 including a perturbative triples correction (CCSD(T)),[6−8] in combination with the correlation-consistent basis sets[9] 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 rotor-harmonic oscillator approximation[10] and appropriate corrections for the heat of formation of the atoms.[11]

In the current work, we have calculated the heats of formation of the halosilanes SiH_3X, the methylhalosilanes CH_3SiH_2X, and the halomethylsilanes XCH_2SiH_3 for X = F, Cl, Br, and I at the CCSD(T)/CBS level as well as a range of radicals relevant to breaking the C−H, Si−H, Si−C, C−X, and Si−X bonds. This work was made possible by the availability of the new effective core potential/correlation consistent basis sets developed by Peterson and co-workers.[12] These basis sets were developed in combination with effective core potentials from the Stuttgart/Köln group and allow us to study all of the main group elements with high quality basis sets that can be extrapolated to the CBS limit.

Computational Methods

The standard aug-cc-pV*n*Z basis sets were used for H, C, and F. It has recently been found that tight *d* functions are

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* Address correspondence to this author. E-mail: dadixon@bama.ua.edu.

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necessary for calculating accurate atomization energies for second row elements,[9d] 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 in analogy to the original augmented correlation consistent basis sets. We use aug-cc-pV($n+d$)Z to represent the combination of aug-cc-pV($n+d$)Z (on the second row atoms Si and Cl) and aug-cc-pVnZ (on H, C, F) basis sets and abbreviate this as aV(n+d)Z. For heavier elements, the effects of relativity need to be included in the basis sets. A small core relativistic effective core potential (RECP) was used for Br and I. For Br, the RECP subsumes the ($1s^2$, $2s^2$, $2p^6$) orbital space into the 10-electron core set, leaving the ($3s^2$, $3p^6$, $4s^2$, $3d^{10}$, $4p^5$) space with 25 electrons to be handled explicitly; only the ($4s^2$, $4p^5$) electrons are active in our valence correlation treatment. For I, the RECP subsumes the ($1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^6$, $3d^{10}$) orbital space into the 28-electron core set, leaving the ($4s^2$, $4p^6$, $5s^2$, $4d^{10}$, $5p^5$) space with 25 electrons to be handled explicitly; only the ($5s^2$, $5p^5$) electrons are active in our valence correlation treatment. Even though the 4s and 4p inner shell occupied orbitals may have similar energies with the inner shell occupied 3d orbitals, there is good spatial separation between the 3d and the 4s and 4p orbitals so the 3d electrons are included in the RECP and the 4s and 4p are included as active electrons with the 4d in the inner core-valence region for the small core RECPs.[13] The polarized relativistic basis sets are labeled as aug-cc-pV*n*Z-PP.[12] We use the shorthand notation of aV*n*Z-PP to denote the combination of the aug-cc-pV*n*Z basis set on H, C, and F, the aug-cc-pV($n+d$)Z basis set on Cl and Si, and the aug-cc-pV*n*Z-PP basis set on Br and I. Only the spherical component subset (e.g., 5-term *d* functions, 7-term *f* functions, etc.) of the Cartesian polarization functions was used. All CCSD(T) calculations were performed with the MOLPRO-2002[14] program system on a single processor of an SGI Origin computer, the Cray XD-1 at the Alabama Supercomputer Center, or a Dell Cluster at the University of Alabama.

For the open shell atomic calculations, we used restricted Hartree−Fock for the starting wave function 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[15]

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

where $n = 2$ (aVDZ-PP), 3 (aVTZ-PP), and 4 (aVQZ-PP).

Most correlated electronic structure calculations based on molecular orbital theory are done in the frozen core approximation with the energetically lower lying orbitals, e.g., the 1s in fluorine, excluded from the correlation treatment. 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.[16] The cc-pwCVTZ-PP basis set for Br and I is based on the cc-pVTZ-PP basis set and accompanying small core RECP. For Br and I, the cc-pwCVTZ-PP basis set includes up through *g*-functions in order to provide a consistent degree of angular correlation for the active 4d electrons.[17] Core-valence calculations for Br and I involve all 25 electrons outside the RECP core, i.e., $3s^2$, $3p^6$, $4s^2$, $3d^{10}$, $4p^5$ and $4s^2$, $4p^6$, $5s^2$, $4d^{10}$, $5p^5$, respectively.

Two adjustments to the total atomization energy (TAE = $\sum D_0$) are necessary in order 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 wave functions. The atomic spin−orbit corrections are $\Delta E_{\mathrm{SO}}(\mathrm{C}) = 0.09$ kcal/mol, $\Delta E_{\mathrm{SO}}(\mathrm{F}) = 0.39$ kcal/mol, $\Delta E_{\mathrm{SO}}(\mathrm{Si}) = 0.43$ kcal/mol, $\Delta E_{\mathrm{SO}}(\mathrm{Cl}) = 0.84$ kcal/mol, $\Delta E_{\mathrm{SO}}(\mathrm{Br}) = 3.50$ kcal/mol, and $\Delta E_{\mathrm{SO}}(\mathrm{I}) = 7.24$ kcal/mol from the tables of Moore.[18] 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 CISD wave function with a VTZ-PP basis set at the CCSD(T)/aVTZ-PP 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. A potential problem arises in computing the scalar relativistic corrections for the molecules in this study as there is the possibility of "double counting" the relativistic effect on Br and I when applying a MVD correction to an energy that already includes most of the relativistic effects via the RECP. Because the MVD operators mainly sample the core region where the pseudo-orbitals are small, we assume any double counting to be small.

Numerical geometry optimizations were performed with a convergence threshold on the gradient of approximately $10^{-4} E_{\mathrm{h}}$/bohr or smaller. Geometries were optimized at the aVDZ-PP and aVTZ-PP. The geometry obtained with the aVTZ-PP basis set was then used in single point aVQZ-PP calculations. The harmonic frequencies for use in the zero point energy (ΔE_{ZPE}) calculations were obtained at the CCSD(T) level with the aVTZ-PP basis set. The C−H and Si−H stretching frequencies contain the most anharmonicity so to calculate the ΔE_{ZPE} correction, the calculated harmonic C−H and Si−H stretching frequencies were scaled by factors of 0.980 and 0.990, respectively. The scale factors for the C−H and Si−H bonds are obtained by taking the average of the theoretical CCSD(T)/aVTZ-PP values and the experimental values[19] for the C−H and Si−H stretches for CH_4 and SiH_4 and dividing the average by the theoretical value. In the ΔE_{ZPE} calculations, the remaining calculated harmonic frequencies were not scaled. ΔE_{ZPE} was calculated as 0.5 the sum of the calculated frequencies with the C−H and Si−H frequencies scaled.

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

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

with the known[1] heats of formation at 0 K for the elements, $\Delta H_{\mathrm{f}}^0(\mathrm{H}) = 51.63$ kcal/mol, $\Delta H_{\mathrm{f}}^0(\mathrm{C}) = 169.98$ kcal/mol, $\Delta H_{\mathrm{f}}^0(\mathrm{F}) = 18.47 \pm 0.07$ kcal/mol, $\Delta H_{\mathrm{f}}^0(\mathrm{Si}) = 107.4 \pm 0.6$ kcal/mol,[5e] $\Delta H_{\mathrm{f}}^0(\mathrm{Cl}) = 28.59$ kcal/mol, $\Delta H_{\mathrm{f}}^0(\mathrm{Br}) = 28.18$ kcal/mol, and $\Delta H_{\mathrm{f}}^0(\mathrm{I}) = 25.61$ kcal/mol, we can derive ΔH_{f}^0 values for the molecules under study at 0 and 298 K.[11] The experimental heat of formation of Si is not as well-established as one would like with significant error bars in the standard tabulations. The NIST-JANAF tables[1] list $\Delta H_{\mathrm{f}}^0(0\mathrm{K,Si}) = 106.6 \pm 1.9$ kcal/mol, while the CODATA tables contain a slightly smaller value, at 106.5 ± 1.9 kcal/mol.[20] For the present work, we have chosen to use a value of 107.4 ± 0.6 kcal/mol for $\Delta H_{\mathrm{f}}^0(0\mathrm{K,Si})$, as recommended by Feller and Dixon[5e] in a computational study of small silicon-containing molecules. This value is in excellent agreement with the 107.2 ± 0.2 kcal/mol value of Karton and Martin,[21] which was derived from W4 calculations of the total atomization energies for SiH_4, Si_2H_6, and SiF_4 whose experimental values can be obtained separately without referencing the gaseous heat of formation of the Si atom. These values all fall within our estimated error bars of ±1.0 kcal/mol for the heats of formation.

Results and Discussion

The total energies used in this study are given as Supporting Information (Table SI-1). The calculated geometries and frequencies are also given as Supporting Information in Tables SI-2 to SI-5 and Table SI-6 respectively, where they are compared with the available experimental values.

Geometries and Frequencies. The experimental molecular structure data are available for a few of the molecules under study,[22,23] and they are in excellent agreement with our calculated theoretical values. Comparing the CCSD(T)/aVTZ-PP calculations with experiment, the C−X bond distances for the fluoromethyl and chloromethyl radicals are too long by ~0.01 Å. For the H_3SiX compounds, the largest error is for the Si−X bond distance, with the largest error for SiH_3I, where the Si−I bond distance was predicted to be too long by 0.021 Å. Structural data for the methylhalosilanes also show good agreement with experiment, and in general, the Si−C and Si−X (halogen) bond distances are calculated to be too long by 0.01 to 0.03 Å. The calculated theoretical data are also in excellent agreement with the available experimental structure data for SiH_3CH_2Cl and SiH_3CH_2Br with the largest difference for the Si−Cl bond distance.

The experimental vibrational frequencies are available for the silyl radical,[24−26] the halosilanes[19] (other than iodosilane), methylsilane,[27] and the halomethyl radicals other than the iodomethyl radical,[28−31] and allow us to benchmark our calculated values. The largest difference for SiH_3 is for the e Si−H stretch. The biggest differences for the halosilanes are for the Si−H stretches as expected due to the fact that the calculated values are harmonic and the experimental values include anharmonic effects. For methylsilane, the largest differences between the calculated and experimental values are for the C−H and Si−H stretches as expected. The CH_3 asymmetric deformation e mode was calculated to be 71 cm^{-1} greater than the experimental value.[27] For the halomethyl radicals, the largest differences between the calculated and experimental values are for the umbrella out-of-plane mode, which could be due to the measurements being in an Ar matrix.

Heats of Formation. The energetic components for predicting the TAEs are given in Table 1 with the electronic state symmetry labels. The core-valence corrections (ΔE_{CV}) for the molecules are positive, except for those of SiH_3, SiH_2F, SiH_2Cl, SiH_3F, and SiH_3Cl. The ΔE_{CV} values range from −0.41 (SiH_3) to 2.06 (SiH_2ICH_3) kcal/mol. The scalar relativistic corrections (ΔE_{SR}) are all negative with values that range from −0.17 (CH_3) to −1.18 (SiH_2FCH_3) 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 wave function can be obtained from the T_1 diagnostic[32] for the CCSD calculation. The values for the T_1 diagnostics are small (<0.02) showing that the wave function is dominated by a single configuration.

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

molecule	CBS[b]	ΔE_{ZPE}[c]	ΔE_{CV}[d]	ΔE_{SR}[e]	ΔE_{SO}[f]	ΣD_0(0K)[g]
CH_3 ($^2A_2''$-D_{3h})	306.80	18.38	0.94	−0.17	−0.09	289.10
CH_2F ($^2A'$-C_s)	313.32	15.37	0.96	−0.45	−0.48	297.97
CH_2Cl ($^2A'$-C_s)	287.95	14.00	1.11	−0.41	−0.93	273.71
CH_2Br ($^2A'$-C_s)	274.64	13.72	1.33	−0.22	−3.89	258.13
CH_2I ($^2A'$-C_s)	263.33	13.39	1.67	−0.18	−7.33	244.11
SiH_3 ($^2A_1$ C_{3v})	228.75	13.25	−0.41	−0.48	−0.43	214.18
SiH_2F ($^2A'$-C_s)	284.59	11.00	−0.36	−0.86	−0.82	271.56
SiH_2Cl ($^2A'$-C_s)	244.21	10.36	−0.28	−0.71	−1.27	231.60
SiH_2Br ($^2A'$-C_s)	229.95	9.99	0.05	−0.58	−3.93	215.49
SiH_2I ($^2A'$-C_s)	215.81	9.86	0.61	−0.49	−7.67	198.40
SiH_3F ($^1A_1$-C_{3v})	383.96	17.20	−0.31	−0.95	−0.82	364.69
SiH_3Cl ($^1A_1$-C_{3v})	341.22	16.43	−0.24	−0.80	−1.27	322.47
SiH_3Br ($^1A_1$-C_{3v})	326.30	16.12	0.19	−0.67	−3.93	305.76
SiH_3I ($^1A_1$-C_{3v})	310.57	15.85	0.69	−0.58	−7.67	287.15
SiH_3CH_3 ($^1A_1$-C_{3v})	628.54	37.92	0.87	−0.78	−0.52	590.18
SiH_3CH_2 ($^2A'$-C_s)	520.21	29.17	0.65	−0.77	−0.52	490.39
SiH_2CH_3 ($^2A'$-C_s)	531.00	31.89	0.77	−0.71	−0.52	498.65
SiH_2FCH_3 ($^1A'$-C_s)	689.64	35.14	1.37	−1.18	−0.91	653.77
SiH_2ClCH_3 ($^1A'$-C_s)	646.75	34.38	0.99	−1.03	−1.36	610.97
SiH_2BrCH_3 ($^1A'$-C_s)	631.78	34.17	1.44	−0.91	−4.02	594.12
SiH_2ICH_3 ($^1A'$-C_s)	611.70	33.90	2.06	−0.79	−7.76	571.30
SiH_3CH_2F ($^1A'$-C_s)	627.51	33.82	1.28	−1.05	−0.91	593.01
SiH_3CH_2Cl ($^1A'$-C_s)	603.60	33.03	0.93	−1.01	−1.36	569.13
SiH_3CH_2Br ($^1A'$-C_s)	592.57	32.70	1.24	−0.83	−4.02	556.26
SiH_3CH_2I ($^1A'$-C_s)	582.43	32.38	1.71	−0.78	−7.76	543.22

[a] The atomic asymptotes were calculated with the R/UCCSD(T) method. [b] Extrapolated by using eq 1 with aVDZ-PP, aVTZ-PP, and aVQZ-PP. [c] The zero point energies were taken as 0.5 the sum of the CCSD(T) harmonic frequencies. [d] Core-valence corrections were obtained with the cc-pwCVTZ (C, F, Si, Cl) and cc-pwCVTZ-PP (for Br and I) basis sets at the optimized CCSD(T)/aVTZ-PP 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 Moore's tables, ref 18. [g] The theoretical value of ΔD_0(0K) was computed with the CBS estimates.

The calculated heats of formation are presented in Table 2 where they are compared with available experimental data. The estimated[1] heats of formation of SiH_3X for X a halogen are all within 1.5 kcal/mol of our calculated values. The calculated values for $\Delta H_f(SiH_3)$ and $\Delta H_f(CH_3)$ are the same as those previously reported[5e,g] and in excellent agreement with experiment.[1,33] The experimental heats of formation of the halomethyl radicals have been reported, and our calculated theoretical values are in excellent agreement with experiment[2] within 1 kcal/mol. Calculations of the heat of formation of CH_2F and CH_2Cl from isodesmic reactions at the MP2 level with a polarized double-ζ basis set (MP2/DZP)[34] are in good agreement with the current high level value. Our calculated values for the heats of formation of the halosilanes are also in excellent agreement with the reported experimental values[1] within the error bar limits and, as noted above, we expect our values to be accurate to ±1 kcal/mol.

Bond Dissociation Energies. We can use our calculated heats of formation to predict a wide range of various BDEs in the halosilanes, methylhalosilanes, and halomethylsilanes, specifically the C−H, Si−H, Si−C, C−X, and Si−X BDEs (Table 3). The adiabatic BDE is defined as dissociation to the ground state of the separated species. For the BDEs under consideration, the adiabatic BDE is equal to the diabatic BDE, which represents dissociation to a configuration most representing the actual bonding in the reactant;[35,36] the BDE for these molecules is from a closed-shell singlet species to two open-shell doublets as the products. The calculated adiabatic BDEs at 0 K for the

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

molecule	theory 0 K	theory 298 K	exptl/other calcd (298 K)
CH_3 (D_{3h})	35.8	35.0	34.8[a]
CH_2F (C_s)	−6.3	−6.9	−7.6 ± 2[b] (−6.8 ± 1.3)[d]
CH_2Cl (C_s)	28.1	27.4	28.0 ± 0.7[b] 29.4 ± 0.8
CH_2Br (C_s)	43.3	40.8	40.4 ± 2[b]
CH_2I (C_s)	54.7	53.8	
SiH_3 (C_{3v})	48.1	46.8	(47.7 ± 1.2)[c]
SiH_2F (C_s)	−42.4	−43.7	
SiH_2Cl (C_s)	7.6	6.4	
SiH_2Br (C_s)	23.3	20.4	
SiH_2I (C_s)	37.9	36.3	
SiH_3F (C_{3v})	−83.8	−88.8	−90 ± 5[a]
SiH_3Cl (C_{3v})	−31.6	−33.8	−33.9 ± 2[a]
SiH_3Br (C_{3v})	−15.3	−19.2	−19 ± 4[a]
SiH_3I (C_{3v})	0.7	−1.8	−0.5 ± 4[a]
SiH_3CH_3 (C_{3v})	−3.0	−6.9	
SiH_3CH_2 (C_s)	45.1	42.5	
SiH_2CH_3 (C_s)	36.9	34.0	
SiH_2FCH_3 (C_s)	−99.8	−103.4	
SiH_2ClCH_3 (C_s)	−46.9	−50.3	
SiH_2BrCH_3 (C_s)	−30.4	−35.6	
SiH_2ICH_3 (C_s)	−10.2	−14.0	
SiH_3CH_2F (C_s)	−39.0	−42.6	
SiH_3CH_2Cl (C_s)	−5.0	−8.5	
SiH_3CH_2Br (C_s)	7.4	2.1	
SiH_3CH_2I (C_s)	17.9	14.0	

[a] Reference 1. [b] Reference 2. [c] Experimental heat of formation given is at 0 K. Reference 33. [d] Reference 34.

TABLE 3: Calculated Bond Dissociation Energies (BDEs) at 0 K (kcal/mol)

BDE	theory	exptl
$SiH_4 \rightarrow SiH_3 + H$	90.2	90.3 ± 1.2,[a] 91.8 ± 0.5,[b] 91.7 ± 0.5,[c] 91.5 ± 2,[d] 91.8 ± 0.5[e]
$SiH_3F \rightarrow SiH_2F + H$	93.1	
$SiH_3Cl \rightarrow SiH_2Cl + H$	90.9	
$SiH_3Br \rightarrow SiH_2Br + H$	90.3	
$SiH_3I \rightarrow SiH_2I + H$	88.8	
$SiH_3F \rightarrow SiH_3 + F$	150.5	152.5 ± 1.2[e]
$SiH_3Cl \rightarrow SiH_3 + Cl$	108.3	109.5 ± 1.7[e]
$SiH_3Br \rightarrow SiH_3 + Br$	91.6	89.9 ± 2.2[e]
$SiH_3I \rightarrow SiH_3 + I$	73.0	71.5 ± 2.0[e]
$CH_3SiH_3 \rightarrow CH_3SiH_2 + H$	91.5	89.6 ± 2,[f] 92.3 ± 3,[d] 92.7 ± 1.2[e]
$CH_3SiH_2F \rightarrow CH_3SiH_2 + F$	155.1	
$CH_3SiH_2Cl \rightarrow CH_3SiH_2 + Cl$	112.3	
$CH_3SiH_2Br \rightarrow CH_3SiH_2 + Br$	95.5	
$CH_3SiH_2I \rightarrow CH_3SiH_2 + I$	72.7	
$CH_3SiH_3 \rightarrow SiH_3 + CH_3$	86.9	89.6 ± 1.2[e]
$CH_3SiH_2F \rightarrow SiH_2F + CH_3$	93.0	
$CH_3SiH_2Cl \rightarrow SiH_2Cl + CH_3$	90.2	
$CH_3SiH_2Br \rightarrow SiH_2Br + CH_3$	89.5	
$CH_3SiH_2I \rightarrow SiH_2I + CH_3$	83.7	
$CH_3SiH_3 \rightarrow SiH_3CH_2 + H$	99.8	
$SiH_3CH_2F \rightarrow SiH_3CH_2 + F$	102.6	
$SiH_3CH_2Cl \rightarrow SiH_3CH_2 + Cl$	78.7	
$SiH_3CH_2Br \rightarrow SiH_3CH_2 + Br$	65.9	
$SiH_3CH_2I \rightarrow SiH_3CH_2 + I$	52.8	
$SiH_3CH_2F \rightarrow CH_2F + SiH_3$	80.9	
$SiH_3CH_2Cl \rightarrow CH_2Cl + SiH_3$	81.2	
$SiH_3CH_2Br \rightarrow CH_2Br + SiH_3$	83.9	
$SiH_3CH_2I \rightarrow CH_2I + SiH_3$	84.9	

[a] Reference 33. [b] Reference 39. [c] Reference 40. [d] Reference 41. [e] Reference 42. [f] Reference 43.

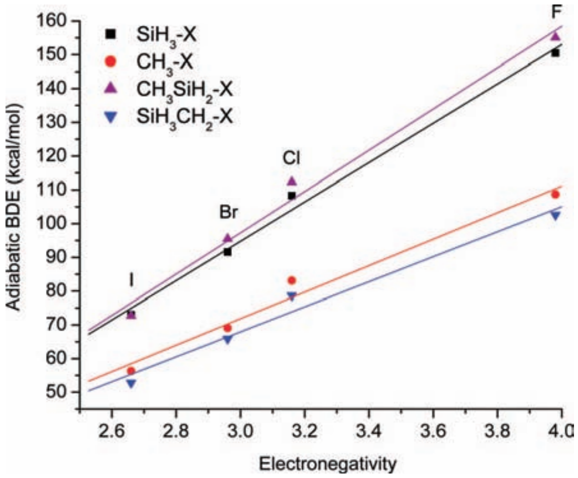

Figure 1. Plot of the calculated adiabatic BDE (kcal/mol) at 0 K as a function of the electronegativity of the halogen substituent.

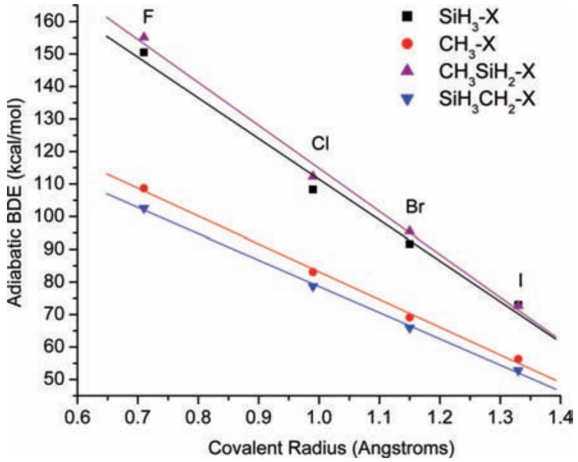

Figure 2. Plot of the calculated adiabatic BDE (kcal/mol) at 0 K as a function of the covalent radii (Å) of the halogen substituent.

halosilanes, methylhalosilanes, halomethanes,[37] and halomethylsilanes as a function of the electronegativity[38] and the covalent radii[38] of the halogen substituent are provided in Figures 1 and 2 respectively.

As expected, the Si−H BDE in SiH_4 is in excellent agreement with the various reported experimental Si−H BDEs.[3,33,39−42] Substitution of a halogen atom for H leads to only a small change (<3 kcal/mol) in the Si−H BDE. Substitution of a fluorine atom leads to a slight increase, of a chlorine or bromine atom to no change, and of an iodine atom to a small decrease. The experimental Si−X BDEs are available and the calculated Si−X BDEs are in excellent agreement with the reported experimental values.[42] The Si−F BDE in SiH_3F is 60 kcal/mol larger than the Si−H BDE in SiH_4 or SiH_3F. The Si−Cl BDE in SiH_3Cl is 42 kcal/mol less than the H_3Si−F BDE and is larger by 17 kcal/mol than the $ClSiH_2$−H BDE. In SiH_3Br, the Si−Br BDE is comparable to the Si−H BDE in SiH_4 and SiH_3Br. The Si−Br BDE in SiH_3Br is 59 kcal/mol smaller than the H_3Si−F BDE. The Si−I BDE in SiH_3I is the smallest of the halosilanes, 78 kcal/mol less than the Si−F BDE in SiH_3F. In contrast to the other halosilanes, the Si−I BDE in SiH_3I is smaller by 16 kcal/mol when compared to the equivalent Si−H BDE in SiH_3I. There is a direct correlation between the increase in the H_3Si−X bond distance and the decrease in H_3Si−X BDE. As illustrated in Figure 1, there is a direct correlation (R^2 value of 0.987) between the decrease in the H_3Si−X BDE and the decrease in the electronegativity of the halogen substituent.[38] There is also an excellent correlation (R^2 value of 0.995) between the H_3Si−X BDE and the covalent radii of the halogen substituent (Figure 2).[38]

The effect of substituting a methyl group for H on the Si−H and Si−X BDEs was also studied. The Si−H BDE in CH_3SiH_3 increases by 1.3 kcal/mol as compared to the Si−H BDE in

TABLE 4: Calculated Si−X and Si−C Stretching Frequencies at the CCSD(T)/aVTZ-PP Level (cm^{-1})

molecule	freq	molecule	freq
$H_3Si{-}F$	870.9	$H_3CSiH_2{-}I$	356.3
$H_3Si{-}Cl$	546.6	$H_3Si{-}CH_3$	703.7
$H_3Si{-}Br$	427.2	$H_3Si{-}CH_2F$	770.7
$H_3Si{-}I$	361.6	$H_3Si{-}CH_2Cl$	758.1
$H_3CSiH_2{-}F$	861.2	$H_3Si{-}CH_2Br$	752.1
$H_3CSiH_2{-}Cl$	524.3	$H_3Si{-}CH_2I$	738.0
$H_3CSiH_2{-}Br$	412.6		

SiH_4 in excellent agreement with the reported experimental values.[3,41,43] The slight increase in the Si−H BDE can be accounted for by the electron donating effect of the methyl group. Except for CH_3SiH_2I, methyl substitution leads to an increase in the Si−X BDE by 4 to 5 kcal/mol when compared to the analogous halosilane, again consistent with the electron donating ability of the methyl group. In CH_3SiH_2I, methyl substitution has no effect on the Si−I BDE compared to SiH_3I. The corresponding $H_3Si{-}X$ bond distances are all shorter on average by ~0.01 Å compared to the $CH_3SiH_2{-}X$ bond distance. This is opposite to what would be expected given the larger Si−X BDEs of the CH_3SiH_2X molecules showing that bond strength near the minimum may not directly correlate with the adiabatic BDE. The $H_3Si{-}X$ and $CH_3SiH_2{-}X$ stretching frequencies (Table 4) decrease with increasing atomic number with the $H_3Si{-}X$ stretching frequencies on average 14 cm^{-1} larger than those of $CH_3SiH_2{-}X$, which is again not consistent with the larger Si−X BDE found for the methylhalosilanes but is consistent with the change in the geometry. There are excellent correlations of the electronegativity[38] and covalent radii[38] (Figures 1 and 2) of the halogen substituent with the $CH_3SiH_2{-}X$ BDE.

For the methylhalosilanes, the effect of halide substitution at the silyl group on the Si−C BDE can be studied. The calculated Si−C BDE in methylsilane is in good agreement with the reported experimental value.[42] Except for CH_3SiH_2I, halide substitution leads to increases in the Si−C BDEs in CH_3SiH_2X (X = F, Cl, Br) by 6.1, 3.3, and 2.6 kcal/mol, respectively. In CH_3SiH_2I, the Si−C BDE decreases by 3.2 kcal/mol. The trends in the Si−C BDEs are not consistent with the change in the Si−C bond distance in the $H_3C{-}SiH_2X$ molecules, which are longer than those in $H_3Si{-}CH_3$. The trends in the Si−C BDEs are consistent with the Si−C stretching frequencies in the methylhalosilanes, which are all larger than the equivalent frequency in methylsilane (Table 4). The largest difference in the Si−C stretching frequency was predicted to be 67 cm^{-1} for $H_3C{-}SiH_2F$ at the CCSD(T)/aVTZ-PP level, consistent with H_3CSiH_2F having the largest Si−C BDE predicted.

The effect of silyl substitution for H on the C−H and C−X BDEs in methylsilane and the halomethanes and the halomethylsilanes can also be studied. The C−H BDE decreases by 4 kcal/mol compared to the C−H BDE in methane on substitution of the electropositive silyl group, SiH_3 for H.[5g] In the halomethylsilanes, the C−F BDE in SiH_3CH_2F is the largest of the halide substituents. The C−I BDE in SiH_3CH_2I is the smallest of the C−X BDEs in the halomethysilanes, 50 kcal/mol less than the C−F BDE in SiH_3CH_2F. Only for fluoromethylsilane is the C−X BDE larger than the corresponding C−H BDE in methylsilane. Using the previously calculated heats of formation of the halomethanes,[37] we have calculated the $H_3C{-}X$ BDEs and predict that the electropositive silyl group decreases the strength of the C−X BDEs in the halomethylsilanes by an average of 4.3 kcal/mol. The largest effect was predicted for the $SiH_3CH_2{-}F$ BDE, which was calculated to be 6.1 kcal/mol less than the $H_3C{-}F$ BDE. There is an excellent correlation (Figure 1) between the decrease in electronegativity ($R^2 = 0.976$) of the halide substituent and the increase in $SiH_3CH_2{-}X$ bond distance, as well as between the BDE and the covalent radii ($R^2 = 0.998$) (Figure 2). The halomethanes[37] exhibit the same dependence on the electronegativity and covalent radii of the halogen substituent (Figures 1 and 2).

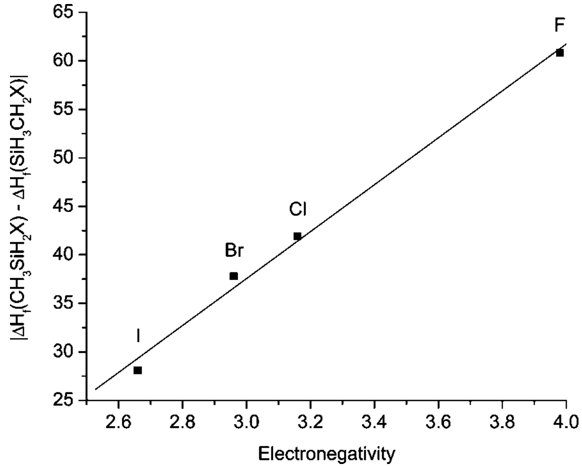

Figure 3. Plot of the magnitude of the energy difference between the calculated $\Delta H_f(CH_3SiH_2X)$ and $\Delta H_f(SiH_3CH_2X)$ of the different isomers (in kcal/mol) at 0 K as a function of the electronegativity of the halogen substituent.

We investigated the effect of halide substitution at the methyl group on the Si−C BDE in the halomethylsilanes. Unlike the methylhalosilanes, the halomethylsilanes all show a decrease in the Si−C BDE when compared to the Si−C BDE in methylsilane. In addition to the electropositive silyl unit, each respective halide substituent has a larger electronegativity compared to that of H leading to a further weakening of the Si−C BDE with the largest effect of halide substitution found for flouromethylsilane. For the halomethylsilanes, the larger the electronegativity of the halide, the larger is the decrease in the Si−C BDE. The predicted trends in the Si−C BDE are consistent with the Si−C bond distances in the H_3SiCH_2X molecules, which are all longer than the corresponding Si−C bond distance in $H_3Si{-}CH_3$. The predicted trends in the Si−C BDEs are not consistent with the Si−C stretching frequencies in the methylhalosilanes as those for the halomethysilanes are all consistently larger than that of methylsilane (Table 4).

The SiH_3CH_2X isomers are always less stable than the SiH_2XCH_3 isomers and this energy difference correlates linearly with the electronegativity of the halogen as shown in Figure 3. The difference in the isomer energies is due to the fact that the C−H BDE is 8.3 kcal/mol larger than the Si−H BDE in CH_3SiH_3 and that the Si−X BDEs are much larger than the C−X BDEs. For the isomer pairs SiH_3CH_2X/SiH_2XCH_3, the difference in the Si−X and C−X BDEs is 52.5, 33.6, 29.6, and 19.9 kcal/mol for X = F, Cl, Br, and I, respectively. The larger Si−X BDE as compared to the C−X BDE is consistent with the smaller electronegativity of Si leading to a larger electronegativity difference between Si and X and a larger BDE with more ionic character. The respective isomer energy differences of 60.8, 41.9, 37.8, and 28.1 kcal/mol for X = F, Cl, Br, and I, respectively, are to a good approximation given by 8.3 kcal/mol plus the difference in the Si−X and C−X BDEs given above.

Conclusions

We have predicted the heats of formation of the halosilanes, the methylhalosilanes, and the halomethylsilanes, as well as radicals involved in the various bond breaking processes, at the CCSD(T)/CBS level plus additional corrections. The calculated values should be good to ±1.0 kcal/mol, and are in excellent agreement with the available experimental data. Our accurately calculated heats of formation allow us to predict the various adiabatic BDEs for all of the substituted silane compounds to within ±1.0 kcal/mol, dramatically improving the estimates of these important quantities. The Si−H BDE in SiH_3F is the largest of the halosilanes. Only in iodosilane is the Si−H BDE larger than the corresponding Si−X BDE. Except for methyliodosilane, methyl substitution leads to an increase in the Si−X BDE when compared to the Si−X BDE in the halosilanes. Except for methyliodosilane, halide substitution leads to an increase in the Si−C BDE when compared to the Si−C BDE in methylsilane. Fluoromethylsilane has the strongest Si−X BDE of 155.1 kcal/mol at 0 K. Unlike the methylhalosilanes, the halomethylsilanes all show a decrease in the Si−C BDE when compared to the Si−C BDE in methylsilane. The various trends can be explained in terms of the electronegativity of the substituent, the atomic sizes, and the electron donating properties of the methyl substituent.

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Supporting Information Available: Total CCSD(T) energies as a function of basis set, CCSD(T) geometry parameters for CH_2X, SiH_3, SiH_2X, SiH_3CH_2, and SiH_2CH_3; SiH_3X; SiH_3CH_3 and SiH_2XCH_3; and SiH_3CH_2X where (X = F, Cl, Br, and I), and CCSD(T) calculated frequencies (cm^{-1}). This material is available free of charge via the Internet at http://pubs.acs.org.

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