Theoretical study of the thermochemistry of molecules in the Si–C–Cl–H system

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

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Ab initio electronic structure calculations coupled with empirical corrections are used to obtain a self-consistent set of heats of formation for molecules in the series CH_nSiCl_m (n, m = 0–3) and for selected molecules in the series $(CH_3)_nSiH_mCl_p$. Heats of formation are also reported for the series $Cl_nSiSiCl_m$ (m, n = 0–3) and for $HC{\equiv}CSiCl_2H$ and $H_2C{=}CH(SiCl_2H)$. Gibbs free energies as a function of temperature and standard entropies are given for all molecules in the study. Heats of formation are used to evaluate potential pathways for the decomposition of Cl_3SiCH_3, a common silicon carbide chemical vapor deposition precursor. The analysis includes the calculation of the transition state for the 1,2-elimination of HCl from Cl_3SiCH_3.

I. Introduction

Chlorinated silanes are commonly used by industry as reactants in a wide variety of materials synthesis processes. For example, chlorinated organosilanes are used as precursors to polydimethylsiloxanes. In addition, these compounds are used to deposit silicon carbide (SiC) by chemical vapor deposition (CVD). Methylated chlorosilanes such as CH_3SiCl_3 and $(CH_3)_2SiCl_2$ are of particular interest for this application.[1-6] Chlorosilanes such as SiH_2Cl_2, $SiCl_4$, and Si_2Cl_6 can also be used instead of silane and disilane in the chemical vapor deposition (CVD) of silicon because homogeneous nucleation of fine particulates is less likely to occur with these reactants.[1] This broad interest in chlorinated silicon compounds has produced the need for a reliable base of thermodynamic data, which is an important prerequisite for the development of computational models that can assist in developing new manufacturing processes.

Thermodynamic data for compounds in the Si–C–Cl–H and Si_2Cl_m (m = 1–6) systems is very limited. Heats of formation are available only for stable, saturated compounds.[7,8] This makes it particularly difficult to study the gas-phase chemistry occurring during materials synthesis, since the high temperatures that are often used (typically above 1200 K for SiC deposition) produce large numbers of short-lived gas-phase species. Only a few such species have been detected, so that experimental measurements of thermodynamic properties are not often possible.

Ab initio calculations can be used to provide temperature-dependent thermodynamic properties for both stable and unstable species.[9] We have used these methods combined with empirical bond additivity corrections (BAC's) to calculate thermodynamic data for a wide range of silicon compounds, including molecules in the Si–H–Cl,[10] Si_2H_n,[11] Si–C–H,[12] Si–H–F,[13] and Si–N–H–F[14] systems. In this paper we extend our investigations to compounds in the Si–C–Cl–H and Si_2Cl_n (n = 1–6) systems to develop a self-consistent set of heats of formation and other high-temperature thermodynamic data.

II. Theoretical Methods

The theoretical methods used in these calculations have been presented in detail elsewhere.[9,13] A general discussion is provided here, however, for the reader who is not familar with the computational technique.

Molecular geometries, vibrational frequencies, and electronic energies were obtained using the Gaussian series of codes developed by Pople et al.[15] The equilibrium molecular geometry was determined using restricted Hartree–Fock (RHF) theory for closed-shell molecules and unrestricted Hartree–Fock (UHF) theory for open-shell molecules. A 6-31G* split-valence basis set with polarization functions on the heavy atoms was used to describe the electronic wave function. Vibrational frequencies obtained at this level of theory were divided by a factor of 1.12, since they are known to be systematically larger than experimental values.[16]

To obtain accurate electronic energies, higher levels of theory incorporating electron correlation must be used. For this purpose, calculations employing fourth-order Møller–Plesset perturbation theory with single, double, triple, and quadruple excitations were performed (MP4(SDTQ)), using a split-valence basis set with polarization functions on all atoms (6-31G**). The electronic energies obtained from MP4 calculations are still not sufficiently accurate to provide useful heats of formation, however. This is primarily a result of the finite basis set. Fortunately, the errors incurred are systematic and can be removed by the application of empirical correction factors. These factors are called bond additivity corrections (BAC's) in the method used here. Their values depend primarily on bond type and bond distance, but are also a function of the identity of neighboring atoms. For a molecule $X_k–X_i–X_j$ the BAC is given by

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

where

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

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

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

A_{ij} and α_{ij} are empirically derived parameters that depend on the X_i–X_j bond type and R_{ij} is the bond distance (angstroms). The factor B_k in eq 4 depends on the identity of atom k. The values of A_{ij} and α_{ij} used in these calculations are given in Table I. Neighboring-atom B_k factors used in this work are B_H = 0.00, B_C = 0.31, B_{Si} = 0.20, and B_{Cl} = 0.42.

In the case of open-shell molecules an additional correction was made for spin contamination of the ground state by excited electronic states. The error in the electronic energy caused by this effect was estimated using the approach of Schlegel[17] and is given by $E_{BAC}(\text{spin}S^2) = E(\text{UMP3}) - E(\text{PUMP3})$, where $E(\text{UMP3})$ is the third-order MP energy using the UHF wavefunction and $E(\text{PUMP3})$ is the projected UMP3 energy. This correction, though generally small (≤ 0.5 kcal mol^{-1}), may become large for molecules containing a high degree of unsaturation or low-lying electronic excited states. Closed-shell molecules that are UHF-unstable, such as SiH_2, also require an additional correction. The form of the correction is $E_{BAC}(\text{spin}_{UHF\text{-unstable}}) = K_{UHF\text{-}1}S(S+1)$, where $K_{UHF\text{-}1}$ is 10.0 kcal mol^{-1} (based on the

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

bond	A	ref species	$\alpha^{a,b}$
Si–Cl	721.93	$SiCl_4$	2.0
Si–C	847.99	SiH_3CH_3	2.5
Si–H	97.79	SiH_4	2.0
C–H	38.61	CH_4	2.0

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

heat of formation of O_3) and S is the spin obtained from the UHF/6-31G** calculation. The BAC's for all molecules in the study are given in Table II with the associated bond length, spin contamination, and UHF-unstable corrections.

The heat of formation at 0 K is obtained by combining the unscaled zero-point energy with the BAC-MP4(STDQ) energy. The entropy, heat capacity, and internal energy are then calculated by applying standard expressions from statisical mechanics, using the HF/6-31G* geometries and scaled frequencies as input. The abbrevation BAC-MP4 is used here to refer to heats of formation determined from the MP4(STDQ) energies.

A major source of error in the thermochemical data is the determination of the molecular heat of formation at 0 K. An estimate of this error was obtained, using the results of calculations made at lower levels of perturbation theory during the determination of the MP4(SDTQ) electronic energy.[9] Bond additivity corrections are applied to the MP2, MP3, and MP4(SDQ) electronic energies to obtain $\Delta H°_f(0)$ at these levels of theory, resulting in the following definition for the estimated error:

$$error(BAC\text{-}MP4) = \{1.0 \text{ kcal mol}^{-1} + (\Delta H_{BAC\text{-}MP4} -$$

$$\Delta H_{BAC\text{-}MP3})^2 + (\Delta H_{BAC\text{-}MP4} - \Delta H_{BAC\text{-}MP4SDQ})^2 +$$

$$0.25(E_{BAC}(spin_S^2) \text{ or } E_{BAC}(spin_{UHF\text{-}I}))^2\}^{1/2} \quad (5)$$

It can be seen from this expression that convergence of $\Delta H°_f(0)$ to a fixed value as the level of theory increases from BAC-MP2 to BAC-MP4 will result in a low value for the calculational error. The magnitude of error(BAC-MP4) also reflects spin and UHF-unstable errors which tend to increase as the molecule becomes more unsaturated. This error estimate does not account for possible inaccuracies in the values of reference heats of formation. In particular, since there are no reference data for molecules containing Si–C double bonds, a potential systematic error exists for this class of compounds.

III. Results and Discussion

The results of applying the BAC-MP4 method to compounds in the Si–C–Cl–H system are given in Tables III–V. Table III lists the values of $\Delta H°_f(0)$ at different levels of theory, from which BAC-MP4 error estimates are calculated. Computed electronic energies, vibrational frequencies, moments of inertia, and Z-matrices are not given here but are available in the supplementary material (see paragraph at the end of the paper). Table IV gives the computed values of $\Delta H°_f(298)$ and BAC-MP4 error estimates, with relevant literature values for comparison. Table V lists $S°(298)$ and values of $\Delta G°_f$ at various temperatures.

A. Heats of Formation and Bond Dissociation Enthalpies. Table III lists the heat of formation at several levels of theory for all the compounds in this study. In almost all cases, $\Delta H°_f(0)$ (the heat of formation at 0 K) is essentially the same at all levels of theory or converges to an approximately constant value. This indicates that error estimates for the BAC-MP4 heats of formation, as measured by eq 5, are usually small. Table IV lists standard heats of formation at 298 K ($\Delta H°_f(298)$) for species in this study; the calculated uncertainties are generally ≤2.5 kcal mol^{-1} for molecules without a high degree of unsaturation. In cases such as CHSiCl, larger uncertainties are found, which are
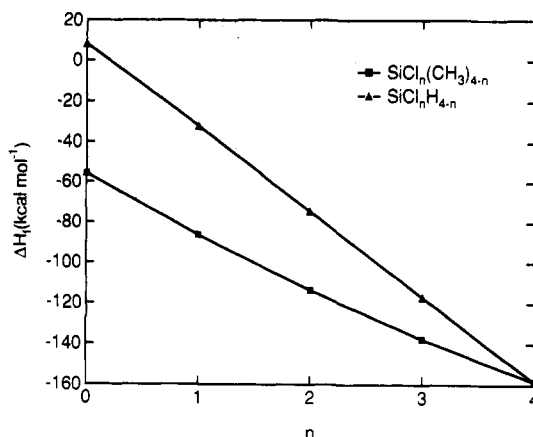

Figure 1. Calculated heats of formation for $SiCl_n(CH_3)_{4-n}$ species compared with those for $SiCl_nH_{4-n}$ species. The slight curvature of the line for the $SiCl_n(CH_3)_{4-n}$ species is indicative of nonlocalized bonding in these molecules.

caused by either spin contamination or UHF-unstable corrections, resulting in a large spin contribution (Table II) to the error estimate.

Trends in the heats of formation of the methylchlorosilanes are observable in the data given in Table IV. Chlorine substitution for methyl groups has a strong stabilizing influence on these compounds. This is consistent with earlier studies that demonstrated this effect in $SiCl_nH_{4-n}$ compounds. Unlike the $SiCl_nH_{4-n}$ species, however, the amount of stabilization decreases as the number of methyl groups replaced by chlorine increases. This is shown in Figure 1, in which the $\Delta H°_f(298)$ is plotted for $SiCl_n(CH_3)_{4-n}$ and $SiCl_nH_{4-n}$ ($n = 0$–4). For the latter compounds,[13] the successive replacement of hydrogen by chlorine decreases $\Delta H°_f(298)$ by 42 kcal mol^{-1} per chlorine. The amount of stabilization that results from chlorine replacement of methyl starts at 30.6 kcal mol^{-1} for the first chlorine and decreases to 20.6 kcal mol^{-1} for the fourth chlorine. This nonlinearity implies that bonding in these systems is not completely localized, which complicates efforts to develop group additivity methods for these compounds. Luo and Benson have addressed this issue by accounting for the ability of the chlorine ligand to π-back-bond to silicon via overlap between the filled Cl(3p) orbital and the empty Si(3d) orbital.[18,19] This produces a significant amount of double-bond character in the silicon–halide bond. It should be noted, however, that π-back-bonding alone cannot explain the nonlinearity of stabilization by chlorine in $SiCl_n(CH_3)_{4-n}$ compounds, since π-back-bonding is possible for both $SiCl_n(CH_3)_{4-n}$ and $SiCl_nH_{4-n}$ compounds. This implies that Si–H bonds are relatively localized, but methyl groups can interact with chlorine ligands in a manner not available to hydrogen.

Reduction of the heat of formation by chlorine substitution can also be observed in unsaturated organosilicon compounds and in organosilicon radicals. For example, chlorine substitution for hydrogen has a large stabilizing effect on silaethylenes. Replacement of each hydrogen bound to silicon in $H_2Si=CH_2$ by chlorine stabilizes the molecule by 37.5 kcal mol^{-1}, a much larger effect than observed when methyl is substituted for hydrogen.[12] Heats of formation for the radical species in this study follow similar trends when chlorine is substituted for methyl. For silyl radicals ($Si(CH_3)_{3-n}Cl_n$, $n = 0$–3), chlorine stabilizes the molecule when it replaces methyl, but the amount of stabilization decreases with increasing numbers of chlorine ligands. This trend does not extend to the silylenes (SiX_nY_{2-n}, $n = 0$–2), where substitution of chlorine for methyl decreases $\Delta H°_f(298)$ by about 34 kcal mol^{-1} in the series $Si(CH_3)_2$, $ClSiCH_3$, $SiCl_2$ (32.2, −2.9, and −36.2 kcal mol^{-1}, respectively).

Among the radical species in this study the silylene $ClSiCH_3$ is of particular interest since silylenes are in general expected to

TABLE II: Bond Additivity Corrections for the MP4(SDTQ) Level of Theory (kcal mol⁻¹)

species	spin or UHF-unstable correction[a]	Si–C bond length[b] (no.)[c]	BAC	Si–Cl bond length (no.)	BAC	Si–H bond length (no.)	BAC	Si–Si bond length	BAC	C–H bond length (no.)	BAC	C–C bond length	BAC
Cl_3SiCH_3		1.858	8.30	2.047 (3)	11.58					1.085 (3)	4.41		
$Cl_2Si(CH_3)_2$		1.867 (2)	8.14	2.069 (2)	11.14					1.085 (6)	4.41		
$ClSi(CH_3)_3$		1.879 (3)	7.93	2.094	10.63					1.086 (6)	4.40		
										1.088 (3)	4.38		
$H_2ClSiCH_3$		1.874	8.16	2.075	11.25	1.470 (2)	4.90			1.087	4.39		
										1.085 (2)	4.41		
HCl_2SiCH_3		1.864	8.27	2.059 (2)	11.47	1.463	4.98			1.085	4.41		
										1.086 (2)	4.40		
$HClSi(CH_3)_2$		1.876 (2)	8.05	2.085	10.93	1.472	4.88			1.085 (2)	4.41		
										1.086 (2)	4.40		
										1.088 (2)	4.39		
Cl_2SiCH_3	u 0.16	1.877	8.02	2.067 (2)	11.30					1.085 (2)	4.41		
										1.086	4.40		
$ClSi(CH_3)_2$	u 0.13	1.886 (2)	7.87	2.091	10.81	1.085				1.085 (2)	4.41		
										1.087 (4)	4.39		
$HClSiCH_3$	u 0.13	1.883	7.98	2.080	11.17	1.475	4.85			1.085	4.41		
										1.086 (2)	4.40		
$ClSiCH_3$	s 2.05	1.903	7.61	2.108	10.56					1.086	4.40		
										1.089 (2)	4.37		
CH_2SiCl_3	u 0.60	1.832	8.84	2.044 (2)	11.64					1.076 (2)	4.49		
					2.048	11.56								
CH_2SiHCl_2	u 0.60	1.840	8.78	2.057 (2)	11.51	1.461	4.99			1.077 (2)	4.48		
CH_2SiH_2Cl	u 0.61	1.847	8.72	2.078	11.18	1.468 (2)	4.92			1.077 (2)	4.48		
$Cl_2Si=CH_2$		1.675	13.08	2.028 (2)	12.09					1.075 (2)	4.50		
$HClSi=CH_2$	s 1.58	1.682	13.09	2.044	11.91	1.459	5.02			1.075	4.50		
										1.076	4.49		
$Cl(CH_3)Si=CH_2$	s 0.09	1.683	12.89	2.054	11.53					1.075	4.50		
		1.868	8.16							1.077	4.48		
										1.085 (3)	4.41		
CH_2SiCl	u 6.86	1.748	11.16	2.064	11.47					1.076	4.49		
										1.077	4.48		
$CHSiCl_3$	u 0.85	1.812	9.26	2.038	11.77					1.072	4.53		
				2.043 (2)	11.65								
$CHSiHCl_2$	u 0.85	1.818	9.26	2.056 (2)	11.53	1.458	5.03			1.072	4.53		
$CHSiH_2Cl$	u 0.87	1.828	9.16	2.073	11.30	1.465	4.95			1.072	4.52		
						1.468	4.92						
$CHSiCl_2$	u 8.69	1.795	9.79	2.056 (2)	11.51					1.073	4.52		
$CHSiHCl$	u 9.20	1.787	10.12	2.072	11.31	1.466	4.94			1.072	4.52		
$CHSiCl$	s 10.12	1.738	11.44	2.130	10.07					1.070	4.55		
$CSiCl_3$	u –2.22	1.886	7.76	2.036	11.84								
				2.038 (2)	11.80								
$CSiHCl_2$	u 0.18	1.825	9.10	2.048 (2)	11.71	1.458	5.03						
$CSiH_2Cl$	u 0.19	1.835	8.98	2.064	11.50	1.465 (2)	4.95						
$CSiCl_2$	u 4.09	1.811	9.42	2.053 (2)	11.58								
$CSiHCl$	s 10.81	1.755	10.95	2.036	12.11	1.462	4.99						
$CSiCl$	u 6.96	1.804	9.70	2.089	10.93								
$HClSi(CH_3)CH_2$	u 0.61	1.850	8.58	2.088	10.87	1.470	4.90			1.077	4.48		
		1.875	8.08							1.078	4.47		
										1.085	4.41		
										1.086	4.40		
										1.087	4.39		
$Cl_2Si(CH_3)CH_2$	u 0.61	1.842	8.66	2.066	11.19					1.076	4.48		
		1.865	8.17	1.070	11.11					1.078	4.47		
										1.085	4.41		
										1.086 (2)	4.40		
$ClSi(CH_3)_2CH_2$	u 0.61	1.854	8.43	2.098	10.56					1.078 (2)	4.47		
		1.877 (2)	7.96							1.086 (4)	4.40		
										1.087 (2)	4.39		
$HC\equiv CSiCl_2H$		1.815	8.87	2.048 (2)	11.70	1.457	5.04			1.059	4.65	1.193	14.78
$H_2C=CH(SiCl_2H)$		1.850	8.34	2.059 (2)	11.48	1.462	4.99			1.077 (2)	4.48	1.326	9.13
										1.079	4.47		
$Cl_3SiCH_3 \rightarrow$ $Cl_2SiCH_2 + HCl^d$		1.729	11.45	1.997 (2)	12.86			1.594[e]	4.37[e]	1.398	2.15		
										1.079 (2)	4.46		
Si_2Cl_6				2.040 (6)	11.84			2.348	5.82				
Si_2Cl_5	u 0.28			2.042	11.81			2.356	5.70				
				2.044 (2)	11.76								
				2.056 (2)	11.66								
$Cl_2SiSiCl_2$	s 7.68			2.064 (4)	11.48			2.459	4.34				
$Cl_3SiSiCl$	s 3.31			2.054 (2)	11.54			2.425	4.74				
				2.059	11.44								
				2.083	11.18								
$Cl_2SiSiCl$	u 4.59			2.062	11.51			2.385	5.29				
				2.070	11.34								
				2.085	11.15								

TABLE II (Continued)

species	spin or UHF-unstable correction[a]	Si–C bond length[b] (no.)[c]	BAC	Si–Cl bond length (no.)	BAC	Si–H bond length (no.)	BAC	Si–Si bond length	BAC	C–H bond length (no.)	BAC	C–C bond length	BAC
Cl$_3$SiSi	u 1.49			2.059 (2)	11.44			2.390	5.23				
				2.065	11.31								
Cl$_2$SiSi				2.049 (2)	11.80			2.202	8.67				
ClSiSiCl	s 5.80			2.125 (2)	10.28			2.437	4.62				
ClSiSi	u 10.03			2.074	11.37			2.263	7.38				
Si$_2$Cl$_5$H				2.041	11.84	1.462	4.98	2.348	5.83				
				2.046 (2)	11.79								
				2.050 (2)	11.71								
HCl$_2$SiSiCl$_2$H				2.056 (4)	11.65	1.462 (2)	4.98	2.348	5.84				
H$_2$ClSiSiCl$_3$				2.047 (2)	11.70	1.467 (2)	4.93	2.346	5.87				
				2.054	11.55								
				2.063	11.65								
HClSiSi	s 5.98			2.063	11.64	1.470	4.91	2.194	8.88				
HSiSiCl	s 3.25			2.163	9.54	1.513	4.50					2.375	5.46

[a] u, UHF-unstable correction; s, spin-contamination correction. [b] In angstroms. [c] Number of bonds. [d] Transition state for this reaction. [e] Bond length and BAC for H–Cl in transition state.

TABLE III: Calculated $\Delta H^\circ_f(0)$ for Si–C–Cl–H Compounds at Various Levels of Theory (kcal mol⁻¹)

species	MP4	BAC-MP2	BAC-MP3	BAC-MP4 SDQ	BAC-MP4 SDTQ	species	MP4	BAC-MP2	BAC-MP3	BAC-MP4 SDQ	BAC-MP4 SDTQ
Cl$_3$SiCH$_3$	−79.3	−135.8	−135.5	−135.5	−135.6	CSiH$_2$Cl	137.5	105.6	105.8	106.1	106.9
Cl$_2$Si(CH$_3$)$_2$	−44.8	−110.1	−109.6	−109.7	−109.8	CSiCl$_2$	125.3	88.3	88.5	88.3	88.6
ClSi(CH$_3$)$_3$	−6.6	−80.8	−80.5	−80.7	−80.6	CSiHCl	158.2	125.6	121.9	121.0	119.4
H$_2$ClSiCH$_3$	−4.2	−46.8	−46.5	−46.5	−46.6	CSiCl	172.7	153.5	153.5	149.4	145.1
HCl$_2$SiCH$_3$	−41.9	−91.5	−91.1	−91.1	−91.3	HClSi(CH$_3$)CH$_2$	39.7	−15.6	−16.0	−16.1	−15.5
HClSi(CH$_3$)$_2$	−5.3	−63.8	−63.5	−63.6	−63.6	Cl$_2$Si(CH$_3$)CH$_2$	0.7	−61.4	−61.8	−61.9	−61.2
Cl$_2$SiCH$_3$	−6.8	−51.6	−50.1	−50.2	−50.8	ClSi(CH$_3$)$_2$CH$_2$	38.4	−32.6	−33.0	−33.2	−32.4
ClSi(CH$_3$)$_2$	30.6	−23.4	−22.1	−22.2	−22.5	HC≡CSiCl$_2$H	25.9	−30.1	−30.2	−31.0	−30.9
HClSiCH$_3$	30.8	−7.3	−6.2	−6.2	−6.5	H$_2$C=CH(SiCl$_2$H)	−4.7	−62.5	−63.1	−63.2	−63.6
ClSiCH$_3$	32.2	0.6	0.8	0.2	−1.2	Cl$_3$SiCH$_3$ → Cl$_2$SiCH$_2$ + HCl[a]	10.0	−43.7	−42.0	−41.2	−42.6
CH$_2$SiCl$_3$	−33.2	−86.4	−87.0	−87.1	−86.4	Si$_2$Cl$_6$	−155.7	−232.7	−230.1	−230.6	−232.6
CH$_2$SiHCl$_2$	3.6	−42.9	−43.3	−43.2	−42.7	Si$_2$Cl$_5$	−87.1	−152.2	−149.0	−149.5	−151.7
CH$_2$SiH$_2$Cl	40.9	1.4	1.1	1.1	1.6	Cl$_2$SiSiCl$_2$	−38.2	−92.8	−89.7	−90.6	−96.2
Cl$_2$Si=CH$_2$	13.3	−31.6	−32.4	−32.6	−32.9	Cl$_3$SiSiCl	−45.8	−97.7	−95.4	−96.4	−99.6
HClSi=CH$_2$	45.1	5.7	5.5	5.2	4.5	Cl$_2$SiSiCl	19.0	−24.0	−20.9	−22.1	−24.8
Cl(CH$_3$)Si=CH$_2$	44.8	−8.9	−9.3	−9.6	−10.1	Cl$_3$SiSi	14.5	−25.7	−24.0	−24.8	−26.4
CH$_2$SiCl	85.0	47.2	48.1	46.7	46.6	Cl$_2$SiSi	64.6	36.3	35.0	34.5	32.4
CHSiCl$_3$	14.9	−35.3	−36.0	−36.0	−34.9	ClSiSiCl	63.8	36.6	38.1	36.6	32.8
CHSiHCl$_2$	51.0	7.7	7.3	7.4	8.3	ClSiSi	127.4	100.1	101.0	99.6	98.6
CHSiH$_2$Cl	87.9	51.6	51.3	51.3	52.2	Si$_2$Cl$_5$H	−118.4	−188.2	−186.0	−186.3	−188.1
CHSiCl$_2$	75.8	30.2	29.7	29.2	29.7	HCl$_2$SiSiCl$_2$H	−81.2	−143.8	−141.8	−142.0	−143.6
CHSiHCl	108.7	69.0	68.6	68.0	68.6	H$_2$ClSiSiCl$_3$	−82.7	−145.3	−143.3	−143.5	−145.0
CHSiCl	125.0	94.8	92.6	90.6	88.9	HClSiSi	98.7	71.2	69.1	68.8	67.3
CSiCl$_3$	49.6	37.9	15.8	10.6	8.6	HSiSiCl	102.0	82.8	83.1	81.9	79.2
CSiHCl$_2$	101.4	62.4	62.4	62.8	63.6						

[a] Transition state for the indicated reaction.

be products of the thermal decomposition of silanes. The singlet–triplet splitting in these molecules has been correlated with silylene reactivity with respect to insertion into single and double bonds.[12,20,21] In an earlier paper it was shown that the magnitude of this splitting increases with the electronegativity of the substituents.[12] In ClSiCH$_3$, ΔH° (singlet–triplet) is 37.2 kcal mol⁻¹, which is nearly the mean of the splittings for Si(CH$_3$)$_2$ and SiCl$_2$. This is consistent with localized bonding in the molecules and indicates that measurement of activation energies for insertion for a few SiX$_2$ species should allow those for mixed species to be predicted.

Table V gives entropies and free energies of formation at selected temperatures. Polynomial fits to the temperature dependence of the enthalpy, entropy, and heat capacity, in the format used by the NASA[22] and CHEMKIN[23,24] thermochemical data bases, are given in Table XII of the supplementary material.

Bond dissociation energies (BDE) for most of the species in this study are given in Table VI. As is the case with the heats of formation, patterns can be discerned that reflect the nonlocalized nature of the bonding in the compounds containing both methyl and chlorine ligands. For example, substitution of methyl

for chlorine strengthens the Si–Cl bond by about 2.5 kcal mol⁻¹; in contrast, hydrogen substitution has a much weaker effect and can even weaken the Si–Cl bond. These effects are illustrated in Figure 2, which shows two different views of the surface of Si–Cl bond strengths formed from all possible combinations of H, Cl, and CH$_3$ ligands. The dashed lines in the figure correspond to constant numbers of methyl groups, showing that varying the number of hydrogen and chlorine ligands typically has little effect on the Si–Cl BDE. In contrast, exchanging methyl for hydrogen with a constant number of chlorine ligands increases the Si–Cl BDE by about 3.5 kcal mol⁻¹ (solid line, Figure 2A). Note that this case corresponds to constant d-pπ back-bonding. Exchanging methyl for Cl also increases the Si–Cl BDE, but by a smaller amount, roughly 2.3 kcal mol⁻¹ per methyl (solid line Figure 2B).

The high–low–high variation of the Si–Cl BDE in the Cl-Si(CH$_3$)$_n$ ($n = 1$-3) series and of the Si–C BDE in the H$_3$C–SiCl$_n$ series ($n = 1$-3) has been observed in other related molecules (SiH$_n$,[10] SiCl$_n$,[10] and Si(CH$_3$)$_n$,[12] $n = 1$-4) and is indicative of the added stability associated with the singlet relative to the triplet divalent state of silicon. Walsh has defined the divalent-state stabilization energy (DSSE) as DSSE = BDE(R$_3$Si–R) –

TABLE IV: Calculated $\Delta H°_f(298)$ for Si–C–Cl–H Compounds at the BAC–MP4(SDTQ) Level of Theory with Error Estimates[a] (kcal mol⁻¹)

species	BAC–MP4(SDTQ)	lit. values	species	BAC–MP4(SDTQ)	lit. values
Cl_3SiCH_3	−137.8 ± 1.0	−136 ± 3;[b] −126.4[c]	$Cl_3SiCH_3 \rightarrow$	−44.8 ± 1.8	
$Cl_2Si(CH_3)_2$	−113.7 ± 1.0	111 ± 2[b]	$Cl_2SiCH_2 + HCl$		
$ClSi(CH_3)_3$	−86.3 ± 1.0	−84.6 ± 1;[b] −85.1[d]	Si_2Cl_6	−232.8 ± 3.4	−228.9;[e] −243.5[g]
$H_2ClSiCH_3$	−50.1 ± 1.0	−50.2 ± 2;[b] −51.3[d]	Si_2Cl_5	−151.7 ± 3.7	
HCl_2SiCH_3	−94.2 ± 1.0	−93.9 ± 2[b]	$Cl_2SiSiCl_2$	−95.7 ± 9.4	−129.5[i]
$HClSi(CH_3)_2$	−68.2 ± 1.0	−67.4 ± 2;[b] −68.2[d]	$Cl_3SiSiCl$	−99.6 ± 5.6	−127.0[i]
Cl_2SiCH_3	−52.8 ± 1.4	−58.1[e]	$Cl_2SiSiCl$	−24.4 ± 5.4	
$ClSi(CH_3)_2$	−26.2 ± 1.1	−33.1[e]	Cl_3SiSi	−26.2 ± 3.2	
$HClSiCH_3$	−9.1 ± 1.1	−17.0[e]	Cl_2SiSi	32.7 ± 3.5	
$ClSiCH_3$	−2.9 ± 2.8	−13.6[e]	$ClSiSiCl$	33.5 ± 7.2	
CH_2SiCl_3	−87.7 ± 1.4		$ClSiSi$	99.1 ± 5.7	
CH_2SiHCl_2	−44.7 ± 1.3		Si_2Cl_5H	−189.0 ± 3.0	−193.1[h]
CH_2SiH_2Cl	−0.9 ± 1.2		$HCl_2SiSiCl_2H$	−145.2 ± 2.6	−157.8[h]
$Cl_2Si{=}CH_2$	−34.2 ± 1.2		$H_2ClSiSiCl_3$	−146.6 ± 2.5	−152.8[h]
$HClSi{=}CH_2$	2.6 ± 1.8		$HClSi$	67.1 ± 3.9	
$Cl(CH_3)Si{=}CH_2$	−13.1 ± 1.3		$HSiSiCl$	79.1 ± 5.1	
CH_2SiCl	45.7 ± 3.9		$SiCl_3$	−76.0 ± 1.6[j]	
$CHSiCl_3$	−35.3 ± 2.0		$SiHCl_2$	−33.4 ± 1.4[j]	
$CHSiHCl_2$	7.2 ± 1.7		SiH_2Cl	7.9 ± 1.1[j]	
$CHSiH_2Cl$	50.5 ± 1.7		$SiCl_2$	−36.2 ± 3.7[j]	
$CHSiCl_2$	29.6 ± 4.5		$SiCl$	37.8 ± 2.3[j]	
$CHSiHCl$	67.9 ± 4.8		$HSiCl$	15.9 ± 2.6[j]	
$CHSiCl$	89.1 ± 6.6		SiH	91.0 ± 1.1[j]	
$CSiCl_3$	9.0 ± 7.6		SiC	171.9[c]	
$CSiHCl_2$	63.2 ± 1.8		Si	107.4 ± 0.0[j]	
$CSiH_2Cl$	105.9 ± 1.7		CH_3	34.9 ± 1.2[k]	
$CSiCl_2$	89.1 ± 2.3		CH_2	92.8 ± 1.4[k]	
$CSiHCl$	119.5 ± 6.3		CH	143.4 ±2.0[k]	
$CSiCl$	146.1 ± 10.1		C	171.2 ± 0.0[k]	
$HClSi(CH_3)CH_2$	−19.2 ± 1.3		$CHCH_2$	71.0 ± 3.5[k]	
$Cl_2Si(CH_3)CH_2$	−64.3 ± 1.3		C_2H	132.2 ± 6.4[k]	
$ClSi(CH_3)_2CH_2$	−37.2 ± 1.4		Cl	29.0 ± 0.0[k]	
$HC{\equiv}CSiCl_2H$	−31.8 ± 1.2		H	52.1 ± 0.0[k]	
$H_2C{=}CH(SiCl_2H)$	−66.3 ± 1.2	−95.1[f]			

[a] Error estimates indicate only relative appliability of the calculational methods. See text for discussion. [b] Reference 7. [c] Reference 31. [d] Reference 19. [e] Reference 34. [f] Reference 33. [g] Reference 26. [h] Reference 35. [i] Reference 36. [j] Reference 13. [k] Reference 24.

BDE(R_2Si–R). The strong stabilizing influence of Cl is illustrated by the increase in DSSE from 29.2 to 42.6 kcal mol⁻¹ in going from $Si(CH_3)_2$ to $SiCl_2$ as the divalent state.

Bonds to hydrogen in these compounds are less affected by substitution at silicon than are the Si–C and Si–Cl bonds. The BDE for Si–H bonds is essentially the same as those in the methylsilanes, with little change observed when chlorine is substituted for methyl. This illustrates the remarkable constancy of the Si–H BDE, which has been remarked upon previously.[12,25] The C–H bonds in CH_3 groups are also essentially unaffected by substitution at silicon and are only slightly weaker than their hydrocarbon analogues. For example, BDE(H–CH_2CCl_3) = 104.4 kcal mol⁻¹, while BDE(H–CH_3SiCl_3) = 102.2 kcal mol⁻¹.

The strength of Si–C double bonds in Cl-substituted silaethylenes decreases dramatically with chlorine substitution at silicon. The BDE's for $H_2Si{=}CH_2$, $HClSi{=}CH_2$, and $Cl_2Si{=}CH_2$ are 116.9, 106.0, and 90.9 kcal mol⁻¹, respectively; the double bond in the last compound is actually weaker than the SiC single bond in H_3SiCH_3. It is expected that the double bond in these compounds, which is weak relative to those found in hydrocarbons (BDE(C_2H_4) = 172 kcal mol⁻¹), should be further weakened by chlorine substitution, since electrons in the filled 3p orbitals of chlorine can overlap with the π-antibonding orbitals centered on silicon. This can be quantified by calculating the π-bond strength D_π, defined as $D_\pi = D_\sigma(Si-H) + D_\sigma(C-H) - D(H-H) + \Delta H_{hyd}$, which is based on reactions of the type $CH_3SiHCl_2 \rightarrow Cl_2Si{=}CH_2 + H_2$. In this equation, ΔH_{hyd} is the hydrogenation energy of the $Si{=}C$ bond and $D_\sigma(SiCl)$ and $D_\sigma(C-H)$ are bond dissociation energies in CH_3SiHCl_2. In the series $H_2Si{=}CH_2$, $HClSi{=}CH_2$, $Cl_2Si{=}CH_2$, the values of D_π are 41.1, 37.5, and 30.9 kcal mol⁻¹, respectively. From these values it is clear that the σ-bond is weakened as well as the π-bond. Substracting D_π from the total DBE yields 75.8, 68.5, and 60.0 kcal mol⁻¹, respectively, for the

$H_2Si{=}CH_2$, $HClSi{=}CH_2$, and $Cl_2Si{=}CH_2$ σ-bond strengths. This is in contrast with the effect upon Si–C single bonds when chlorine is substituted for hydrogen, where the bond strength actually *increases* from about 2.5 kcal mol⁻¹ for every new chlorine ligand.

In addition to the chlorinated organosilicon species discussed above, we have also included chlorinated disilanes in the series $Cl_nSiSiCl_m$ ($n, m = 1-3$) as well as a few mixed disilicon species containing both Cl and H. As in the other compounds studied, chlorine ligands exert a large stabilizing influence on the molecule. Comparing the heats of formation of Si_2H_6 and Si_2Cl_6, each chlorine on average stabilizes the disilane by 42.0 kcal mol⁻¹, the same as is found for $SiCl_nH_{4-n}$ species. The heats of formation of Si_2Cl_5H and $H_2ClSiSiCl_3$ relative to Si_2Cl_6 demonstrate that the 42.0 kcal mol⁻¹ stabilization is not affected by the number of chlorine ligands in the molecule. Thus, like the related molecules containing only one silicon atom, chlorine replacement of hydrogen results in an essentially fixed amount of thermodynamic stabilization, indicating that heats of formation for higher silanes containing only silicon, hydrogen, and chlorine should be calculable within 1–3 kcal mol⁻¹ using group additivity methods.

The Si–Cl BDE's display a similar high–low–high pattern for the Si_2Cl_n ($n = 1-6$) series. The silylene $Cl_3SiSiCl$, like other silylenes studied, is a ground-state singlet with a DSSE of 29.0 kcal mol⁻¹. This represents a substantial stabilization of the divalent state, as expected, but not as large as observed for $SiCl_4$, where the DSSE is 42.6 kcal mol⁻¹. The Si–Si bonds in these compounds are marginally stronger than the one in disilane (81 kcal mol⁻¹ in Si_2Cl_6 vs 76 kcal mol⁻¹ in Si_2H_6), which is in reasonable agreement with an estimate derived from appearance potentials of 77 kcal mol⁻¹.[26] This result shows that Si–Si bonds are essentially unaffected by substitution at silicon. Bonds between silicon and hydrogen are about the same in the chlorinated

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

species	$\Delta H_f^{\circ a}$ 298	$S^{\circ b}$ 298	$\Delta G_f^{\circ a}$ 300	600	1000	1500	2000	2500
Cl$_3$SiCH$_3$	−137.8	84.5	−123.5	−108.8	−89.0	−64.8	−38.8	−12.0
Cl$_2$Si(CH$_3$)$_2$	−113.7	88.7	−94.3	−73.9	−46.1	−11.9	23.7	59.7
ClSi(CH$_3$)$_3$	−86.3	90.8	−61.0	−34.3	2.1	47.3	93.6	139.9
H$_2$ClSiCH$_3$	−50.1	72.0	−38.7	−26.4	−9.1	12.3	35.5	59.4
HCl$_2$SiCH$_3$	−94.2	79.6	−81.8	−68.6	−50.6	−28.4	−4.5	20.2
HClSi(CH$_3$)$_2$	−68.2	81.6	−49.9	−30.4	−3.7	29.6	64.3	99.3
Cl$_2$SiCH$_3$	−52.8	80.8	−45.3	−37.4	−26.4	−12.8	2.8	19.3
ClSi(CH$_3$)$_2$	−26.2	82.7	−12.9	1.4	21.1	45.8	72.1	99.0
HClSiCH$_3$	−9.1	72.9	−2.6	4.6	14.9	27.8	42.7	58.5
ClSiCH$_3$	−2.9	71.0	−0.4	2.2	6.6	12.3	20.3	29.4
CH$_2$SiCl$_3$	−87.7	90.2	−79.8	−72.2	−62.2	−50.1	−36.1	−21.2
CH$_2$SiHCl$_2$	−44.7	83.3	−38.0	−31.4	−22.3	−11.2	1.8	15.7
CH$_2$SiH$_2$Cl	−0.9	74.2	5.2	11.5	20.5	31.6	44.6	58.5
Cl$_2$Si=CH$_2$	−34.2	75.2	−29.7	−25.1	−18.5	−10.3	0.0	11.4
HClSi=CH$_2$	2.6	68.5	5.8	9.4	14.9	21.9	30.9	41.1
Cl(CH$_3$)Si=CH$_2$	−13.1	78.4	−3.2	7.4	22.2	40.9	61.3	82.4
CH$_2$SiCl	45.7	69.4	43.9	42.4	40.8	39.1	39.6	41.5
CHSiCl$_3$	−35.3	88.4	−31.5	−28.3	−24.3	−19.7	−13.1	−5.5
CHSiHCl$_2$	7.2	80.9	10.0	12.4	15.7	19.7	25.6	32.7
CHSiH$_2$Cl	50.5	73.1	52.3	54.1	56.7	60.0	65.3	71.6
CHSiCl$_2$	29.6	81.1	27.6	25.2	21.9	17.8	15.9	15.3
CHSiHCl	67.9	70.6	65.7	63.5	60.6	57.1	55.9	55.9
CHSiCl	89.1	70.3	82.4	75.7	67.1	56.7	48.8	42.3
CSiCl$_3$	9.0	86.8	8.7	8.0	6.7	5.0	5.5	7.2
CSiHCl$_2$	63.2	77.5	62.3	61.4	60.3	58.9	59.7	61.8
CSiH$_2$Cl	105.9	69.9	103.9	102.3	100.5	98.3	98.4	99.7
CSiCl$_2$	89.1	76.7	83.8	78.3	70.9	61.9	55.4	50.2
CSiHCl	119.5	67.7	113.6	107.7	100.1	90.9	84.1	78.8
CSiCl	146.1	68.1	135.4	124.5	110.3	93.0	78.4	65.4
HClSi(CH$_3$)CH$_2$	−19.1	83.8	−6.2	7.3	25.8	48.7	73.2	98.2
Cl$_2$Si(CH$_3$)CH$_2$	−64.3	92.2	−50.5	−36.6	−17.7	5.5	30.2	55.5
ClSi(CH$_3$)$_2$CH$_2$	−37.2	92.9	−17.2	3.5	31.8	66.7	102.9	139.2
HC≡CSiCl$_2$H	−31.8	82.0	−28.9	−26.1	−22.3	−17.4	−10.4	−2.5
H$_2$C=CH(SiCl$_2$H)	−66.3	84.7	−54.9	−43.0	−26.7	−6.5	15.5	38.2
Cl$_3$SiCH$_3$ → Cl$_2$SiCH$_2$ + HCl^c	−44.8	90.4	−32.3	−19.4	−2.0	19.5	43.0	67.4
Si$_2$Cl$_6$	−232.7	111.1	−215.5	−198.9	−177.5	−152.0	−122.7	−91.2
Si$_2$Cl$_5$	−151.7	109.1	−141.8	−132.4	−120.5	−106.5	−88.4	−67.9
Cl$_2$SiSiCl$_2$	−95.7	102.1	−91.7	−88.1	−83.6	−78.4	−68.9	−56.8
Cl$_3$SiSiCl	−99.6	101.5	−95.4	−91.9	−87.4	−82.1	−72.6	−60.4
Cl$_2$SiSiCl	−24.4	92.4	−25.5	−26.8	−28.5	−30.8	−28.4	−23.3
Cl$_3$SiSi	−26.2	89.4	−26.4	−26.7	−27.1	−27.7	−23.7	−16.9
Cl$_2$SiSi	32.7	79.9	27.4	22.1	15.4	7.3	4.1	3.8
ClSiSiCl	33.5	81.8	27.6	21.6	14.0	4.6	0.2	−1.5
ClSiSi	99.1	71.4	88.3	77.7	64.2	48.0	36.7	28.7
Si$_2$Cl$_5$H	−189.0	108.0	−174.2	−159.5	−140.7	−118.2	−91.8	−63.2
HCl$_2$SiSiCl$_2$H	−145.3	99.8	−131.3	−117.4	−99.0	−76.9	−51.0	−22.9
H$_2$ClSiSiCl$_3$	−146.6	100.6	−132.9	−119.1	−101.1	−79.5	−54.1	−26.4
HClSiSi	67.1	71.3	61.0	55.1	48.0	39.4	35.6	34.8
HSiSiCl	79.1	73.0	72.5	66.1	58.1	48.3	43.2	41.0

^{a} In kcal mol^{-1}. ^{b} In cal mol^{-1} K^{-1}. ^{c} Transition state.

disilanes as in disilane itself (88.4 kcal mol^{-1} in Si$_2$H$_6$ vs 89.4 kcal mol^{-1} in Si$_2$Cl$_5$H).

B. Methyltrichlorosilane Decomposition. An important motivation for this study is to provide data required to evaluate the importance of organosilicon compounds in the CVD of SiC from chlorosilanes. A common precursor in this process is methyltrichlorosilane (Cl$_3$SiCH$_3$; MTS). Table VII lists reaction enthalpies for several possible decomposition pathways for MTS. As expected from the BDE's discussed earlier, the least favorable pathways from a thermodynamic point of view are reactions 3 and 6, which both involve the breaking of strong Si–Cl bonds. An energetically more favorable path is the simple fission of the Si–C bond to produce a methyl radical and a trichlorosilyl radical (reaction 1). The two lowest energy paths, the extrusion of SiCl$_2$ (reaction 4) and the 1,2-elimination of HCl to give the silaethylene Cl$_2$Si=CH$_2$ (reaction 5), share the same enthalpy of reaction.

The six reactions can be subdivided into two categories: simple bond fission (reactions 1–3) and elimination/insertion reactions (reactions 4–6). The former have activation energies comparable to the bond strength but also high A-factors (typically $\geq 10^{16}$ s^{-1}).[27] The latter type often have activation energies lower than those for bond fission but also have lower A-factors, typically 10^{12}–10^{15} s^{-1}, which is characteristic of their tight transition states.[27] On this basis it is possible to remove some of these reactions from consideration since their rates are likely to be very slow. Thus, reaction 6, with both a high activation energy and an anticipated low A-factor, can be eliminated. Given A-factors comparable to reaction 1, reactions 2 and 3 will also play minor roles in the decomposition process.

For the lowest energy pathways (reactions 4 and 5) to compete effectively with reaction 1, they must have substantially lower activation barriers since their A-factors are at least a factor of 10 times smaller. We thus performed BAC-MP4 calculations to determine the transition-state energies for these two paths. Attempts to determine $\Delta H^{\circ}_f(298)$ for the transition state of reaction 4 (which can be used to calculate the activation barrier for the reaction at infinite pressure) were unsuccessful, however, probably owing to a large activation barrier that leads to the breakage of the weakest bond in the molecule (the Si–C bond) instead of elimination of SiCl$_2$. Instead, a lower limit to this energy was determined from the heat of reaction (81.5 kcal mol^{-1}

TABLE VI: Calculated Bond Dissociation Enthalpies at 298 K (kcal mol^{-1}) for Selected Molecules

bond	BDE	bond	BDE	bond	BDE	bond	BDE
			(a) Si–Cl Bonds				
Cl–SiCl$_3$[a]	111.4	Cl–SiCl$_2$CH$_3$	114.0	Cl–SiCl(CH$_3$)$_2$	116.5	Cl–Si(CH$_3$)$_3$	118.4
		Cl–SiH$_2$CH$_3$	112.2	Cl–SiH(CH$_3$)$_2$	115.5		
		Cl–SiCH$_3$HCl	114.1				
Cl–SiClCH$_3$	78.9	Cl–SiCl$_2$CH$_2$	82.5	Cl–SiCl$_2$CH	93.9	Cl–SiCl$_2$C	109.0
		Cl–SiHClCH$_2$	76.3	Cl–SiHClCH	89.7	Cl–SiHClC	85.3
		Cl–SiH$_2$CH$_2$	70.6	Cl–SiH$_2$CH	83.9	Cl–SiH$_2$C	90.3
		Cl–SiClCH$_2$	108.9	Cl–SiClCH	88.5	Cl–SiClC	86.0
		Cl–SiHCH$_2$	112.2			Cl–SiHC	94.4
		Cl–SiCH$_2$	57.4	Cl–SiCH	64.3	Cl–SiC	54.8
Cl–Si(CH$_3$)$_2$	87.3						
Cl–SiHCH$_3$	86.9						
Cl–SiCH$_3$	106.4						
Cl–Si(CH$_3$)$_2$CH$_2$	78.5	Cl–SiCl(CH$_3$)CH$_2$	80.1	Cl–SiH(CH$_3$)CH$_2$	74.5		
Cl–Si$_2$Cl$_5$	110.1	Cl–SiCl$_2$Si	87.9	Cl–SiHSi	85.3		
Cl–SiClSiCl$_3$	81.1	Cl–SiSiCl$_2$	86.1	Cl–SiSiH	73.3		
Cl–SiCl$_2$SiCl$_2$	84.9	Cl–SiClSiCl	86.9				
Cl–SiClSiCl$_2$	100.5	Cl–SiClSi	95.4				
Cl–SiSiCl$_3$	102.4	Cl–SiSiCl	94.6				
Cl–SiCl$_2$SiCl	104.1	Cl–SiSi	75.7				
			(b) Si–H Bonds				
H–SiHClCH$_3$	93.1	H–SiCl$_2$CH$_3$	93.5	H–SiCl(CH$_3$)$_2$	94.1		
		H–SiCl$_2$CH$_2$	62.6	H–SiCl$_2$CH	74.5	H–SiCl$_2$C	78.0
		H–SiHClCH$_2$	55.6	H–SiHClCH	69.5	H–SiHClC	65.7
H–SiClCH$_3$	58.3	H–SiClCH$_2$	95.2	H–SiClCH	73.3	H–SiClC	78.7
H–SiCl$_2$SiCl$_3$	89.4			H–SiClSi	84.1	H–SiSiCl	72.1
			(c) C–H Bonds				
H–CH$_2$SiCl$_3$	102.2	H–CHSiCl$_3$	104.5	H–CSiCl$_3$	96.5		
H–CH$_2$SiCH$_3$Cl$_2$	101.6						
H–CH$_2$Si(CH$_3$)$_2$Cl	101.2						
H–CH$_2$SiHCl(CH$_3$)	101.2						
H–CH$_2$SiH$_2$Cl	101.3						
H–CH$_2$SiCl$_2$	70.6	H–CHSiCl$_2$	115.9	H–CSiCl$_2$	111.6		
H–CH$_2$SiHCl	63.8	H–CHSiHCl	117.4				
H–CH$_2$SiCH$_3$Cl	65.2						
H–CH$_2$SiCl	100.6	H–CHSiCl	95.5	H–CSiCl	109.1		
			(d) Si–C Bonds				
H$_3$C–SiCl$_3$	96.7	H$_2$C–SiCl$_3$	104.5	HC–SiCl$_3$	102.7	C–SiCl$_3$	23.4
H$_3$C–SiHCl$_2$	95.1	H$_2$C–SiHCl$_2$	103.5	HC–SiHCl$_2$	102.8	C–SiHCl$_2$	74.0
H$_3$C–SiH$_2$Cl	92.9	H$_2$C–SiH$_2$Cl	101.6	HC–SiH$_2$Cl	100.8	C–SiH$_2$Cl	73.2
H$_3$C–SiH$_3$[b]	89.6						
H$_3$C–SiCH$_3$Cl$_2$	95.9	H$_3$C–Si(CH$_3$)$_2$Cl	95.0	H$_3$C–Si(CH$_3$)$_3$[b]	93.8	H$_3$C–SiHClCH$_3$	94.0
H$_3$C–SiCl$_2$	51.5	H$_2$C–SiCl$_2$	90.9	HC–SiCl$_2$	77.6	C–SiCl$_2$	46.0
H$_3$C–SiHCl	59.8	H$_2$C–SiHCl	106.0	HC–SiHCl	91.4	C–SiHCl	67.6
H$_3$C–SiCH$_3$Cl	58.2	H$_2$C–SiCH$_3$Cl	103.0				
H$_3$C–Si(CH$_3$)$_2$[b]	63.9						
H$_3$C–SiCl	75.5	H$_2$C–SiCl	84.9	HC–SiCl	92.1	C–SiCl	62.9
H$_3$C–SiCl$_2$CH$_2$	64.9			H$_2$C–SiCH$_3$Cl$_2$	104.3		
H$_3$C–SiHClCH$_2$	56.7			H$_2$C–Si(CH$_3$)$_2$Cl	103.8	HC≡C–SiCl$_2$H	130.0
H$_3$C–Si(CH$_3$)ClCH$_2$	59.0			H$_2$C–SiHCH$_3$Cl	102.8	H$_2$C=CHSiCl$_2$H	103.3
H$_3$C–SiCH$_2$Cl	93.7						
			(e) Si–Si Bonds				
Cl$_3$Si–SiCl$_3$	80.8						
Cl$_3$Si–SiCl$_2$H	79.6						
Cl$_3$Si–SiClH$_2$	78.5						
HCl$_2$SiSiCl$_2$H	78.4						
Cl$_3$Si–SiCl$_2$	39.5	Cl$_3$Si–Si	57.5	Cl$_2$Si–Si	38.5	ClSi–Si	46.0
Cl$_2$Si–SiCl$_2$	23.4	Cl$_2$Si–SiCl	26.0	ClSi–SiCl	42.0		
Cl$_3$Si–SiCl	61.3						
		HClSi–Si	56.2	HSi–SiCl	49.7		

[a] Taken from ref 13. [b] Taken from ref 12.

from Table VII) and the activation barrier for the reverse reaction, $E_a(-4)$. The value of $E_a(-4)$, which is expected to be significant on the basis of calculations[21] and experiments,[28–30] can be estimated by comparison with similar reactions. The only similar reaction for which the temperature dependence of the rate is known is SiF$_2$ + Cl$_2$ → SiF$_2$Cl$_2$, with an activation barrier of 8 kcal mol^{-1}.[28] Since the C–Cl bond is considerably stronger than the Cl–Cl bond (83.8 kcal mol^{-1} vs 58.0 kcal mol^{-1}), $E_a(-4)$ is likely to be significantly larger than this. We thus estimate E_a-(4) = $E_a(-4)$ + $\Delta H°_r$ > 90 kcal mol^{-1}, making it unlikely that

reaction 4 competes significantly with reaction 1 at deposition temperatures unless the A-factor for the forward reaction is ≥10^{15} s^{-1}.

For reaction 5, a calculation of the transition-state geometry and energetics (see Tables II–V for BAC's and thermodynamic properties) shows that the reaction proceeds by dissociation of Cl followed by H abstraction from the methyl group. A value of 93.0 kcal mol^{-1} was obtained for $E_a(5)$. The size of this activation barrier is sufficiently large that, even with an A-factor as large as 10^{15} s^{-1}, the rate of reaction 5 would be a factor of
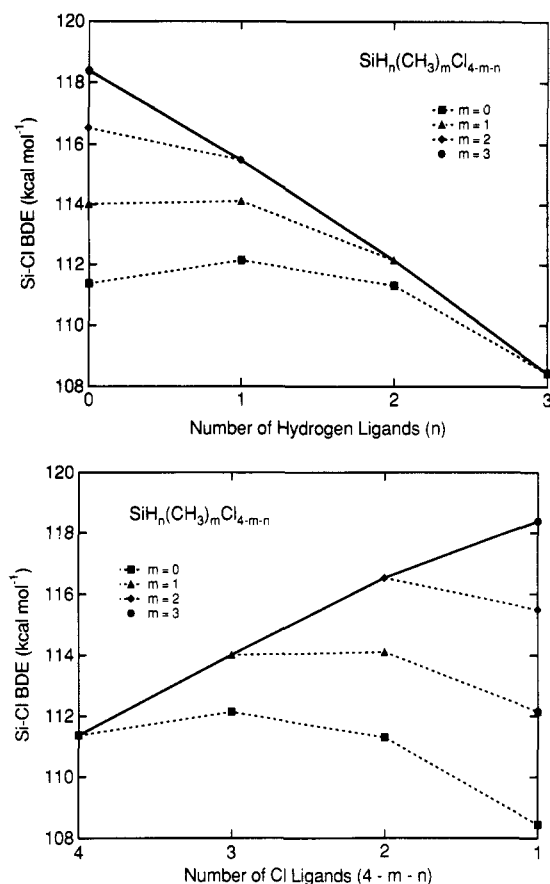
Figure 2. Two views of the surface formed by the Si–Cl bond dissociation energies for all possible compounds in the series $SiH_n(CH_3)_mCl_{4-m-n}$ (n, $m = 0-3$). Dashed lines correspond to constant numbers of methyl groups. A, top: The solid line in this figure corresponds to exchanging methyl for hydrogen with a constant number of chlorine ligands. This case corresponds to constant d–pπ back-bonding. B, bottom: Another view of the same surface. The solid line corresponds to replacement of methyl by chlorine with a constant number of hydrogen ligands.

TABLE VII: Enthalpies of Reaction for Pathways in the Decomposition of Cl_3SiCH_3

no.	reaction	ΔH_r° (kcal mol^{-1})
	bond fission reactions	
1.	$Cl_3SiCH_3 \rightarrow CH_3 + SiCl_3$	96.7
2.	$Cl_3SiCH_3 \rightarrow Cl_3SiCH_2 + H$	102.2
3.	$Cl_3SiCH_3 \rightarrow Cl_2SiCH_3 + Cl$	114.0
	elimination/insertion reactions	
4.	$Cl_3SiCH_3 \rightarrow CH_3Cl + SiCl_2$	81.5
5.	$Cl_3SiCH_3 \rightarrow Cl_2Si{=}CH_2 + HCl$	81.5
6.	$Cl_3SiCH_3 \rightarrow CH_3SiCl + Cl_2$	134.9

2.4 smaller than that of reaction 1 at 1300 K, which is lower temperature bound for SiC CVD. Thus, we estimate that a maximum of 30% of the MTS would decompose by this route (with the remainder of the MTS decomposing through reaction 1).

The combined kinetic and thermodynamic analysis described above indicates that the most favorable pathway for the gas-phase decomposition of MTS is Si–C bond fission. Since SiC deposition typically uses hydrogen as the carrier gas, most of the methyl radical should be converted to methane through the reaction $CH_3 + H_2 \rightarrow CH_4 + H$. The reactivity of the silicon-containing product of reaction 1, $SiCl_3$, is unfortunately not well characterized. One possibility for reaction is the abstraction of chlorine from $SiCl_3$ by the methyl radical formed in reaction 1 ($SiCl_3 + CH_3 \rightarrow SiCl_2 + CH_3Cl$). The heat of reaction for this process is -15.1 kcal mol^{-1}, which partially reflects the stability of the divalent state of silicon, as discussed above. The reactivity of $SiCl_2$ is expected to be relatively low with species such as H_2,

HCl, and CH_4 that are expected to be present in high concentrations in the gas phase of a SiC CVD process.[21,28,30] Thus, we predict that substantial concentrations of this radical could be present during the CVD of SiC.

The analysis also suggests that, under the most favorable circumstances (A-factor for reaction $5 \geq 10^{15}$ s^{-1}), an organosilicon compound ($Cl_2Si{=}CH_2$) could constitute as much as 30% of the initial products of decomposition. This has significant implications for the analysis of gas-phase chemistry in SiC CVD systems, since the identity of the species most responsible for carbon deposition is currently unknown. Unsaturated organosilicon compounds such as $Cl_2Si{=}CH_2$ may have much higher surface reactivities (reactive sticking coefficients > 0.1) than other more abundant carbon-containing compounds such as methane (reactive sticking coefficient $\sim 10^{-4}$). Thus, our results underscore the need for experimental measurements of MTS decomposition rates and product species concentrations in order to assess their importance to the transport of carbon to a growing SiC surface.

C. Comparison with Literature Values. Experimental data and other theoretical predictions for comparison with these results are much more limited than in the case of previously studied compounds in the Si–C–H system.[12] A recent review by Walsh summarizes most of the relevant data.[7] Literature values of ΔH°_f (298) are given in Table IV.

For the chloromethylsilanes, the BAC-MP4 results are in good agreement with the values recommended by Walsh.[7] Other literature sources include a value in the JANAF Tables[31] of -126.4 kcal mol^{-1} for the heat of formation of Cl_3SiCH_3; no source for this number is given. Because of the large difference between this value and the heat of formation recommended by Walsh (which is based on experimental data) as well as the disagreement with the BAC-MP4 prediction, the number given in the JANAF Tables can be safely assumed to be incorrect. Luo and Benson have developed an electronegativity scale that allows heats of formation to be predicted for silanes containing bonds to carbon, hydrogen, and chlorine.[19] Heats of formation predicted by this method for $SiCH_3H_2Cl$ and $Si(CH_3)_2HCl$ compare well with BAC-MP4 predictions for these molecules, lending support to their assumption that the back-bonding energy in these two compounds is the same as that in $Si(CH_3)_3Cl$.

There is one experimental measurement of a BDE available for comparison with our results. Davidson and Dean estimated the strength of the Si–C bond in $(CH_3)_3SiCl$ from low-pressure pyrolysis experiments,[32] with the assumption that there is no activation barrier for the reaction $(CH_3)_2SiCl + CH_3 \rightarrow (CH_3)_3$-SiCl. Their value of 87.5 ± 2 kcal mol^{-1} is significantly smaller than the BAC-MP4 prediction of 95.0 ± 2 kcal mol^{-1}. The pyrolysis may not have occurred at the nonchain limit, as was thought to be the case, which would decrease the measured bond strength somewhat.

In addition to the studies mentioned above, Gadzhiev and Gubareva have measured the enthalpies of formation of five vinylsilanes using the calorimetric combustion method.[33] Combining these values with heats of formation for other silanes available in the literature, they estimated heats of formation for 35 compounds in the $SiH_n(CH_3)_m(CH{=}CH_2)_pCl_{4-n-m-p}$ series ($n, m, p = 0-4$). None of the compounds experimentally studied by them are included in this study. They did, however, estimate $\Delta H^\circ_{f,298}$ for $H_2C{=}CH(SiCl_2H)$, obtaining -95.1 kcal mol^{-1}. This value is substantially different from the BAC-MP4 prediction of -66.3 kcal mol^{-1}. A likely source of this error resides in the combustion calorimetric measurements, which are subject to large errors in the event of incomplete combustion.[7] Thus, further experimental data are needed before these numbers can be assigned confidently.

To our knowledge there are no experimental measurements of thermodynamic quantities for organochlorosilicon radicals. Heats of formation for methylchlorosilyl radicals and CH_3SiCl have

been estimated using the MOBI method.[34] This semiempirical method has been shown previously to be an unreliable method for determining heats of formation for silicon compounds.[7] The values obtained are 5–10 kcal mol^{-1} lower than the BAC-MP4 predictions (Table IV).

A similar dearth of experimental and theoretical information exists for the chlorinated disilanes and related radicals. For Si_2Cl_6, Potzinger et al. derived a value of –243.5 kcal mol^{-1} for the heat of formation, using appearance potential measurements.[26] There is also a MOBI calculation[35] that yielded a value of –228.9 kcal mol^{-1}. Our value is –232.8 ± 3.4 kcal mol^{-1}. Among the radical species, the only data available for comparison are again from MOBI calculations,[36] which are mostly in poor agreement with our results (Table IV).

IV. Summary and Conclusions

Ab inition calculations of the electronic structure of molecules in the Si–C–Cl–H and Si_2Cl_n systems were combined with empirical corrections to yield a self-consistent set of thermodynamic data for these compounds. Although reliable experimental data for comparison are sparse, the predictions for chloromethylsilanes are in good agreement with recommended values,[7] which are based on experimental results. The calculations show that heats of formation in the series $SiCl_n(CH_3)_{4-n}$ (n = 0–4) change nonlinearly with n, in contrast with the constant amount of stabilization that results when chlorine replaces hydrogen in the series $SiCl_nH_{4-n}$ (n = 0–4). This indicates that methyl groups interact with chlorine ligands, showing that bonding in these compounds is not completely localized. Finally, pathways for the decomposition of Cl_3SiCH_3, a compound used to deposit silicon carbide by CVD, have been evalulated using thermodynamic data presented in this study. Included in this analysis is the determination of the energetics and structure of the transition state for the 1,2-elimination of HCl from Cl_3SiCH_3. Analysis of the decomposition of Cl_3SiCH_3, which is a common precursor to silicon carbide in CVD processing, indicates that Si–C bond fission to form CH_3 and $SiCl_3$ is the most likely path for the unimolecular decomposition, with at least 70% of the decomposition occurring by this reaction. The remainder of the Cl_3SiCH_3 is predicted to decompose by 1,2-elimination of HCl, leading to as much as 25% of the product forming as the organosilicon species $Cl_2Si=CH_2$. Experimental results are needed to confirm this prediction and to verify the BAC-MP4 predictions of thermodynamic data.

Appendix

The supplementary data are as follows: Table VIII presents the Z matrices[37] for each of the molecular species obtained from the HF/6-31G* geometry optimization calculations. Molecular geometries can be obtained from these matrices. Table IX gives the moments of inertia in atomic units (amu bohr^2), and Table X lists the scaled vibrational frequencies obtained at the same level of theory. Table XI presents the electronic energies resulting from the various perturbation-theory calculations using the 6-31G** basis set. The projected UHF (PUHF) and projected UMP2 (PUMP2) energies[17] are given for reference, although they are not used in the derivation of the BAC's.

Table XII gives the coefficients for polynomial fits to C_p, H, and S as a function of temperature (300 K $\leq T \leq$ 2500 K) for the species considered in this paper. These fits are used with the CHEMKIN software package[23,24] and are defined by

$$C_p/R = a_1 + a_2T + a_3T^2 + a_4T^3 + a_5T^4$$

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

$$\frac{S}{R} = a_1 \ln T + a_2T + \frac{a_3}{2}T^2 + \frac{a_4}{3}T^3 + \frac{a_5}{4}T^4 + a_7$$

Supplementary Material Available: Tables VIII–XII as described in the Appendix (23 pages). Ordering information is given on any current masthead page.

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