

Heats of Formation of SiH_mCl_n Calculated by ab Initio Molecular Orbital Methods

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Optimized geometries and vibrational frequencies for SiH_mCl_n were calculated at the MP2/6-31G(d,p) level. Energy differences were computed at the MP4/6-31+G(2df,p) level (all structures) and the G-2 level (structures containing no more than two chlorines). The heats of formation of SiH_mCl_n were estimated using the following isodesmic and isogyric reactions: $[(4-n)/4]\text{SiH}_4 + (n/4)\text{SiCl}_4 \rightarrow \text{SiH}_{4-n}\text{Cl}_n$, $\text{SiH}_m + \text{SiH}_{4-n}\text{Cl}_n \rightarrow \text{SiH}_{m-n}\text{Cl}_n + \text{SiH}_4$, $3/4\text{Si} + 1/4\text{H}_2 + \text{SiH}_3\text{Cl} \rightarrow \text{SiCl} + 1/2\text{H} + 3/4\text{SiH}_4$, $1/2\text{Si} + 1/2\text{H}_2 + \text{SiH}_{4-n}\text{Cl}_n \rightarrow \text{SiH}_{2-n}\text{Cl} + \text{H} + 1/2\text{SiH}_4$, and $1/4\text{Si} + 1/2\text{H} + \text{SiH}_{4-n}\text{Cl}_n \rightarrow \text{SiH}_{3-n}\text{Cl}_n + 1/4\text{H}_2 + 1/4\text{SiH}_4$. The calculated heats of formation (kcal/mol; 298 K, 1 atm) are as follows: SiCl , 36.5 ± 1.5 ; SiHCl , 15.0 ± 1.5 ; SiCl_2 , -38.6 ± 1.5 ; SiH_2Cl , 8.0 ± 1.5 ; SiHCl_2 , -34.0 ± 1.5 ; SiCl_3 , -75.8 ± 1.5 ; SiH_3Cl , -32.0 ± 1.5 ; SiH_2Cl_2 , -74.2 ± 1.5 ; SiHCl_3 , -116.8 ± 1.5 (based on experimental values for SiH_n and SiCl_4). The present study uses a significantly higher level of theory than that used in earlier work and confirms the heats of formation predicted by the best previous theoretical studies to within ± 0.8 kcal/mol. The theoretical heats of formation are within the error bars of the most recent experimental values except for SiCl (46 ± 5 kcal/mol), suggesting that a new experimental value would be desirable for SiCl .

Introduction

Chlorosilanes are important reagents in chemical vapor deposition processes used in the semiconductor industry,¹ and reliable heats of formation are essential for any discussion of the mechanistic details of chemical vapor deposition. The thermochemistry of small silicon compounds has been the subject of a number of recent reviews.^{2,3} The heats of formation of the chlorosilanes are fairly well-known experimentally, and reasonable experimental estimates are available for the subchlorides, SiCl_n . The thermochemistry of SiH_mCl_n has also been the subject of a number of theoretical studies.⁴⁻⁷ In general there is good agreement between the recent experimental and theoretical values. In the course of a study of the pathways for thermal decomposition of chlorosilanes,⁸ we had the opportunity to re-examine the heats of formation of SiH_mCl_n ($n + m = 1-4$) at a higher level of theory than that used in previous studies.

The heat of formation of tetrachlorosilane has been measured directly from the heat of chlorination of silicon.⁹ Farber and Srivastava¹⁰ determined ΔH_f° for $\text{SiH}_{4-m}\text{Cl}_m$ and SiCl_n from effusion/mass spectroscopy studies. Walsh et al.^{2b,11} obtained $\Delta H_f^\circ(\text{SiCl}_3)$ from $\text{SiHCl}_3 + \text{I}$, calling into question the value from the effusion/mass spectrometric study. Experimental estimates of $\Delta H_f^\circ(\text{SiCl})$ are also available from spectroscopic studies¹² and from studies on $\text{Si}^+ + \text{SiCl}_4$.¹³

Theoretical studies on the heats of formation of SiH_mCl_n have been carried out with the bond additivity method at the MP4/6-31G(d,p) level (BAC-MP4) with⁴ and without⁵ bond length or spin corrections. These estimates are expected to have error bars of ± 3 kcal/mol. Heats of formation have also been computed using isodesmic reactions at the MP4/6-31G(d) level.^{6,7} Both sets of calculations support Walsh's value for $\Delta H_f^\circ(\text{SiCl}_3)$. Good agreement with experimental is also found for $\text{SiH}_{4-n}\text{Cl}_n$ and SiCl_2 , but SiCl is calculated to be 10 kcal/mol more stable than inferred experimentally.

Computational Method

Ab initio molecular orbital (MO) calculations were carried out with the GAUSSIAN 92 series of programs.¹⁴ Geometries were fully optimized using analytical gradients by second-order Møller-Plesset perturbation theory with the 6-31G(d,p) basis set.¹⁵ Vibrational frequencies, zero-point energies, and thermal

corrections (298 K, 1 atm) were calculated at the MP2/6-31G(d,p) levels using analytical second derivatives.¹⁶ Energy differences for isodesmic reactions were computed by fourth-order Møller-Plesset perturbation theory¹⁷ (MP4SDTQ, frozen core) with the 6-31+G(2df,p) basis set and the G-2 level of theory.¹⁸ In the G-2 method,¹⁸ the energy computed at MP4/6-311G(d,p) is corrected for the effect of diffuse functions obtained at MP4/6-311+G(d,p) and MP2/6-311+G(3df,2p), for the effect of higher polarization functions obtained at MP4/6-311G(2df,p) and MP2/6-311+G(3df,2p), and for the effect of electron correlation beyond fourth-order obtained at QCISD(T)/6-311G(d,p). The average absolute error of the additivity assumptions in the G-2 level of theory is only 0.30 kcal/mol.^{18b} Higher level corrections for deficiencies in the energy are estimated empirically by comparing with well-established atomization energies, ionization energies, electron affinities, and proton affinities. At the G-2 level of theory, the mean absolute error in these energy differences is 1.3 kcal/mol.¹⁸ A similar level of accuracy can be expected in the present study. Because of computational cost, the G-2 level was used only for molecules containing at most two chlorines.

Results and Discussion

The calculated total energies, zero-point energies, and thermal corrections are listed in Table I. The optimized geometries are given in Table II. The MP2/6-31G(d,p) optimized Si-Cl bond lengths are ca. 0.005-0.010 Å shorter than the HF/6-31G(d) values. The valence angles and Si-H bond lengths are within 0.5° and 0.005 Å of the HF/6-31G(d) values. The experimental and theoretical vibrational frequencies are listed in Table III and plotted in Figure 1. The calculated harmonic frequencies are ca. 6% too high, primarily due to the neglect of vibrational anharmonicity. Figure 1 shows a very good linear correlation between theory and experiment ($R^2 = 0.997$). The only significant exceptions are the Si-H stretching modes in SiH_3 . An earlier assignment¹⁹ of the SiH_3 spectrum has been questioned.²⁰⁻²⁴ Accurate experimental values are available for the umbrella and degenerate deformation modes,^{21,22} but the Si-H stretching region is difficult to observe directly because of overlap with SiH_4 . The present MP2 calculations and previous studies^{5a,24} predict the symmetric and degenerate stretches at 2140-2150 and 2180-2190 cm^{-1} , respectively. If the Si-H stretches of SiH_3 are dropped,

TABLE I: Total Energies^a

molecule	6-31G(d,p)	6-31+G(2df,p)		G-2	MP2/6-31G(d,p)	
	MP2	MP2	MP4		ZPE	thermal
SiH (2II)	-289.481 22	-289.489 97	-289.514 04	-289.546 00	3.07	1.48
SiCl (2II)	-748.587 25	-748.643 35	-748.684 74	-748.768 62	0.78	1.60
SiH ₂ (1A ₁)	-290.093 98	-290.106 22	-290.134 49	-290.167 71	7.77	1.80
SiHCl (1A')	-749.195 37	-749.255 01	-749.300 33	-749.385 96	5.10	1.94
SiCl ₂ (1A ₁)	-1208.301 79	-1208.409 87	-1208.472 01	-1208.610 39	1.84	2.37
SiH ₃ (2A ₁)	-290.708 70	-290.721 20	-290.748 64	-290.773 51	14.07	1.87
SiH ₂ Cl (2A')	-749.792 19	-749.852 34	-749.896 98	-749.975 83	10.99	2.04
SiHCl ₂ (2A')	-1208.878 38	-1208.986 56	-1209.048 53	-1209.181 95	7.38	2.49
SiCl ₃ (2A ₁)	-1667.964 35	-1667.120 54	-1668.199 97		3.32	3.18
SiH ₄	-291.349 86	-291.364 78	-291.396 56	-291.419 04	20.57	1.90
SiH ₃ Cl	-750.434 14	-750.496 47	-750.545 32	-750.621 81	17.31	2.10
SiH ₂ Cl ₂	-1209.520 71	-1209.630 82	-1209.696 86	-1209.828 17	13.54	2.56
SiHCl ₃	-1668.607 26	-1668.765 26	-1668.848 59		9.31	3.22
SiCl ₄	-2127.691 64	-2127.897 26	-2127.997 99		4.81	3.99

^a Total energies in atomic units (1 au = 627.51 kcal/mol), zero-point energies (ZPE) and thermal energies (298 K, 1 atm) in kilocalories per mole; G-2 values for SiH_n and SiCl from ref 18. Note that the definition of the G-2 energy includes ZPE.

TABLE II: MP2/6-31G(d,p) Optimized Geometries^a

molecule	symmetry	R(SiH)	R(SiCl)	∠HSiH	∠HSiCl	∠ClSiCl
SiH	C _{∞v}	1.515				
SiCl	C _{∞v}	2.072				
SiH ₂	C _{2v}	1.508		92.33		
SiHCl	C _s	1.509	2.077		95.25	
SiCl ₂	C _{2v}		2.073			101.7
SiH ₃	C _{3v}	1.473		111.2		
SiH ₂ Cl	C _s	1.472	2.056	111.0	109.1	
SiHCl ₂	C _s	1.473	2.047		108.3	110.8
SiCl ₃	C _{3v}		2.043			109.7
SiH ₄	T _d	1.472				
SiH ₃ Cl	C _{3v}	1.468	2.056	110.3	108.6	
SiH ₂ Cl ₂	C _{2v}	1.463	2.042	112.5	108.5	110.5
SiHCl ₃	C _{3v}	1.459	2.032	109.2	109.7	
SiCl ₄	T _d		2.025			

^a Bond lengths in angstroms; angles in degrees.

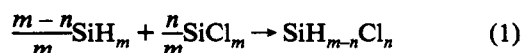
TABLE III: MP2/6-31G(d,p) Vibrational Frequencies^a

molecule	frequencies (cm ⁻¹)
SiH	2144 (1970)
SiCl	547 (534)
SiH ₂	1078 (1004), 2178 (1964), 2178 (1973)
SiHCl	545 (522), 859 (808), 2162
SiCl ₂	208 (202), 540 (502), 540 (514)
SiH ₃	822 (723), 985' (870'), 2325 (1955), 2362' (1999')
SiH ₂ Cl	569, 680, 781, 976, 2324, 2359
SiHCl ₂	185, 538, 608, 700, 802, 2327
SiCl ₃	171', 253, 494 (470), 617' (582')
SiH ₄	974'' (913''), 1018' (972'), 2348 (2186), 2360'' (2189'')
SiH ₃ Cl	572 (551), 691' (663'), 1003' (952'), 1016 (945), 2366 (2201), 2382' (2211')
SiH ₂ Cl ₂	193 (188), 548 (527), 617 (590), 623 (602), 746 (710), 936 (876), 1008 (954), 2390 (2224), 2408 (2237)
SiHCl ₃	180' (176'), 262 (254), 511 (499), 628' (600'), 852' (811'), 2420 (2261)
SiCl ₄	151' (149'), 229'' (220''), 434 (425), 647'' (620'')

^a Experimental (anharmonic) values in parentheses; doubly degenerate marked with a prime; triply degenerate marked with a double prime.

a scale factor of 0.945 ± 0.002 is obtained at the MP2/6-31G(d,p) level. A similar value (0.93) was found in HF/6-31G(d) calculations on SiH_mCl_n⁵ (frequencies below 1900 cm⁻¹ only) and SiH_mF_n²⁵ (all frequencies).

Table IV summarizes the enthalpy differences for three sets of isodesmic and isogyric reactions used in the estimation of the heats of formation of SiH_mCl_n. The first set interpolates between SiH_n and SiCl_n.



Since the experimental ΔH_f° of SiH₄ and SiCl₄ are firmly established,⁹ this reaction is used to estimate the heats of formation

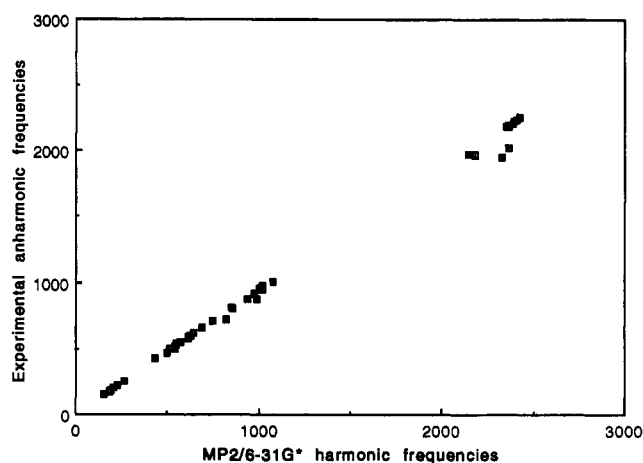
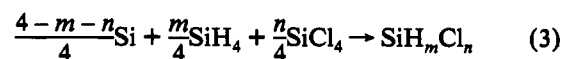


Figure 1. Comparison of experimental anharmonic vibrational frequencies and MP2/6-31G(d,p) calculated harmonic vibrational frequencies.

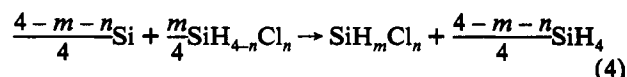
of SiH₃Cl, SiH₂Cl₂, and SiHCl₃. The experimental and theoretical ΔH_f° of SiH, SiH₂, and SiH₃ are in close agreement,^{2,3} but the experimental ΔH_f° of SiCl, SiCl₂, and SiCl₃ are less well-known.² Hence, a different set of reactions must be used. Given the ΔH_f° of SiH, SiH₂, and SiH₃, the heats of formation of SiCl, SiHCl, SiCl₂, SiH₂Cl, SiHCl₂, and SiCl₃ can be computed by transferring the chlorines from SiH_{4-n}Cl_n.



Previous studies have used the bond additivity method^{4,5} to estimate the ΔH_f° of SiH_mCl_n at the MP4/6-31G(d,p) level of theory. Cast into the form of an isodesmic reaction, the bond additivity method uses the following reaction to compute the heat of formation:



This assumes that the corrections for a given bond are independent of the number and nature of the other substituents. There is some evidence that a variety of properties, including the energy, are not linear with the number of halogen substituents.⁶ Since reliable values for the ΔH_f° of SiH_{4-n}Cl_n can be determined from (1), reaction 3 can be modified to keep the number of chlorines bonded to a silicon the same in reactants and products:



Although reactions 3 and 4 are isodesmic, they are not isogyric (i.e. reactants and products do not have the same number of unpaired electrons). This can be remedied by adding the

TABLE IV: Isodesmic Reactions^a

reaction	6-31G(d,p)		6-31+G(2df,p)		G-2	expt ^b
	MP2	MP4	MP2	MP4		
$1/2\text{SiH}_2 + 1/2\text{SiCl}_2 \rightarrow \text{SiHCl}$	1.73		2.05	1.98	1.80	
$2/3\text{SiH}_3 + 1/3\text{SiCl}_3 \rightarrow \text{SiH}_2\text{Cl}$	1.32		1.47	1.56		
$1/3\text{SiH}_3 + 2/3\text{SiCl}_3 \rightarrow \text{SiHCl}_2$	0.70		0.77	0.85		
$3/4\text{SiH}_4 + 1/4\text{SiCl}_4 \rightarrow \text{SiH}_3\text{Cl}$	1.15		1.31	1.42		-0.5
$1/2\text{SiH}_4 + 1/2\text{SiCl}_4 \rightarrow \text{SiH}_2\text{Cl}_2$	0.63		0.73	0.86		-1.5
$1/4\text{SiH}_4 + 3/4\text{SiCl}_4 \rightarrow \text{SiHCl}_3$	-0.15		-0.19	-0.09		-1.9
$\text{SiH} + \text{SiH}_3\text{Cl} \rightarrow \text{SiCl} + \text{SiH}_4$	-12.75		-12.71	-12.87	-12.54	-1.0
$\text{SiH}_2 + \text{SiH}_3\text{Cl} \rightarrow \text{SiHCl} + \text{SiH}_4$	-10.20		-10.19	-10.18	-9.77	
$\text{SiH}_2 + \text{SiH}_2\text{Cl}_2 \rightarrow \text{SiCl}_2 + \text{SiH}_4$	-22.18		-22.59	-22.35	-21.14	-21.0
$\text{SiH}_3 + \text{SiH}_3\text{Cl} \rightarrow \text{SiH}_2\text{Cl} + \text{SiH}_4$	0.66		0.51	0.42	0.25	
$\text{SiH}_3 + \text{SiH}_2\text{Cl}_2 \rightarrow \text{SiHCl}_2 + \text{SiH}_4$	1.03		0.73	0.56	0.39	
$\text{SiH}_3 + \text{SiHCl}_3 \rightarrow \text{SiCl}_3 + \text{SiH}_4$	1.60		1.22	0.94		-1.2
$3/4\text{Si} + 1/4\text{H}_2 + \text{SiH}_3\text{Cl} \rightarrow \text{SiCl} + 1/2\text{H} + 3/4\text{SiH}_4$	20.70		19.92	19.73	19.73	31.4
$1/2\text{Si} + 1/2\text{H}_2 + \text{SiH}_3\text{Cl} \rightarrow \text{SiHCl} + \text{H} + 1/2\text{SiH}_4$	49.51		48.08	48.49	48.86	
$1/2\text{Si} + 1/2\text{H}_2 + \text{SiH}_2\text{Cl}_2 \rightarrow \text{SiCl}_2 + \text{H} + 1/2\text{SiH}_4$	37.53		35.68	36.32	37.49	38.7
$1/4\text{Si} + 1/2\text{H} + \text{SiH}_3\text{Cl} \rightarrow \text{SiH}_2\text{Cl} + 1/4\text{H}_2 + 1/4\text{SiH}_4$	-9.30		-9.49	-9.92	-10.88	
$1/4\text{Si} + 1/2\text{H} + \text{SiH}_2\text{Cl}_2 \rightarrow \text{SiHCl}_2 + 1/4\text{H}_2 + 1/4\text{SiH}_4$	-8.92		-9.27	-9.78	-10.74	
$1/4\text{Si} + 1/2\text{H} + \text{SiHCl}_3 \rightarrow \text{SiCl}_3 + 1/4\text{H}_2 + 1/4\text{SiH}_4$	-8.35		-8.78	-9.40		-8.7

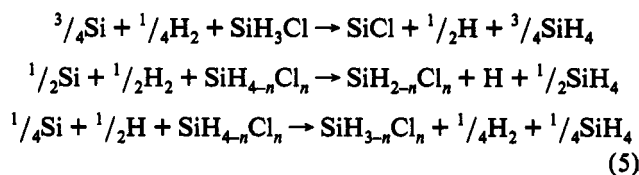
^a Calculated enthalpy differences (298 K, 1 atm) in kilocalories per mole. ^b Using the experimental heats of formation listed in Table V (first entry is used in cases where there is more than one value).

TABLE V: Heats of Formation and Entropies^a

molecule	expt ΔH_f° ₂₉₈	present calc ΔH_f° ₂₉₈	previous calc ΔH_f° ₂₉₈	calc S_{298}
SiH	89.6 ± 1.2 ^b		91.7, ^f 91.0, ^f 89.9, ^k 87.8 ^l	46.0
SiCl	46 ± 5, ^c 47.4 ± 1.6 ^d	36.5	37.9, ^f 37.8, ^f 36.6 ^m	55.6
SiH ₂	65.5 ± 1.0 ^e		68.1, ^f 64.8, ^f 65.7, ^k 62.4 ^l	50.9
SiHCl		15.0	17.0, ^f 15.8 ^l	59.9
SiCl ₂	-40.3 ± 0.8, ^d -39.4 ± 3.4 ^c	-38.6	-37.6, ^l -36.2, ^l -38.9 ^m	68.5
SiH ₃	47.9 ± 0.6 ^d		47.8, ^f 47.4, ^f 47.7, ^k 46.7 ^l	53.9
SiH ₂ Cl		8.0	7.8, ^f 7.9 ^l	62.4
SiHCl ₂		-34.0	-34.3, ^l -34.0 ^l	70.5
SiCl ₃	-80.1 ± 2.2 ^f	-75.8	-76.5, ^l -76.4, ^l -76.4 ^m	75.9
SiH ₄	8.2 ± 0.5 ^e		6.0 ^l	53.7
SiH ₃ Cl	-33.9 ± 2, ^e -32.4 ± 2.5 ^h	-32.0	-32.2, ^l -32.0 ^l	61.9
SiH ₂ Cl ₂	-76.6 ± 3, ^e -75.3 ± 2 ^h	-74.2	-74.5, ^l -74.4 ^l	69.6
SiHCl ₃	-118.6 ± 1.5, ^e -119.3 ± 1.5 ^h	-116.8	-117.0, ^l -117.1 ^l	76.8
SiCl ₄	-158.4 ± 1.3 ^e			83.9

^a 298 K, 1 atm; enthalpies in kilocalories per mole, entropies in calories per mole Kelvin. ^b Reference 26. ^c Reference 13. ^d References 9, and 10a. ^e Reference 27. ^f References 2a, and 11. ^g Reference 9. ^h Reference 10b. ⁱ Reference 5. ^j Reference 4. ^k Reference 25. ^l Reference 18. ^m Reference 7.

appropriate multiple of the reaction $\text{H}_2 \rightarrow 2\text{H}$ to reaction 4 to balance the number of unpaired spins:



Although not as simple as reaction 2, reaction 5 has the advantage that the ΔH_f° for SiH_mCl_n can be computed without reference to the ΔH_f° for SiH, SiH₂, and SiH₃.

For the reactions collected in Table IV, there is generally very good agreement among all of the levels of theory listed (including MP2/6-31G(d,p)). The average absolute difference between the MP4/6-31G(2df,p) and G-2 energies is 0.5 kcal/mol; the largest difference is 1.2 kcal/mol for SiCl₂. This level of agreement illustrates the capabilities of carefully selected isodesmic and isogyric reactions, and validates earlier calculations of the heats of formation of SiH_mF_n based on similar isodesmic reactions.²⁵

The final estimates of the ΔH_f° for $\text{SiH}_{4-n}\text{Cl}_n$ listed in Table V, are obtained from reaction 1 using the MP4/6-31+G(2df,p) energies; the ΔH_f° for the remaining SiH_mCl_n are calculated as an average of the values obtained from reactions 2 and 5 using the G-2 energies for SiCl, SiHCl, SiCl₂, SiH₂Cl, and SiHCl₂ and the MP4/6-31+G(2df,p) energies for SiCl₃. The estimated error in the heats of formation is ±1.5 kcal/mol. The ΔH_f° for SiCl_n are within 0.6 kcal/mol of the values obtained from isodesmic reactions at the MP4/6-31G(d,p) level.⁷ The values for $\text{SiH}_{4-n}\text{Cl}_n$

and $\text{SiH}_{3-n}\text{Cl}_n$ are within 0.7 kcal/mol of the BAC-MP4 calculations.^{4,5} The differences for SiCl₂, SiHCl, and SiCl are somewhat larger but are still inside the ±3 kcal/mol error estimated for BAC-MP4.

Most of the present calculations are within the error bounds of the experimental heats of formation, with the exception of SiCl and SiCl₃. In a kinetic iodination study, Walsh^{2b,11} measured $D_0(\text{Cl}_3\text{Si}-\text{H}) = 91.3 \pm 1.5$ kcal/mol and obtained ΔH_f° ₂₉₈(SiCl₃) = -80.1 ± 2.2 kcal/mol using ΔH_f° ₂₉₈(SiHCl₃) = -119.3 ± 1.6 kcal/mol. The present calculations give $D_0(\text{Cl}_3\text{Si}-\text{H}) = 93.1$ kcal/mol and ΔH_f° ₂₉₈(SiHCl₃) = -116.8 kcal/mol. Thus, the apparent discrepancy for SiCl₃ is due to the value used for the heat of formation of SiHCl₃. Since isodesmic reaction 1 is quite reliable, especially at the level of theory used in the present work, the calculated heat of formation of SiHCl₃ can be combined with the measured $D_0(\text{Cl}_3\text{Si}-\text{H})$ to yield ΔH_f° ₂₉₈(SiCl₃) = -77.6 ± 2.5 kcal/mol.

The experimental ΔH_f° ₂₉₈ for SiCl has been questioned previously.^{2-5,7} Mass spectral/effusion studies give 47.4 ± 1.6 kcal/mol;^{10a} analysis of spectroscopic data yields 32, 33, and 43 kcal/mol;¹² thresholds for $\text{Si}^+ + \text{SiCl}_4 \rightarrow \text{SiCl} + \text{SiCl}_3^+$ give 46 ± 5 kcal/mol.¹³ On the basis of the available data, Walsh^{2b} recommended 37 ± 10 kcal/mol "with caution but not with great confidence". Theoretical calculations consistently predict a heat of formation in the range of 36–38 kcal/mol.³ Until an accurate value for heat of formation for SiCl can be determined experimentally, the present theoretical estimate, ΔH_f° ₂₉₈(SiCl) = 36.5 ± 1.5 kcal/mol, is recommended.

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References and Notes

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