

An ab Initio MO Study of the Thermal Decomposition of Chlorinated Monosilanes, $\text{SiH}_{4-n}\text{Cl}_n$ ($n = 0-4$)

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The reactants, clusters, transition structures, and products for the various channels for the thermal decomposition of $\text{SiH}_{4-n}\text{Cl}_n$ were optimized at the HF/6-31G(d) and MP2/6-31G(d,p) levels. The electron correlation contributions were calculated at the MP4/6-31G(d,p), MP4/6-31+G(2df,p), MP2/6-31++G(3df,3pd), and G-2 levels of theory. In the decomposition of SiH_4 , $\text{SiH}_2 + \text{H}_2$ is favored over $\text{SiH}_3 + \text{H}$. For SiH_3Cl , the $\text{SiHCl} + \text{H}_2$ channel is preferred over the $\text{SiH}_2 + \text{HCl}$ channel, with fragmentation into $\text{SiH}_2\text{Cl} + \text{H}$ and $\text{SiH}_3 + \text{Cl}$ lying significantly higher. The barriers for SiH_2Cl_2 decomposition are $\text{SiCl}_2 + \text{H}_2 \approx \text{SiHCl} + \text{HCl} < \text{SiHCl}_2 + \text{H} < \text{SiH}_2\text{Cl} + \text{Cl} < \text{SiH}_2 + \text{Cl}_2$. For SiHCl_3 , decomposition into $\text{SiCl}_2 + \text{HCl}$ is favored over $\text{SiCl}_3 + \text{H}$, with the $\text{SiHCl}_2 + \text{Cl}$ and $\text{SiHCl} + \text{Cl}_2$ channels lying substantially higher. In tetrachlorosilane, $\text{SiCl}_4 \rightarrow \text{SiCl}_3 + \text{Cl}$ is favored over $\text{SiCl}_4 \rightarrow \text{SiCl}_2 + \text{Cl}_2$.

Introduction

The gas-phase thermochemistry and reactivity of small silicon compounds are of considerable importance in the semiconductor industry, especially for processes such as chemical vapor deposition (CVD).¹ In silicon CVD, materials such as SiH_4 , Si_2H_6 , SiH_2Cl_2 , SiCl_4 , etc., or various mixtures of these, are heated to 400–800 °C. Thermal decomposition of the starting materials is the initial step in the deposition. Kruppa, Shin, and Beauchamp² studied the vacuum flash pyrolysis of SiH_2Cl_2 and SiHCl_3 under heterogeneous conditions and found SiCl_2 and HCl to be the major products. Sausa and Ronn³ used IR multiphoton dissociation to study SiH_2Cl_2 under collision-free conditions and found only SiCl_2 and H_2 ; likewise, Walker, Ring, and O'Neal⁴ found no evidence of HCl in the thermal decomposition of SiH_2Cl_2 in static pyrolysis experiments. Ho, Breiland, and Carr⁵ generated SiHCl from SiH_2Cl_2 by excimer laser photolysis. Lavrushenko, Baklanov, and Strunin⁶ measured the temperature dependence of $\text{SiHCl}_3 \rightarrow \text{SiCl}_2 + \text{HCl}$ and estimated 75 kcal/mol for the high-pressure activation energy. Leitner, Mikulec, and Cerny⁷ studied the high-temperature (1300 K) vapor-phase equilibrium in Si–Cl–H systems by matrix isolation.

The reverse reaction of a silane decomposing into a silylene and a diatomic is a silylene insertion reaction. Rates for silylene insertions have been reviewed recently by Bell and co-workers.⁸ In general, the order of reactivity of the chlorosilylenes is $\text{SiH}_2 > \text{SiHCl} > \text{SiCl}_2$. Jasinski and co-workers⁹ measured the rate of SiH_2 reacting with a variety of diatomics and obtained the order $\text{Cl}_2 > \text{HCl} > \text{H}_2$. Moore et al.¹⁰ found the activation energies for SiH_2 inserting into SiH_4 and HCl to be similar, ca. 1.3 kcal/mol. Ho et al.⁵ determined that the rate of reaction of $\text{SiHCl} + \text{SiH}_4$ is 2–4 orders of magnitude slower than that of $\text{SiH}_2 + \text{SiH}_4$ and found the rate of $\text{SiHCl} + \text{H}_2$ too slow to measure. Safarik et al.⁸ observed that SiCl_2 did not react with H_2 . Doncaster and Walsh¹¹ found SiCl_2 to be unreactive with HCl and SiH_4 .

The experimental thermochemistry of chlorosilanes, -silyl radicals, and -silylenes has been reviewed by Walsh;¹² theoretical calculations of the heats of formation of these species were recently reviewed by Gordon, Francisco, and Schlegel.¹³ Previous theoretical studies have dealt with the thermal decompositions of SiH_4 ,¹⁴ $\text{SiH}_{4-n}\text{F}_n$,¹⁵ Si_2H_6 ,¹⁶ and $\text{Si}_2\text{H}_{6-n}\text{F}_n$ ¹⁷ and the heats of formation of SiH_mF_n ,^{18–21} SiH_mCl_n ,^{22–24} and $\text{SiH}_{4-m-n}\text{F}_m\text{Cl}_n$.²⁵ In connection with the present investigation, we have recalculated the heats of formation of SiH_mCl_n ²⁴ at a level of theory higher

than that used in previous studies and have confirmed earlier theoretical estimates. In contrast to the values for the fluorosilanes, there is good agreement between the experimental and theoretical heats of formation for most SiH_mCl_n species (ΔH_f° (SiCl) is the primary exception). The present paper outlines a theoretical study of the pathways, transition structures, and barriers for thermal decomposition of SiH_3Cl , SiH_2Cl_2 , SiHCl_3 , and SiCl_4 into silyl radicals and atoms and into silylenes and diatomics. Simple radical–radical recombination for neutral species, i.e. the reverse of a single-bond dissociation, should have no activation barrier; hence only the heats of formation of the corresponding silanes and the silyl radicals are required to compute the barriers for thermal decomposition for these channels. On the other hand, silylene insertion reactions generally have small to moderate barriers. Because the thermal decomposition channels involving Cl_2 are significantly higher in energy than most other modes, only insertions into H_2 and HCl are considered in the present study. In the previous work, we have examined the effect of fluorine substitution on the barriers for silylene insertion into H_2 , HF , F_2 , SiH_4 , and $\text{SiH}_{4-n}\text{F}_n$.^{15,17,26,27} Of the insertion reactions considered in this paper, only $\text{SiH}_2 + \text{H}_2$ and $\text{SiH}_2 + \text{HCl}$ have been studied perviously.^{14,28}

Computational Method

Ab initio MO calculations were carried out with the GAUSSIAN 92 series of programs.²⁹ Geometries were fully optimized using analytical gradients at the Hartree–Fock level with the 6-31G(d) basis set and second-order Møller–Plesset perturbation theory with the 6-31G(d,p) basis set.³⁰ Vibrational frequencies and zero-point energies were obtained at the HF/6-31G(d) and MP2/6-31G(d,p) levels using analytical second derivatives.³¹ Energy differences were calculated using second-order and fourth-order Møller–Plesset perturbation theory³² (MP2 and MP4SDTQ, frozen core) and the G-2 level of theory. Because of computational cost, the G-2 calculations were carried out only for molecules containing at most two chlorines. In the G-2 method,³³ 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 additivity assumptions in the G-2 level of theory were tested by computing the energy of the $\text{SiH}_2 + \text{H}_2$ transition state at QCISD(T)/6-311+G(3df,2p); like that of equilibrium geometries, the error due to the

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TABLE I: Total Energies^a

	6-31G(d,p)			6-31+G(2df,p)		MP2/6-311++G(3df,3pd) ^c	G-2
	MP2 ^b	MP4 ^b	MP2 ^c	MP2 ^c	MP4 ^c		
Transition Structures							
SiH ₂ + H ₂	-291.234 62	-291.264 87	-291.245 95	-291.264 55	-291.298 96	-291.304 77	-291.327 85
SiHCl + H ₂	-750.294 84	-750.335 46	-750.316 23	-750.382 90	-750.435 05	-750.455 87	-750.518 33
SiCl ₂ + H ₂	-1209.356 17	-1209.407 20	-1209.387 76	-1209.502 43	-1209.572 38	-1209.608 36	-1209.711 17
SiH ₂ + HCl	-750.283 32	-750.323 61	-750.304 18	-750.367 06	-750.419 97	-750.442 10	-750.505 53
SiHCl + HCl	-1209.361 79	-1209.411 89	-1209.393 90	-1209.506 07	-1209.575 45	-1209.613 45	-1209.714 64
SiCl ₂ + HCl	-1668.439 89	-1668.499 82	-1668.483 07	-1668.645 02	-1668.731 10		
Clusters							
SiH ₂ + H ₂	-291.242 48	-291.273 29	-291.257 55			-291.314 56	
SiHCl + H ₂	-750.332 63	-750.373 61	-750.353 83			-750.484 27	
SiCl ₂ + H ₂	-1209.428 56	-1209.479 44	-1209.459 89			-1209.670 18	
SiH ₂ + HCl	-750.295 10	-750.337 18	-750.317 05			-750.450 19	
SiHCl + HCl	-1209.384 21	-1209.436 51	-1209.415 92			-1209.686 81	
SiCl ₂ + HCl	-1668.478 94	-1668.541 25					

^a Total energies in au; the corresponding total energies are, for H₂, -1.157 65, -1.164 54, -1.157 66, -1.157 66, -1.164 57; for HCl, -460.205 44, -460.223 92, -460.215 62, -460.257 26, -460.284 61; and, for Cl₂, -919.171 14, -919.203 82, -919.191 22, -919.284 23, -919.334 12. ^b Using the HF/6-31G(d)-optimized geometry. ^c Using the MP2/6-31G(d,p)-optimized geometry.

TABLE II: Calculated Vibrational Frequencies

molecule	level ^a	ZPE ^b	frequencies ^c
Transition States			
SiH-H ₂	HF	18.13	1630i, 837, 863, 1027, 1125, 1782, 2263, 2382, 2400
	MP2	17.84	1231i, 810, 821, 1009, 1095, 1774, 2260, 2340, 2367
SiHCl-H ₂	HF	14.79	1742i, 553, 631, 778, 819, 1116, 1720, 2294, 2435
	MP2	14.52	1350i, 550, 616, 744, 811, 1084, 1691, 2283, 2375
SiCl ₂ -H ₂	HF	10.89	1871i, 197, 539, 608, 640, 641, 1025, 1641, 2327
	MP2	10.67	1479i, 187, 527, 592, 628, 633, 978, 1599, 2322
SiH ₂ -HCl	HF	13.60	1475i, 207, 485, 720, 767, 1104, 1506, 2358, 2370
	MP2	13.42	701i, 272, 494, 663, 711, 1083, 1598, 2272, 2292
SiHCl-HCl	HF	10.13	1524i, 88, 227, 581, 623, 693, 925, 1543, 2404
	MP2	10.05	896i, 108, 305, 569, 624, 674, 890, 1558, 2306
SiCl ₂ -HCl	HF	6.15	1538i, 92, 92, 219, 328, 572, 628, 760, 1611
	MP2	6.24	1024i, 108, 133, 207, 393, 575, 604, 685, 1659
Clusters			
SiH ₂ --H ₂	HF	15.93	94, 95, 209, 236, 345, 1129, 2208, 2219, 4611
	MP2	19.17	503, 592, 805, 872, 1048, 1375, 2203, 2212, 3795
SiHCl--H ₂	HF	12.46	19, 34, 60, 100, 205, 532, 901, 2230, 4634
	MP2	12.74	54, 110, 119, 184, 302, 543, 859, 2163, 4582
SiCl ₂ --H ₂	HF	8.88	14, 22, 43, 47, 159, 219, 532, 540, 4638
	MP2	8.98	21, 37, 78, 84, 177, 208, 539, 541, 4596
SiH ₂ --HCl	HF	14.26	76, 99, 247, 363, 480, 1130, 2195, 2207, 3178
	MP2	14.42	106, 144, 296, 463, 577, 1070, 2162, 2165, 3103
SiHCl--HCl	HF	10.81	48, 55, 92, 245, 294, 518, 899, 2237, 3174
	MP2	10.68	42, 67, 103, 246, 359, 527, 856, 2168, 3105
SiCl ₂ --HCl	HF	6.97	24, 43, 52, 84, 208, 224, 523, 538, 3178
	MP2	6.90	32, 53, 69, 89, 192, 212, 527, 540, 3110

^a HF frequencies calculated with the 6-31G(d) basis set at the HF/6-31G(d)-optimized geometry; MP2 frequencies, with the 6-31G(d,p) basis at the MP2/6-31G(d,p)-optimized geometry. ^b In kcal/mol. ^c In cm⁻¹.

additivity assumption is only 0.3 kcal/mol.^{33b} Note that the empirical corrections used in G-2 theory for higher level correlation contributions cancel for the thermal decomposition reactions considered in the present study. Because silylene insertions are very sensitive to the level of calculation, additional calculations were carried out at the MP2/6-311++G(3df,3pd) level to assess the effect of additional diffuse and polarization functions on hydrogen.

Results and Discussion

The calculated total energies for clusters and transition states are given in Table I. The vibrational frequencies and zero-point energies for clusters and transition states are listed in Table II. The corresponding energies and frequencies for the reactants and products are available in previous papers.²²⁻²⁵

Geometries for SiXY + H₂. The transition states for chlorosilylene insertions into H₂ shown in Figure 1 are very similar to those of their fluorine analogues. Optimization of the SiH₂ + H₂ transition state at the MP2/6-311G(2d,2p) level results in

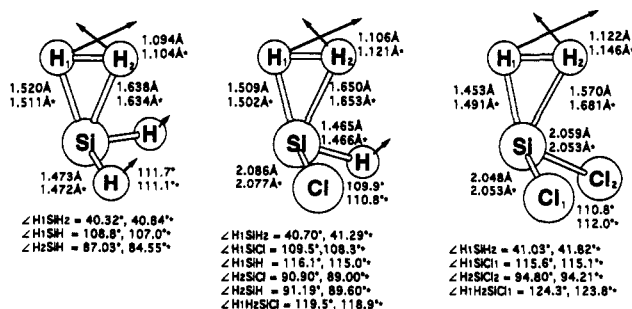


Figure 1. Optimized geometries for the transition structures for elimination of H₂ for SiH₄, SiH₃Cl, and SiH₂Cl₂: HF/6-31G(d), no superscript; MP2/6-31G(d,p), asterisk. Arrows indicate the transition vectors.

only very small changes in the geometry.¹⁴ With halogen substitution on the silylene, the H-H distance lengthens somewhat; the effect of chlorine substitution is smaller than that for fluorine.^{15,26} The average Si-H₂ distance in the transition state increases with both fluorine and chlorine substitution, but effects

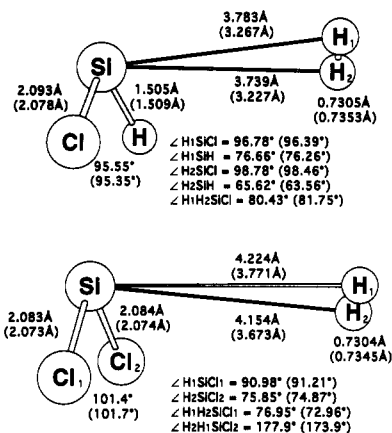


Figure 2. Optimized geometries for the clusters of SiHCl and SiCl₂ with H₂: HF/6-31G(d), no parentheses; MP2/6-31G(d,p), parentheses.

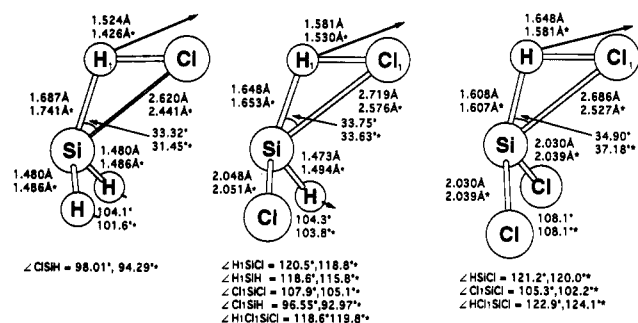


Figure 3. Optimized geometries for the transition structures for the elimination of HCl from SiH₂Cl, SiHCl₂, and SiCl₃: HF/6-31G(d), no superscript; MP2/6-31G(d,p), asterisk. Arrows indicate the transition vectors.

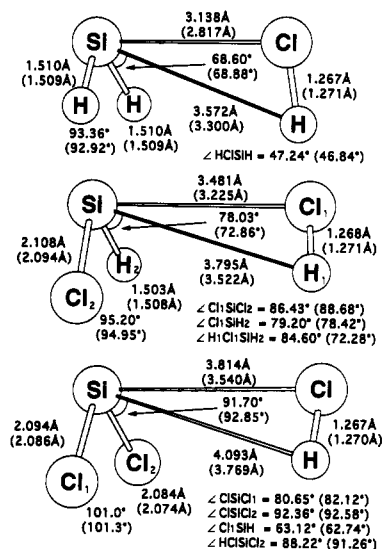


Figure 4. Optimized geometries for the clusters of SiH₂, SiHCl, and SiCl₂ with HCl: HF/6-31G(d), no parentheses; MP2/6-31G(d,p), parentheses.

are small. The clusters between H₂ and the chlorosilylenes (Figure 2) have longer Si-H₂ distances than the corresponding fluorosilylene clusters calculated at the same level; in turn, all of the halosilylene clusters have considerably longer Si-H₂ distances than the SiH₂ + H₂ cluster.

Geometries for SiXY + HCl. Similar to the fluorine case, insertion into HCl can also be viewed as a 1,2 hydrogen shift across an Si-Cl bond (Figure 3). Chlorine substitution results in a longer H-Cl distance and a shorter H-Si distance, i.e. a later transition state for insertion of 1,2 shift. The effect is considerably larger than seen for F substitution or insertion into HF.¹⁵ The

clusters between HCl and the chlorosilylenes have much longer Si-X distances than their fluorine analogues (even after taking into account the difference in the van der Waals radii).

Energetics. The barriers for the insertion reactions are presented in Table III, and well depths for the clusters are collected in Table IV. Chlorine substitution raises the barrier for silylene insertion into H₂ by 17–22 kcal/mol per Cl, whereas fluorine substitution raises the barrier by 22–30 kcal/mol per F.^{15,26} Because the potential energy surface is rather flat in the neighborhood of the transition state, the change in the barrier on re-optimizing the geometry at the MP2 level is rather small. The MP2/6-31G(d,p) barriers at the HF/6-31G(d)- and MP2/6-31G(d,p)-optimized geometries differ by only about 0.5 kcal/mol. However, expanding the basis set to 6-31+G(2df,p) lowers the barrier by ca. 4 kcal/mol. The barrier for SiH₂ + H₂ insertion is 3.5 kcal/mol at the MP4/6-31+G(2df,p)//MP2/6-31G(d,p) level. This is in good agreement with the 3.9 kcal/mol barrier calculated at the G-2 level of theory, which approximates the value obtained at the QCISD(T)/6-311++G(3df,2p) level. Direct calculations at QCISD(T)/6-311++G(3df,2p) yield a barrier of 4.2 kcal/mol, indicating that the additivity approximations in the G-2 method are valid for this transition state. Further expansion of the basis set to 6-311++G(3df,3pd) lowers the barrier by 1.3 kcal/mol at the MP2 level. The 2.9 kcal/mol barrier at the estimated QCISD(T)/6-311++G(3df,3pd) level is 1.2 kcal/mol higher than the best previous estimate, 1.7 kcal/mol at the MP4/6-311++G(3df,3pd) level.¹⁴ The SiXY + H₂ barriers listed in Table V are calculated using the G-2 values corrected for the effect of increasing the basis set to 6-311++G(3df,3pd) (the corrections are -1.3, -1.5, and -1.5 kcal/mol for H₂ + SiH₂, SiHCl, and SiCl₂, respectively). The most recent analysis of the experimental data³⁴ yielded an activation energy of 0.5 kcal/mol; this suggests that the best calculated values for insertion into H₂ might be too high by up to 2 kcal/mol.

For SiH₂, SiHCl, and SiCl₂ insertion into HCl, the barriers are small and the increase in barrier on halogenation is about 6–10 kcal/mol per Cl, much less than that for the analogous silylene insertions into H₂. This is similar to the effect of fluorine substitution on silylene insertion into HF (4–11 kcal/mol per F¹⁵). Similar to the case for the SiXY + H₂ insertion barriers, re-optimizing the geometry at MP2/6-31G(d,p) has little effect but increasing the basis set to 6-31+G(2df,p) causes a 4–5 kcal/mol change. The barriers at the G-2 level are similar to the values obtained at MP4/6-31+G(2df,p), and increasing the basis set to 6-311++G(3df,3pd) lowers the barrier by only 0.5 kcal/mol at the MP2 level. The G-2 values corrected for the effect of increasing the basis set to 6-311++G(3df,3pd) are used in Table V. There are no accurate experimental estimates of the activation energy for comparison, but indirect studies¹⁰ suggest an activation energy of 1.3 kcal/mol or less, in agreement with the present calculations. Similar to the H₂ insertion barriers, the HCl insertion barriers are possibly also 1–2 kcal/mol too high.

Silylene forms a fairly stable complex with H₂ (binding energy of 7.7 kcal/mol at MP4/6-311++G(3df,3pd) without zero-point energy¹⁴); however, both the fluorosilylenes and the chlorosilylenes form weakly bound clusters with H₂ (<1 kcal/mol at MP2/6-311++G(3df,3pd) without zero-point energy; Table IV) and the binding energy decreases with substitution. The binding of the chlorosilylenes with HCl is somewhat stronger (3–7 kcal/mol) but not as strong as the interaction between the fluorosilylenes and HF (8–10 kcal/mol).¹⁵

The barriers for thermal decomposition of the chlorosilanes are summarized in Table V and Figure 5. The heats of reaction are computed from the theoretical heats of formation determined in ref 24. The forward barriers are obtained by adding the reverse barriers (i.e. silylene insertion and radical recombination) to the heats of reaction. The silylene insertion barriers were discussed above, and the radical recombinations are assumed to be

TABLE III: Calculated Barriers for Silylene Insertion Reactions^a

	6-31G(d,p)			6-31+G(2df,p)		MP2/6-311++G(3df,3pd) ^c	G-2
	MP2 ^b	MP4 ^b	MP2 ^c	MP2 ^c	MP4 ^c		
SiH ₂ + H ₂ → SiH ₄	7.6	7.9	7.1	3.1	3.5	1.7	3.9
SiHCl + H ₂ → SiH ₃ Cl	26.3	26.5	25.9	21.5	21.6	19.7	21.3
SiCl ₂ + H ₂ → SiH ₂ Cl ₂	47.6	47.5	47.2	43.1	42.5	40.4	41.1
SiH ₂ + HCl → SiH ₃ Cl	4.6	5.9	4.6	-1.1	0.6	-0.7	1.5
SiHCl + HCl → SiH ₂ Cl ₂	11.7	13.3	11.2	4.4	6.4	4.6	7.2
SiCl ₂ + HCl → SiHCl ₃	22.4	24.0	21.5	13.8	15.9		

^a ΔE in kcal/mol, with ΔZPE included. ^b Using the optimized geometry and unscaled ΔZPE computed at HF/6-31G(d). ^c Using the optimized geometry and unscaled ΔZPE computed at MP2/6-31G(d,p).

TABLE IV: Calculated Cluster Well Depths^a

	6-31G(d,p)				ZPE ^d
	MP2 ^b	MP4 ^b	MP2 ^c	MP2/6-311++G(3df,3pd) ^c	
SiH ₂ --H ₂ → SiH ₂ + H ₂	0.9	0.9	3.7	7.9	-4.8
SiHCl--H ₂ → SiHCl + H ₂	0.3	0.3	0.5	1.0	-1.0
SiCl ₂ --H ₂ → SiCl ₂ + H ₂	0.2	0.2	0.3	0.6	-0.6
SiH ₂ --HCl → SiH ₂ + HCl	3.9	3.7	4.7	6.9	-2.2
SiHCl--HCl → SiHCl + HCl	2.7	2.5	3.1	4.3	-1.1
SiCl ₂ --HCl → SiCl ₂ + HCl	1.8	1.7	2.3		-0.6

^a ΔE in kcal/mol, with ΔZPE *not* included. ^b Using the HF/6-31G(d)-optimized geometries. ^c Using the MP2/6-31G(d,p)-optimized geometries. ^d Unscaled ΔZPE at MP2/6-31G(d,p).

TABLE V: Thermal Decomposition Barriers of SiH_nCl_{4-n}^a

reaction	ΔH _r (298)	forward barrier	reverse barrier
SiH ₄			
→ SiH ₂ + H ₂	57	60	3
→ SiH ₃ + H	92	92	0
SiH ₃ Cl			
→ SiHCl + H ₂	47	67	20
→ SiH ₂ + HCl	75	76	1
→ SiH ₂ Cl + H	92	92	0
→ SiH ₃ + Cl	109	109	0
SiH ₂ Cl ₂			
→ SiCl ₂ + H ₂	36	76	40
→ SiHCl + HCl	67	74	7
→ SiHCl ₂ + H	92	92	0
→ SiH ₂ Cl + Cl	111	111	0
→ SiH ₂ + Cl ₂	140	≥140	≥0
SiHCl ₃			
→ SiCl ₂ + HCl	56	72	16
→ SiCl ₃ + H	93	93	0
→ SiHCl ₂ + Cl	112	112	0
→ SiHCl + Cl ₂	132	≥132	≥0
SiCl ₄			
→ SiCl ₃ + Cl	112	112	0
→ SiCl ₂ + Cl ₂	120	≥120	≥0

^a In kcal/mol.

barrierless. The decomposition of SiH₄ has been studied previously¹⁴ and is shown in Figure 5a for comparison with the decomposition of the chlorosilanes. Decomposition to SiH₂ + H₂ is the preferred path, with a barrier of ca. 60 kcal/mol; the SiH₃ + H channel is higher by about 32 kcal/mol. Figure 5b shows the four lowest energy pathways for the SiH₃Cl decomposition. The SiHCl + H₂ channel is the most favored, with a barrier of 67 kcal/mol; the SiH₂ + HCl path lies ca. 9 kcal/mol higher, with a barrier of 76 kcal/mol. The SiH₂Cl + H and SiH₃ + Cl channels are 92 and 109 kcal/mol above SiH₃Cl, respectively. For the decomposition of SiH₂Cl₂ (Figure 5c), there are two closely competing low-energy channels that cannot be distinguished at the present level of theory: SiHCl + HCl and SiCl₂ + H₂, with forward barriers of 74 and 76 kcal/mol, respectively. The other three channels, SiHCl₂ + H, SiH₂Cl + Cl, and SiH₂ + Cl₂, are considerably higher, with barriers of 92, 111, and ≥140 kcal/mol, respectively. Elimination of HCl is the preferred pathway for SiHCl₃ decomposition, with Si-H bond cleavage 20 kcal/mol higher (Figure 5d). For SiCl₄ decomposition, the heat of reaction for breaking a single Si-Cl bond is 8 kcal/mol lower

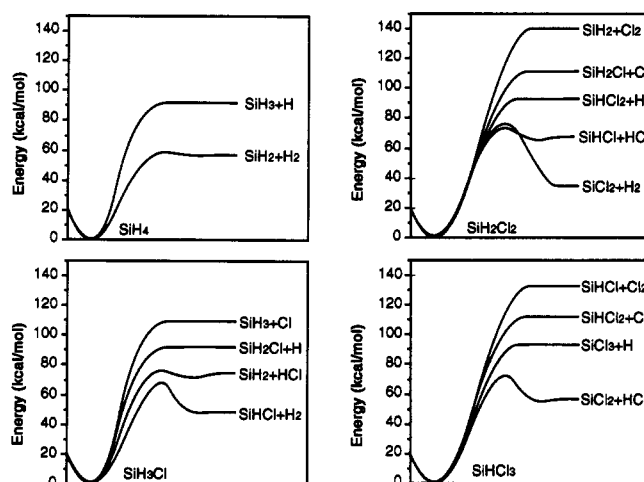


Figure 5. Potential energy profiles for the various channels for the thermal decomposition of (a) SiH₄, (b) SiH₃Cl, (c) SiH₂Cl₂, and (d) SiHCl₃.

TABLE VI: Rates of H₂ and HCl Elimination at 600 °C Calculated by Transition-State Theory^a

reaction	log A	E _a (kcal/mol)	rate (s ⁻¹)
SiH ₄ → SiH ₂ + H ₂	14.68	61.4	2.0 × 10 ⁻¹
SiH ₃ Cl → SiHCl + H ₂	14.39	68.4	1.8 × 10 ⁻³
SiH ₂ Cl ₂ → SiCl ₂ + H ₂	13.92	77.4	3.4 × 10 ⁻⁶
SiH ₃ Cl → SiH ₂ + HCl	14.71	78.0	1.5 × 10 ⁻⁵
SiH ₂ Cl ₂ → SiHCl + HCl	14.84	75.8	7.2 × 10 ⁻⁵
SiHCl ₃ → SiCl ₂ + HCl	14.69	73.7	1.7 × 10 ⁻⁴

^a Reaction path degeneracies are 12, 6, 2, 3, 4, and 3, respectively.

than that for Cl₂ elimination. The lowest energy channels for SiH₃Cl, SiH₂Cl₂, and SiHCl₃ have barriers that are quite similar to those of their fluorine analogues (70–90 kcal/mol); only SiCl₄ has a barrier that is substantially lower than that for its fluorine counterpart (112 vs 163 kcal/mol for Si-X cleavage).

Except for those of SiCl₄, the lowest energy pathways for thermal decomposition of SiH_{4-n}Cl_n involve the elimination of H₂ or HCl. Since these reactions have distinct transition states, conventional transition-state theory³⁵ can be used to obtain estimates of the rates under chemical vapor deposition conditions. Table VI lists the high-pressure unimolecular rates, activation energies, and pre-exponential factors for SiH_{4-n}Cl_n → SiH_{2-n}Cl_n + H₂ and SiH_{4-n}Cl_n → SiH_{3-n}Cl_{n-1} + HCl at 600 °C. Because there is uncertainty in the barrier heights (±2 kcal/mol) and

because the harmonic oscillator approximation was used for all vibrations, the magnitudes of the rate constants should be regarded with caution. Silane decomposition should probably be treated by variational transition-state theory because of its small exit channel barrier and strongly bound cluster. The A factor computed from the theoretical transition state is an order of magnitude smaller than the experimentally derived value³⁴ (log $A = 15.8$), suggesting that the rate is governed by a variational transition state between the cluster and the product. For SiH_3Cl decomposition, the rate of H_2 elimination is greater than that of HCl elimination due to a significantly lower activation energy. Although the activation energies for H_2 and HCl elimination from SiH_2Cl_2 are nearly equal, the calculated A factors favor HCl elimination over H_2 elimination, in contrast to IR multiphoton dissociation³ and pyrolysis⁴ experiments. The computed values for SiHCl_3 decomposition are in good agreement with a preliminary analysis of the experimental data ($E_a = 71.4$ kcal/mol, log $A = 14.52$).⁴

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