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Thermal Decomposition Pathways and Rates for Silane, Chlorosilane, Dichlorosilane, and Trichlorosilane

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Calculations have been carried out for the thermal decomposition of silane, chlorosilane, dichlorosilane, and trichlorosilane. In each case, the stationary point geometries and harmonic frequencies were characterized using CASSCF/derivative methods and the cc-pVDZ basis set. Accurate energetics were obtained by combining the CCSD(T) results using the a-cc-pVTZ basis set with an extrapolation to the basis set limit using the a-cc-pVDZ, a-cc-pVTZ, and a-cc-pVQZ basis sets at the MP2 level. The geometries, energetics, and harmonic frequencies were used to obtain rate constants using conventional transition state theory. The barrier heights obtained in the present work (kcal/mol) are the following: $SiH_4 \rightarrow SiH_2 + H_2$ (61.9); $SiClH_3 \rightarrow SiClH + H_2$ (66.7); $SiClH_3 \rightarrow SiH_2 + HCl$ (76.9); $SiCl_2H_2 \rightarrow SiCl_2 + H_2$ (77.2); $SiCl_2H_2 \rightarrow SiClH + HCl$ (74.8); $SiCl_3H \rightarrow SiCl_2 + HCl$ (72.7). The computed barrier heights are believed to be accurate to within 1 kcal/mol. The rate coefficients obtained in the present work are in fair accord with most of the experimental results.

I. Introduction

As part of a project to create a reliable database in microelectronic processing, calculations of gas-phase reaction rates have been carried out for use in modeling thermal chemical vapor deposition (CVD) reactors. We first investigated the thermal decomposition of silane, chlorosilane, dichlorosilane, and trichlorosilane with H_2 as an additional feed gas. In this paper, we report on the important reaction pathways and reaction rate coefficients for the thermal decomposition of silane and Cl-substituted silane. Since we are also interested in trends in reactivity, we also discuss reactions of silylenes (SiH_2, SiHCl, and $SiCl_2$) and silylidynes (SiH and SiCl) with H_2. In a future paper, we will discuss the reaction of the initial decomposition products with H and Cl. This work will eventually lead to a reaction set (i.e. the group of reactions that are important in the mechanism) and accurate thermal rate coefficients for all the reactions in the set.

Su and Schlegal[1] studied the decomposition of silane, chlorosilane, dichlorosilane, and trichlorosilane using transition state theory (TST) on the basis of calculations at the G2 level. Wittbrodt and Schlegel[2] improved on the original calculations using the QCISD(T) method. These studies, while carefully carried out, used smaller basis sets than in the present work. Also in our studies we carried out basis set extrapolations, which in effect take the calculations to the limit of a complete basis set. Thus, the present studies are more reliable than previous work. Previous experimental work on this system includes the nonlinear regression analysis of Moffat et al.,[3] the experiments of Newman et al.,[4] and the empirically adjusted RRKM calculations of Meyerson and Jasinski.[5] Also rate coefficients derived from modeling reactor and shock tube experiments for the chlorosilane decomposition and the reverse reactions were recently reported by Walker et al.[6] Related work on Cl-substituted silanes has been reported by Osterheld, Allendorf, and Melius,[7] who studied the thermal decomposition of methyltrichlorosilane.

The reactivities of SiH and SiH_2 have been reviewed by Jasinski, Becerra, and Walsh.[8] This paper references a number of studies on the reactions of SiH and SiH_2 with H_2. On the theory side, Grev and Schaefer[9] reported accurate heats of formation for SiH_n, $n = 1-4$. Gordon, Xie, Yamaguchi, Grev, and Schaefer[10] reported a calculation of the barrier height for SiH plus H_2, and Gordon, Gano, Binkley, and Frish[11] reported on the barrier height for $SiH_2 + H_2$. Becerra and Walsh[12] discuss the reactivity of substituted silylenes including the Cl-substituted species discussed here.

The details of the calculations are described in section II. Section III discusses the results obtained, and the conclusions are given in section IV.

II. Calculational Details

The geometries and harmonic frequencies for all the stationary points (minima or saddle points) were determined using the complete active space self-consistent field (CASSCF)/derivative method with the correlation consistent polarized valence double-ζ (cc-pVDZ) basis sets.[13] In these calculations all the bond pairs were included in the active space; e.g. for the silanes, this consists of 8 electrons distributed over 8 orbitals. The energetics were obtained using the coupled cluster single and double excitation with perturbational estimate of triple excitations (CCSD(T)) method using the augmented cc-pVTZ basis set (a-cc-pVTZ) and extrapolated to the complete basis set (CBS) limit using the Moller−Plesset second-order perturbation theory method (MP2) with the a-cc-pVDZ, a-cc-pVTZ, and a-cc-pVQZ basis sets.[14] (The CCSD(T) and MP2 calculations made use of the closed shell methods[15] for singlet states and open shell methods[16] for cases with open shells.) The MP2 results were extrapolated to the basis set limit using the Martin−Schwartz three-point extrapolation.[17] The results of the MP2 extrapolation were combined with CCSD(T) results obtained with the a-cc-pVTZ basis set to obtain an estimate of the CCSD(T) results in the limit of a complete basis set. The basis for this was described by Ricca and Bauschlicher,[18] who noticed that for bond strengths the ratio D_e(CCSD(T))/D_e(MP2) was constant for a series of correlation consistent basis sets. Thus, for barrier heights and

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SCHEME 1

$SiCl_2H_2 \rightarrow SiCl_2 + H_2$ (77.2)
$\rightarrow SiClH + HCl$ (74.8)

$SiCl_3H \rightarrow SiCl_2 + HCl$ (72.7)

$SiCl_2 + H \rightarrow SiCl_2H \rightarrow SiCl + HCl$(abstraction(16.3) or complex(29.5))
$SiHCl + H \rightarrow SiCl + H_2$ (0.0) or $SiH + HCl$(0.0)
$SiHCl + Cl \rightarrow SiCl + HCl$ (abstraction (0.0) or complex(4.5))

$SiH_2 + H_2 \rightarrow SiH_4$ (0.0)
$SiHCl + H_2 \rightarrow SiClH_3$ (15.3)
$SiCl_2 + H_2 \rightarrow SiCl_2H_2$ (37.8)

$SiH + H_2 \rightarrow SiH_3$ (6.0)
$SiCl + H_2 \rightarrow SiClH_2$ (59.2)

$SiH_2 + SiH_2 \rightarrow Si_2H_4 \rightarrow SiH_3 + SiH$
$\rightarrow SiH_4 + Si$ (triplet surface)

$SiCl_2 + SiCl_2 \rightarrow Si_2Cl_4 \rightarrow SiCl_3 + SiCl$ (not likely)

other relative energy quantities, the value in the limit of a complete basis set was obtained as

$$\frac{\Delta E(\text{a-cc-pVTZ/CCSD(T)})}{\Delta E(\text{a-cc-pVTZ/MP2})} \times \Delta E\ (\text{CBS/MP2}) \qquad (1)$$

where ΔE(a-cc-pVTZ/CCSD(T) and ΔE(a-cc-pVTZ/MP2) are the values obtained with the a-cc-pVTZ basis set for CCSD(T) amd MP2, respectively, and ΔE(CBS/MP2) is the MP2 value extrapolated to the complete basis set limit (CBS).

In these calculations the 10 electron Ne core was not correlated. For SiH_4 we relaxed this restriction to determine the magnitude of core−valence effects.

Here the 8 electron calculations are done with a frozen Ne core, while the 16 electron calculations are done with a frozen He core. (The basis set for the core−valence calculations has the two exponents which dominate the Si 2s and 2p orbitals uncontracted, and additional tight d (exponents 1.443 and 4.329) and tight f (exponents 1.008 and 3.024) functions are added.) The mass-velocity and Darwin scalar relativistic corrections were also computed using perturbation theory at the CASSCF level as implemented in DALTON.[19]

For the reactions with barriers (i.e., those with well-defined saddle points), rate coefficients as a function of temperature were obtained using conventional transition state theory. (Note that in the text and figures a saddle point is denoted by sp.) For reactions without barriers (e.g. $SiH_2 + H_2$), rate coefficients have to be obtained using variational transition state theory on the basis of computed energetics and force constant matrixes along the reaction pathway obtained as discussed above. This will be the subject of a future publication.

The CASSSCF/derivative calculations were carried out using DALTON,[19] the CCSD(T) calculations were carried out using MOLPRO,[20] and the MP2 calculations were done using Gaussian94.[21] The transition state theory calculations were carried out using POLYRATE.[22]

III. Discussion

A. Electronic Structure Calculations. The overall reaction set we are currently considering for the $SiCl_xH_y/H_2$ system is given in Scheme 1. (Note that this reaction set is most likely not complete and other reactions may have to be included.) For each reaction, the best estimates of the barrier heights (in kcal/mol) from our calculations are included in parentheses. This reaction set is designed to model the gas-phase CVD process for thermal decomposition of dichlorosilane or trichlorosilane and subsequent reaction of the decomposition products with H/H_2. Here it is seen that the primary decomposition products are $SiCl_2$ and SiClH for dichlorosilane and $SiCl_2$ for trichlorosilane, respectively. The reactions of $SiCl_2$ and SiHCl with H and Cl are complex. There are both direct abstraction pathways and pathways which proceed through formation and decomposition of a complex. An important observation is that H atom can convert SiHCl to SiCl or SiH with no barrier. Thus, the silylenes $SiCl_2$ and SiHCl and the silylidynes SiCl and SiH will all be important gas-phase species produced in this system. The reactions of SiH_2, SiClH, and $SiCl_2$ with H_2 illustrate a decreased reactivity of the silylene as hydrogens are substituted by chlorines. A similar trend is seen for SiH and SiCl. (See the discussion in section III.) Finally, the $SiH_2 + SiH_2$ system was studied, since it is a possible source of Si atoms. However, preliminary studies show that the analogous reaction of $SiCl_2 + SiCl_2$ is unlikely (due to larger barriers for migrating Cl atoms

TABLE 1: $SiH_4 \rightarrow SiH_2 + H_2$ CCSD(T) Energetics

	a-cc-pVDZ		a-cc-pVTZ		a-cc-pVQZ		CBS[a]	
	E_H (Hartree relative to −291 E_H)	kcal/mol	E_H (Hartree relative to −291 E_H)	kcal/mol	E_H (Hartree relative to −291 E_H)	kcal/mol	E_H (Hartree relative to −291 E_H)	kcal/mol
$SiH_3 + H$			−0.287 94	94.7				96.9
$SiH_2 + H_2$	−0.307 18	57.8	−0.344 18	59.4	−0.353 34	60.8	−0.3589	61.9
sp1	−0.305 91	58.6	−0.344 79	59.0	−0.355 33	59.5	−0.3620	59.9[b]
SiH_4	−0.399 25	0.0	−0.438 89	0.0	−0.450 17	0.0	−0.4575	0.0

[a] CBS is the energy in the limit of a complete basis set obtained by basis set extrapolation. [b] MP2 extrapolation (as discussed in the text) gives 59.7 kcal/mol as compared to 59.9 kcal/mol from direct extrapolation of the CCSD(T) results.

TABLE 2: $SiH_4 \rightarrow SiH_2 + H_2$ MP2 Energetics

	a-cc-pVDZ		a-cc-pVTZ		a-cc-pVQZ		CBS[a]	
	E_H (Hartree relative to −291 E_H)	kcal/mol	E_H (Hartree relative to −291 E_H)	kcal/mol	E_H (Hartree relative to −291 E_H)	kcal/mol	E_H (Hartree relative to −291 E_H)	kcal/mol
$SiH_3 + H$	−0.223 42	88.3	−0.257 94	92.3	−0.269 15	93.5	−0.2768	94.4
$SiH_2 + H_2$	−0.266 58	61.2	−0.305 03	62.7	−0.316 51	63.8	−0.3241	64.8
sp1	−0.267 71	60.5	−0.307 79	61.0	−0.320 37	61.4	−0.3289	61.7
SiH_4	−0.364 18	0.0	−0.404 96	0.0	−0.418 21	0.0	−0.4273	0.0

[a] CBS is the energy in the limit of a complete basis set obtained by basis set extrapolation.

TABLE 3: SiH_4 Core−Valence CCSD(T) Calculation (Barrier Height)

	8 electrons		16 electrons	
	E^a	ΔE^b	E^a	ΔE^b
$SiH_2 + H_2$	−0.346 06	60.2	−0.591 76	59.7
sp1	−0.346 67	59.8	−0.592 56	59.2
SiH_4	−0.441 95	0.0	−0.686 97	0.0

[a] Energy in E_H relative to −291 E_H. [b] Relative energy in kcal/mol.

TABLE 4: Scalar Relativistic Correction (Mass-Velocity and Darwin Terms) for SiH_4 at the SiH_4 Minimum and Saddle Point at the CASSCF Level

	$SiH_4{}^a$	sp^a	ΔE^b
nonrelativistic	−0.299 64	−0.197 40	64.2
relativistic	−0.899 16	−0.797 24	64.0

[a] Energy in E_H relative to −291 E_H. [b] Relative energy in kcal/mol.

TABLE 5: $SiClH_3$ → Products CCSD(T) Energetics

	a-cc-pVDZ		a-cc-pVTZ		CBS[a] from mp2
	E_H (Hartree relative to −750 E_H)	kcal/mol	E_H (Hartree relative to −750 E_H)	kcal/mol	kcal/mol
$SiH_3 + Cl$			−0.464 31	106.4	111.4
$SiClH_2 + H$			−0.482 50	94.9	97.2
$H_2 + SiClH$	−0.450 22	47.1	−0.555 28	49.3	51.4
$HCl + SiH_2$	−0.415 83	68.7	−0.515 30	74.4	78.1
sp2	−0.412 79	70.6	−0.515 06	74.5	76.9
sp1	−0.422 26	64.7	−0.529 12	65.7	66.7
$SiClH_3$	−0.525 33	0.0	−0.633 80	0.0	0.0

[a] CBS estimate obtained by combining the CCSD(T) results with the a-cc-pVTZ basis set with the results of the MP2 extrapolation.

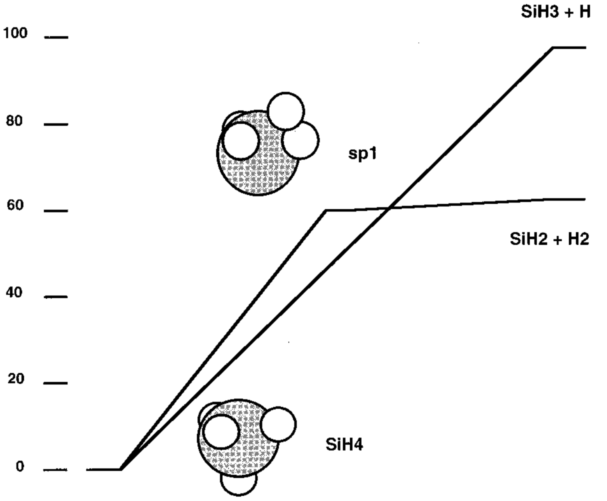

Figure 1. Decomposition pathways for SiH_4. The structures of the SiH_4 minimum and saddle point leading to $SiH_2 + H_2$ are shown. The ordinate is relative energy in kcal/mol.

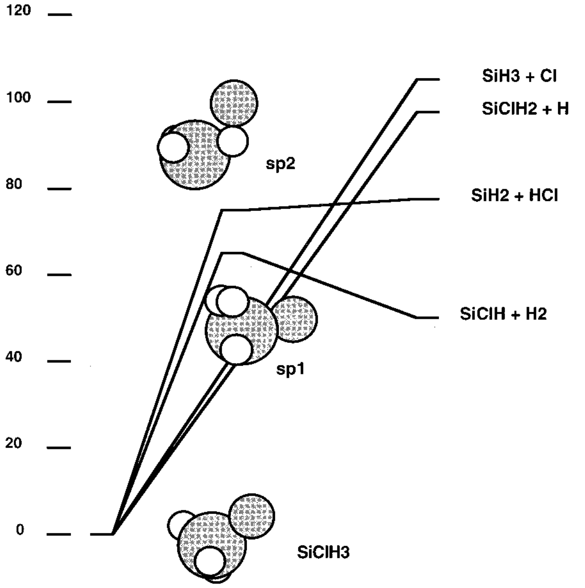

Figure 2. Decomposition pathways for SiH_3Cl. The structures of the SiH_3Cl minimum and of the saddle points leading to $SiClH + H_2$ and $SiH_2 + HCl$ are shown. The ordinate is relative energy in kcal/mol.

as compared to H atoms). In this paper we focus mainly on the thermal decomposition of chlorosilane, dichlorosilane, and trichlorosilane. We also considered thermal decomposition of silane and used this system to benchmark our theoretical methods.

Tables 1−4 and Figure 1 show the results of calculations on the SiH_4 system. (While this system has been discussed elsewhere,[10] we include it here, partly to benchmark our results and partly for completeness, since we are interested in trends in reactivity.) From Figure 1, it is seen that it is more favorable energetically to go to $SiH_2 + H_2$ than to break an SiH bond (leading to $SiH_3 + H$). The pathway for dissociating to $SiH_2 + H_2$ is typical of a carbene insertion pathway (i.e. for the reverse reaction) in that the plane of the SiH_2 molecule is nearly parallel with the H_2 bond and oriented cis. The pathways for carbene insertion are discussed elsewhere[23] and ultimately are understood in terms of the orbital phase continuity principle.[24] (Note also the detailed discussion of silylene chemistry by Becerra and Walsh.[12]) The reaction of SiH_2 with H_2 has no barrier at the highest level of calculation described here (CCSD(T) with MP2 basis set extrapolation). However, there is a barrier on the CASSCF potential energy surface, and this defines a pathway. The rate constant for this reaction was computed using conventional transition state theory on the basis of the CASSCF saddle point. Table 1 gives CCSD(T) energetics for this reaction. In this case, we were able to do the CCSD(T) calculations with the a-cc-pVDZ, a-cc-pVTZ, and a-cc-pVQZ basis sets and extrapolate the results to the basis set limit. As a check on the

TABLE 6: $SiClH_3$ → Products MP2 Energetics

	a-cc-pVDZ		a-cc-pVTZ		a-cc-pVQZ		CBS[a]	
	E_H (Hartree relative to −750 E_H)	kcal/mol	E_H (Hartree relative to −750 E_H)	kcal/mol	E_H (Hartree relative to −750 E_H)	kcal/mol	E_H (Hartree relative to −750 E_H)	kcal/mol
$SiH_3 + Cl$	−0.316 23	104.1	−0.405 45	111.4	−0.434 84	114.4	−0.455 0	116.6
$SiClH_2 + H$	−0.340 86	88.7	−0.435 35	92.7	−0.467 34	94.0	−0.489 5	94.9
$H_2 + SiClH$	−0.401 90	50.4	−0.499 84	52.2	−0.532 05	53.4	−0.554 1	54.4
$HCl + SiH_2$	−0.363 26	74.6	−0.455 86	79.8	−0.486 36	82.1	−0.507 3	83.8
sp2	−0.364 58	73.8	−0.459 75	77.4	−0.491 59	78.8	−0.513 5	79.9
sp1	−0.374 47	67.6	−0.474 04	68.4	−0.507 31	68.9	−0.530 2	69.4
$SiClH_3$	−0.482 19	0.0	−0.583 05	0.0	−0.617 17	0.0	−0.640 8	0.0

[a] CBS is the energy in the limit of a complete basis set obtained by basis set extrapolation.

TABLE 7: $SiCl_2H_2 \rightarrow$ Products CCSD(T) Energetics

	cc-pVDZ		cc-pVTZ	
	E_H (Hartree relative to -750 E_H)	kcal/mol	E_H (Hartree relative to -750 E_H)	kcal/mol
sp2	−0.504 81	70.9	−0.705 35	73.7
sp1	−0.496 57	76.0	−0.700 33	76.8
$SiCl_2H_2$	−0.617 75	0.0	−0.822 79	0.0

	a-cc-pVDZ		a-cc-pVTZ		CBS[a]		CBS from MP2
	E_H (Hartree relative to -750 E_H)	kcal/mol	E_H (Hartree relative to -750 E_H)	kcal/mol	E_H (Hartree relative to -750 E_H)	kcal/mol	kcal/mol
$SiH_2 + Cl_2$			−0.609 11	139.2			143.8
$SiClH_2 + Cl$			−0.658 87	108.0			113.0
$SiCl_2H + H$			−0.679 97	94.9			97.3
$SiCl_2 + H_2$	−0.597 84	34.6	−0.771 76	37.2			39.4
$SiHCl + HCl$	−0.558 87	59.1	−0.726 40	65.6			69.5
sp2	−0.544 29	68.2	−0.715 60	72.4	−0.775 9	73.9	74.8
sp1	−0.534 14	74.6	−0.709 77	76.1	−0.771 6	76.6	77.2
$SiCl_2H_2$	−0.653 02	0.0	−0.831 01	0.0	−0.893 6	0.0	0.0

[a] CBS estimate obtained by combining the CCSD(T) results with the a-cc-pVTZ basis set with the results of the MP2 extrapolation.

TABLE 8: $SiCl_2H_2 \rightarrow$ Products MP2 Energetics

	cc-pVDZ		cc-pVTZ		cc-pVQZ	
	E_H (Hartree relative to -1209 E_H)	kcal/mol	E_H (Hartree relative to -1209 E_H)	kcal/mol	E_H (Hartree relative to -1209 E_H)	kcal/mol
sp2	−0.447 44	74.1	−0.629 47	76.0	−0.690 59	76.6
sp1	−0.436 62	80.9	−0.621 98	80.7	−0.683 72	80.9
$SiCl_2H_2$	−0.565 51	0.0	−0.750 58	0.0	−0.812 72	0.0

	a-cc-pVDZ		a-cc-pVTZ		a-cc-pVQZ		CBS[a]	
	E_H (Hartree relative to -1209 E_H)	kcal/mol	E_H (Hartree relative to -1209 E_H)	kcal/mol	E_H (Hartree relative to -1209 E_H)	kcal/mol	E_H (Hartree relative to -1209 E_H)	kcal/mol
$SiH_2 + Cl_2$	−0.370 93	144.9	−0.526 22	148.9	−0.576 96	151.7	−0.611 7	153.8
$SiClH_2 + Cl$	−0.433 40	105.7	−0.582 86	113.4	−0.633 03	116.5	−0.667 6	118.7
$SiCl_2H + H$	−0.460 59	88.6	−0.615 72	92.8	−0.668 55	94.2	−0.705 2	95.1
$SiCl_2 + H_2$	−0.542 56	37.2	−0.700 82	39.4	−0.753 83	40.7	−0.790 4	41.7
$SiHCl + HCl$	−0.498 58	64.8	−0.650 67	70.8	−0.701 90	73.2	−0.737 3	75.0
sp2	−0.488 77	70.9	−0.644 43	74.7	−0.697 23	76.2	−0.733 8	77.7
sp1	−0.476 16	78.8	−0.636 16	79.9	−0.690 17	80.6	−0.727 5	81.1
$SiCl_2H_2$	−0.601 79	0.0	−0.763 55	0.0	−0.818 63	0.0	−0.856 8	0.0

[a] CBS is the energy in the limit of a complete basis set obtained by basis set extrapolation.

MP2 basis set extrapolation method, we also did the MP2 extrapolation for this system (Table 2) and compared the results to the direct extrapolation of the CSSD(T) results. From Table 1 it is seen that the MP2 extrapolation gives a barrier height of 59.7 kcal/mol, while direct extrapolation of the CCSD(T) results gives a barrier height of 59.9 kcal/mol. Thus, the error introduced by the MP2 extrapolation is only 0.2 kcal/mol and makes this an attractive option for the remaining cases, where we cannot do the direct extrapolation of the CCSD(T) results. From Table 1, it is also seen that the barrier height converges more rapidly with basis set than the endoergicity of reaction. (Note that improving the basis set *increases* the barrier height for this reaction.) The error between the results obtained with the a-cc-pVTZ basis set as compared to the estimated complete basis set limit is 0.9 and 2.5 kcal/mol for the barrier height and heat of reaction, respectively. The difference between the results obtained with the largest basis set and the estimated complete basis set limit is probably a reasonable upper limit estimate of the remaining error in the basis set extrapolation. This predicts errors due to limitations of the basis set of 0.4 and 1.1 kcal/mol for barrier height and heat of reaction, respectively.

Table 3 shows the effect of core-valence correlation on the barrier height and heat of reaction for dissociation of SiH_4. From Table 3 it is seen that core−valence effects lower the barrier height and reaction endoergicity by 0.6 and 0.5 kcal/mol, respectively. Table 4 shows the effect of the mass-velocity and Darwin scalar relativistic corrections. Here it is seen that these relativistic effects lower the barrier by 0.2 kcal/mol. Another relativistic effect that could be important is spin−orbit coupling. Neglect of spin−orbit coupling introduces errors of 0.4 kcal/mol for an SiH bond and 1.3 kcal/mol for an SiCl bond,[25] and we would expect similar errors in cases where we dissociate a single bond to give e.g. a H or Cl atom. However, for the saddle points for dissociation to closed shell species such as $SiCl_2$, SiClH, etc., the reaction stays completely on the singlet surface and there is no first-order spin−orbit effect.

These results suggest a combined error of 0.8 kcal/mol in the barrier height due to core−valence and relativistic corrections. This effect lowers the barrier height, while the effect of basis set incompleteness is to underestimate the barrier height (by up to 0.4 kcal/mol). Thus, the best estimate is that the true barrier height is lower than the estimate of the complete basis set limit by about 0.4 kcal/mol. Thus, even if the errors were

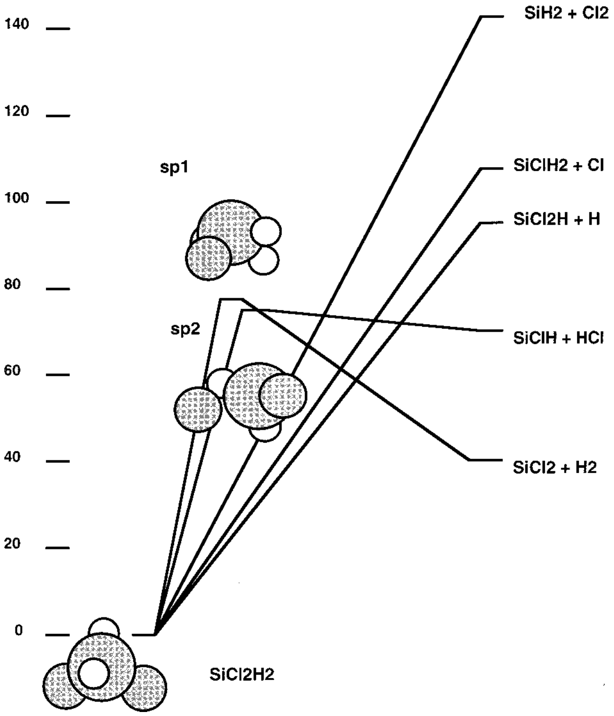

Figure 3. Decomposition pathways for $SiCl_2H_2$. The structures of the $SiCl_2H_2$ minimum and of the saddle points leading to SiClH + HCl and $SiCl_2 + H_2$ are shown. The ordinate is relative energy in kcal/mol.

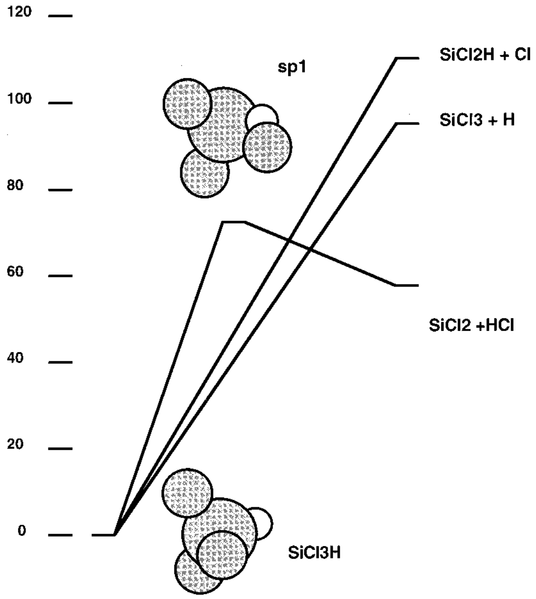

Figure 4. Decomposition pathways for $SiCl_3H$. The structures of the $SiCl_3H$ minimum and of the saddle point leading to $SiCl_2$ + HCl are shown. The ordinate is relative energy in kcal/mol.

twice as large for the Cl substituted silanes, our barriers would still be accurate to within 1 kcal/mol.

Tables 5 and 6 and Figure 2 show the results of calculations on the $SiClH_3$ system. Here it is seen that there are two pathways, one leading to SiClH + H_2 and the other leading to SiH_2 + HCl. The SiClH + H_2 channel is favored both thermodynamically and kinetically. Considering the reverse reactions, it is seen that the reaction SiH_2 + HCl has no barrier but the reaction SiClH + H_2 has a significant barrier. This is an example of the lower reactivity of the chlorine-substituted silylene (vide infra).

Tables 7 and 8 and Figure 3 show the results of calculations on the $SiCl_2H_2$ system. Here there are also two pathways, one leading to $SiCl_2 + H_2$ and the other leading to SiClH + HCl. The pathway leading to $SiCl_2 + H_2$ is favored thermodynamically but has a larger barrier, while the pathway leading to SiClH + HCl has a smaller barrier but the product channel is less favorable thermodynamically. Once again the relative barrier heights are understandable in terms of the lower silylene reactivity upon chlorine substitution.

Tables 9 and 10 and Figure 4 show the results of calculations on the $SiCl_3H$ system. Here the only pathway that is energetically accessible leads to $SiCl_2$ + HCl. The other possible product channel is SiClH + Cl_2. However, this channel is 135.1 kcal/mol above $SiCl_3H$ and was not considered here.

Tables 11 and 12 show energetics for other species which were used in constructing the earlier tables and are included here for completeness.

Table 13 shows energetics for the reactions of SiH_2, SiHCl, and $SiCl_2$ with H_2, and Table 14 shows energetics for the reactions of SiH and SiCl with H_2. These tables also show the low-spin to high-spin excitation energies of the silylenes. Here it is seen that there is a correlation between the low-spin to high-spin excitation energy of the silylene and the barrier to the silylene insertion reaction with H_2. This trend can be understood in terms of the s → p near degeneracy effect in the silylene; i.e., the two lobes of the silylene pair have an overlap that depends on the $s^2 \rightarrow p^2$ excitation energy. In the case of the silylene, this is the energy to promote two electrons from the doubly occupied sp nonbonding orbital in-plane to the empty

TABLE 9: $SiCl_3H \rightarrow$ Products CCSD(T) Energetics

	cc-pVTZ E_H (Hartree relative to −1668 E_H)	cc-pVTZ kcal/mol
sp1	−0.894 59	71.7
min	−1.008 91	0.0

	a-cc-pVDZ E_H (Hartree relative to −1668 E_H)	a-cc-pVDZ kcal/mol	a-cc-pVTZ E_H (Hartree relative to −1668 E_H)	a-cc-pVTZ kcal/mol	CBS[a] from MP2 kcal/mol
SiClH + Cl_2			−0.820 21	130.3	135.1
$SiCl_2H$ + Cl			−0.856 34	107.6	112.7
$SiCl_3$ + H			−0.876 42	95.0	
$SiCl_2$ + HCl	−0.706 49	46.0	−0.942 88	53.3	57.3
sp1	−0.674 17	66.3	−0.915 58	70.5	72.7
$SiCl_3H$	−0.779 80	0.0	−1.027 86	0.0	0.0

[a] CBS estimate obtained by combining the CCSD(T) results with the a-cc-pVTZ basis set with the results of the MP2 extrapolation.

TABLE 10: $SiCl_3H \rightarrow$ Products MP2 Energetics

	cc-pVTZ	
	E_H (Hartree relative to −1668 E_H)	kcal/mol
sp1	−0.808 98	73.5
$SiCl_3H$	−0.926 12	0.0

	a-cc-pVDZ		a-cc-pVTZ		a-cc-pVQZ		CBS[a]	
	E_H (Hartree relative to −1668 E_H)	kcal/mol	E_H (Hartree relative to −1668 E_H)	kcal/mol	E_H (Hartree relative to −1668 E_H)	kcal/mol	E_H (Hartree relative to −1668 E_H)	kcal/mol
$SiClH + Cl_2$	−0.506 25	134.5	−0.721 03	139.9	−0.792 50	142.8	−0.841 7	145.0
$SiCl_2H + Cl$	−0.553 40	104.9	−0.763 23	113.4	−0.834 24	116.6	−0.883 4	118.8
$SiCl_3 + H$	−0.579 38	88.6	−0.795 73	93.0				
$SiCl_2 + HCl$	−0.639 24	51.1	−0.851 65	57.9	−0.923 68	60.5	−0.973 5	62.2
sp1	−0.611 69	68.4	−0.828 98	72.2	−0.902 84	73.5	−0.954 0	74.5
$SiCl_3H$	−0.720 63	0.0	−0.943 96	0.0	−1.020 02	0.0	−1.072 7	0.0

[a] CBS is the energy in the limit of a complete basis set obtained by basis set extrapolation.

TABLE 11: CCSD(T) Energies (in E_H)

	a-cc-pVDZ	a-cc-pVTZ	a-cc-pVQZ	CBS
SiH_3		−290.788 12		
SiH_2	−290.143 57	−290.172 32	−290.180 05	−290.185 0
H_2	−1.163 61	−1.171 86	−1.173 29	−1.174 0
H	−0.499 34	−0.499 82	−0.499 95	
$SiCl_2$	−1208.434 23	−1208.599 90	−1208.650 99	−1208.685 2
SiClH	−749.286 61	−749.383 42	−749.412 78	−0.432 3
HCl	−460.272 26	−460.342 98	−460.363 87	−460.377 6
$SiClH_2$		−749.982 68		
$SiCl_2H$		−1209.180 15		
Cl_2		−919.436 79		
Cl		−459.676 19		

TABLE 12: MP2 Energies (in E_H)

	a-cc-pVDZ	a-cc-pVTZ	a-cc-pVQZ
SiH_3	−290.724 08	−290.758 12	−290.769 20
SiH_2	−290.111 53	−290.141 11	−290.150 69
H_2	−1.155 05	−1.163 92	−1.165 82
H	−0.499 34	−0.499 82	−0.499 95
$SiCl_2$	−1208.387 51	−1208.536 90	−1208.588 01
SiClH	−749.246 85	−749.335 92	−749.366 23
HCl	−460.251 73	−460.314 75	−460.335 67
$SiClH_2$	−749.841 52	−749.935 53	−749.967 39
$SiCl_2H$	−1208.961 25	−1209.115 90	−1209.168 60
Cl	−459.592 15	−459.647 33	−459.665 64
Cl_2	−919.259 40	−919.385 11	−919.426 27

TABLE 13: $SiXY + H_2$ Reactions

	ΔE(S−T)[a]	ΔE_b[b]
SiH_2	20.0	0.0
SiHCl	33.9	15.3
$SiCl_2$	53.4	37.8

[a] Silylene singlet−triplet separation (kcal/mol) CCSD(T). [b] CBS estimate obtained by combining the CCSD(T) results with the a-cc-pVTZ basis set with the results of the MP2 extrapolation.

TABLE 14: $SiX + H_2$ Reactions

	ΔE(D−Q)[a]	ΔE_b[b]
SiH	38.2	6.0
SiCl	69.3	59.2

[a] Silylidene doublet−quartet separation (kcal/mol) CCSD(T). [b] CBS estimate obtained by combining the CCSD(T) results with the a-cc-pVTZ basis set with the results of the MP2 extrapolation.

p orbital perpendicular to the plane. The lower this excitation energy the smaller the overlap of the two lobes of the silylene pair and the more reactive the silylene is. One measure of this excitation energy is the low-spin to high-spin excitation energy in the silylene, since this excitation corresponds to promoting one electron from an s-like to a p-like orbital. Substituting Cl increases the promotion energy and reduces the silylene biradical character, which results in lower reactivity. Walsh[12] explains this in terms of the divalent state stabilization energy (DSSE). This quantity is the difference between the first and second bond dissociation energies for the silane. This is a similar concept, in that it is related to the s → p promotion energy. Becerra and Walsh[12] also tabulate rate constants for reaction of SiH_2 and SiHCl with H_2. The rate for SiHCl in the above reaction is at least 4 orders of magnitude less than for SiH_2, in agreement with the larger barrier in the SiHCl case.

Table 14 shows a barrier height of 6.0 kcal/mol for the reaction of SiH with H_2. This compares with an estimated range of 4.5−6.5 kcal/mol obtained by Gordon et al.[10] Our computed reaction rate at 300 K is 1.6×10^{-16} compared to an estimate of $<1.2 \times 10^{-14}$ from experiment (cm^3 $molecule^{-1}$ s^{-1}). For $SiH_2 + H_2$ we find a barrierless reaction. This compares to a barrier of 1.7 kcal/mol obtained by Gordon et al.[11] Experimentally[8] this reaction has a negative activation energy, which implies an entrance channel SiH_2–H_2 complex. We have not characterized this complex in this case.

B. Rate Coefficient Calculations. Thermal rate coefficients in the high-pressure limit were calculated using conventional transition state theory (TST) employing the POLYRATE program.[22] The TST rate expression is given by

$$k_{uni}^{\infty}(T) = \sigma \frac{kT}{h} \frac{Q^{\ddagger}(T)}{Q(T)} \exp\left(-\frac{E^{\ddagger}}{kT}\right) \qquad (2)$$

where the symmetry factor, σ, gives the reaction path multiplicity (that is the number of equivalent paths that reactants can reach products) and Q and $Q^{\ddagger}$ are the overall partition functions of the reactants and transition state, respectively. The quantity $E^{\ddagger}$ represents the energy of the saddle point relative to the reactants. The partition functions are assumed to be separable into their electronic, vibrational, rotational, and translational degrees of freedom. The harmonic approximation is employed in the calculation of the vibrational partition functions. Data required to calculate the partition functions include rotational constants, harmonic frequencies, and energetics, which are obtained using the ab initio electronic structure methods as described above.

A fundamental assumption of TST involves assigning a “dividing” surface that separates reactants from products. The rate of reaction is related to the flux of reactants passing through this surface. The effects of surface recrossing are ignored,

TABLE 15: Reaction Path Degeneracies σ, Saddle Point Energies $E^{\ddagger}$, and High-Pressure Arrhenius Parameters $k(T) = A\exp[-E_a/kT]$[a]

			present work			other theory		expt	
reaction	σ	$E^{\ddagger}$	A	E_a	n	A	E_a	A	E_a
$SiH_4 \rightarrow SiH_2 + H_2$	12	59.9	5.66(+14)	58.4		4.79(+14)	61.4[b]	6.17(+15)	60.0[d]
								3.55(+15)	59.6[e]
								3.40(+15)	59.8[f]
$SiH_2 + H_2 \rightarrow SiH_4$	4	−2.0	1.74(−18)	−1.9	1.97				
$SiH_3 \rightarrow SiH + H_2$	6	50.8	2.41(+14)	49.1					
$SiH + H_2 \rightarrow SiH_3$	2	6.0	4.45(−11)	7.5					
$SiClH_3 \rightarrow SiClH + H_2$	6	66.6	3.87(+14)	65.0		2.45(+14)	68.4[b]	3.16(+14)	60.6[g]
$SiClH + H_2 \rightarrow SiClH_3$	2	15.3	4.34(−12)	18.1				4.17(−12)	12.1[g]
$SiClH_3 \rightarrow SiH_2 + HCl$	3	76.9	4.89(+14)	75.5		5.13(+14)	78.0[b]		
$SiH_2 + HCl \rightarrow SiClH_3$	2	−1.2	1.81(−20)	−2.0	2.50				
$SiClH_2 \rightarrow SiCl + H_2$	2	92.4	3.98(+13)	92.9					
$SiCl + H_2 \rightarrow SiClH_2$	2	59.2	2.05(−11)	62.9					
$SiCl_2H_2 \rightarrow SiCl_2 + H_2$	2	77.2	1.50(+14)	75.6		8.32(+13)	77.4[b]	3.16(+14)	69.2[g]
						7.94(+13)	74.1[c]		
$SiCl_2 + H_2 \rightarrow SiCl_2H_2$	4	37.8	8.15(−12)	40.5				6.61(−12)	33.4[g]
$SiCl_2H_2 \rightarrow SiClH + HCl$	4	74.8	6.60(+14)	73.7		6.92(+14)	75.8[b]		
						6.76(+14)	72.6[c]		
$SiClH + HCl \rightarrow SiCl_2H_2$	2	5.3	3.76(−12)	8.3					
$SiCl_3H \rightarrow SiCl_2 + HCl$	3	72.8	4.39(+14)	71.9		4.90(+14)	73.7[b]	3.16(+14)	71.9[g]
$SiCl_2 + HCl \rightarrow SiCl_3H$	2	15.5	2.52(−12)	18.5				2.09(−12)	16.7[g]

[a] Units: $E^{\ddagger}$, E_a (kcal/mol); A, unimolecular reactions (s^{-1}); A, bimolecular reactions (cm^3 $molecule^{-1}$ s^{-1}); $1.00(\pm x) \equiv 1.00 \times 10^{\pm x}$. [b] Su and Schlegel.[1] [c] Wittbrodt and Schlegel.[2] [d] Moffat, Jensen, and Carr.[3] [e] Newman, O'Neal, Ring, Leska, and Shipley.[4] [f] Meyerson and Jasinski.[5] [g] Walker, Jardine, Ring, and O'Neal.[6]

resulting in TST giving an upper bound estimate to the reaction rate. The error introduced in this assumption can be reduced by minimizing the rate with respect to the position of this dividing surface, yielding a variational TST result.

Reactions that involve significant atom rearrangement such as elimination/insertion or isomerization reactions are typically characterized by what is termed a "tight" transition state, a well-defined saddle point structure that reactants must pass through to reach products. For tight transition states, the position of the dividing surface usually corresponds closely to the saddle point, and hence, the TST rates can be obtained solely from the reactant and saddle point data. A "loose" transition state can arise from simple bond fission reactions, often resulting in two fragment radicals. For these cases, there is little or no barrier along the minimum energy path from reactants to products. The optimal dividing surface is not known apriori and will change with temperature. For these reactions, data along the minimum energy path of the potential are needed for variational TST calculations. Often, however, it is assumed that the transition state for these cases is close to the asymptotic products and the TST rates are calculated using the data for the separated fragments (the Gorin model). For the few loose transition state reaction rate coefficients reported here, the CASSCF saddle point geometries and frequencies with the CCSD(T)/MP2-extrapolated energies are used to calculate the transition state partition functions.

The CASSCF/cc-pVDZ geometries and frequencies of the species involved in the reactions for which we report TST rate coefficients are given in Table IS (Supporting Information). The rate coefficients for each reaction were calculated for 10 temperatures in the range of 400−2000 K and then fitted to an Arrhenius-like form, $k(T) = AT^n \exp(-E_a/kT)$. For the tight transition state reactions and also for the endothermic loose transition state reactions, the calculated rate coefficients fit nicely to an exponential Arrhenius form with no preexponential temperature dependence ($n = 0$), with the exponent E_a typically falling within a few kilocalories of the saddle point barrier height, $E^{\ddagger}$, or the endothermicity. In the exothermic direction for the loose transition state reactions, the present TST treatment results in rate coefficient expressions with preexponential temperature dependence ($n > 0$) and negative E_a.

For comparison, reported in Table 15 are the results from other studies. Su and Schlegel[1] have performed TST rate calculations using G2 theory on the primary decomposition reactions. As can be seen in Table 15, the G2 results give A factors in good agreement with our present calculations, but the activation energies E_a are overestimated by 1.8−3.4 kcal/mol. This is most likely do to deficiencies in the Moller−Plesset perturbation theory for saddle point regions. For example, with comparison of Tables 1 and 2, it is seen that MP2 overestimates the barrier height by 2.0 kcal/mol as compared to CCSD(T). Wittbrodt and Schlegel[2] improved upon the G2 results for the dichlorosilane decomposition using the QCISD(T) level of theory with larger basis sets. At this level of theory, the activation energies are lower by 1.1 and 1.5 kcal/mol than our results. As noted in section IIIA, a lower barrier height for these reactions is characteristic of a smaller basis set. This is consistent with use of a somewhat smaller basis set than those used in our calculations.

Experimentally derived high-pressure rate coefficient expressions for the silane decomposition are also in good agreement with our calculations. The nonlinear regression analysis of Moffat et al.[3] given in Table 15 and the experiments of Newman et al.,[4] as well as the empirically adjusted RRKM calculations of Meyerson and Jasinski,[5] all give similar agreement with our calculations, though the A factors from experiment are almost 1 order of magnitude larger. This is most likely due to the silane decomposition reaction possessing a loose transition state. Employing the Gorin model[26] for this reaction using our data gives an A factor of 4.89×10^{15} s^{-1} and $E_a = 54.7$ kcal/mol. This gives better agreement with experiment for the A factor but worsens agreement with the activation energy. A better treatment for this system would be to use variational TST.

Finally, rate coefficients derived from modeling reactor and shock tube experiments for the chlorosilane decomposition and the reverse reactions were recently reported by Walker et al.[6] and are given in Table 15. In their model, the A factors for all the chlorosilane decomposition reactions were fixed to the same value. Comparison of the trichlorosilane decomposition and reverse reactions gives good agreement with our calculations. For the chlorosilane and the dichlorosilane reactions, the A

factors are in good agreement, but the experimental values for E_a differ by 4.4 to 7.1 kcal/mol below our calculated values. Given that the experimental numbers are not direct measurements and our estimate that our barrier heights are accurate to within 1 kcal/mol, it is likely that the experimental estimates are in error.

IV. Conclusions

Calculations have been carried out for the thermal decomposition of silane, chlorosilane, dichlorosilane, and trichlorosilane. In each case, the stationary point geometries and harmonic frequencies were characterized using CASSCF/derivative methods and the cc-pVDZ basis set. Accurate energetics were obtained by combining the CCSD(T) results using the a-cc-pVTZ basis set with an extrapolation to the basis set limit using the a-cc-pVDZ, a-cc-pVTZ, and a-cc-pVQZ basis sets at the MP2 level. The geometries, energetics, and harmonic frequencies were used to obtain rate constants using conventional transition state theory.

From the basis set extrapolation plus estimates of core−valence and relativistic effects, we estimate that the basis set extrapolated barrier height for decomposition of silane is too high by about 0.5 kcal/mol. We expect that the errors for the chlorinated silanes will be similar to those for silane. Thus, we believe our computed barrier heights are accurate to within 1 kcal/mol.

Comparison to other calculations indicates that the G2 method overestimates activation energies for these systems by 1.8−3.4 kcal/mol. The QCISD(T) method in conjunction with smaller basis sets underestimates activation energies for dichlorosilane decomposition by 1.0 and 1.5 kcal/mol for the $SiClH + HCl$ and $SiCl_2 + H_2$ channels, respectively. This is probably mostly due to use of a smaller basis set than that used in the present work.

Our computed barrier heights are not in agreement with the experimental estimates of Walker et al. for decomposition of the dichloro and monochloro silanes but do agree for the trichlorosilane case. We believe the experimental estimates are wrong for the dichloro- and monochlorosilane cases.

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Supporting Information Available: Geometries and frequencies from CASSCF calculations (Table IS). This material is available free of charge via the Internet at http://pubs.acs.org.

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