Ab Initio MO Study of the Thermal Decomposition of Fluorinated Disilanes, $Si_2H_{6-n}F_n$ (n = 0, 1, 2)

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The reactants, transition structures, and products for the various channels for the thermal decomposition of $Si_2H_{6-n}F_n$ were optimized at the HF/3-21G and HF/6-31G* levels. The electron correlation contributions were calculated at the MP4/6-31G* level with the zero-point energies at the HF/3-21G level. Isodesmic reactions have been used to estimate the heats of formation of SiH_3SiH_2F, SiH_2FSiH_2F, SiH_3SiHF_2, SiH_2FSiH, $SiHF_2SiH$, SiH_3SiF, and SiH_2FSiF. In the decomposition of disilane, the $SiH_2 + SiH_4$ and $SiH_3SiH + H_2$ paths are favored over other modes of decomposition. For monofluorodisilane, the $SiH_3F + SiH_2$, $SiH_2FSiH + H_2$, and $SiH_3SiF + H_2$ channels are nearly equal in energy and are preferred over $SiH_4 + SiHF$. In the decomposition of the 1,1-difluorodisilane, SiH_3SiHF_2, the barriers for decomposition into $SiH_2F_2 + SiH_2$, $SiHF_2SiH + H_2$, and $SiH_3F + SiHF$ are very close in energy, while the $SiH_4 + SiF_2$ channel is considerably higher. In the decomposition of the 1,2-difluorodisilane, SiH_2FSiH_2F, the barriers for decomposition into $SiH_2F_2 + SiH_2$, $SiH_2FSiF + H_2$, and $SiH_3F + SiHF$ are similar in energy. For all the fluorodisilanes considered, the barriers for the elimination of HF and the homolytic cleavage of the Si-Si bond are considerably higher than those of the elimination of H_2 or the extrusion of a silylene.

Introduction

Fluorinated silanes and disilanes, and reactive intermediates derived from these compounds, are important in chemical vapor deposition and etching of silicon surfaces (for some leading refs, see 1-4). The pathways for thermal decomposition of fluorinated monosilanes were discussed in a previous paper.[5] In addition to these processes, disilanes can undergo homolytic Si-Si bond rupture, SiXY extrusion, and 1,2-elimination of H_2 and HF. A previous study on the thermal decomposition of disilane by Gordon et al.[6] found that 1,1-elimination of H_2 from Si_2H_6 has a much lower barrier than 1,2-elimination, even though $H_2Si{=}SiH_2$ is more stable than H_3SiSiH. Silylene insertion into SiH_4 has been shown to occur with no barrier[7] whereas the barrier for insertion into the SiF bond of SiH_3F[8] is comparable to that of insertion into HF.[9] The addition of HF to silanol and fluorodisilane was studied recently to model etching of silicon surfaces.[10] Accurate theoretical estimates of the heats of formation are available for fluorine-substituted monosilanes[11,12] and for Si_2H_n.[12,13,14] Unimolecular dissociation dynamics have been studied theoretically for disilane.[15]

In this paper, we explore a number of pathways for the thermal decomposition of H_3SiSiH_2F, $H_3SiSiHF_2$, and $H_2FSiSiH_2F$:

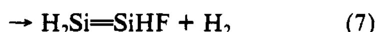
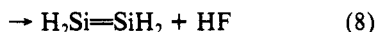
$$H_3Si{-}SiH_2F \rightarrow H_2FSi{-}SiH + H_2 \quad (1)$$

$$\rightarrow H_3Si{-}SiF + H_2 \quad (2)$$

$$\rightarrow H_3Si{-}SiH + HF \quad (3)$$

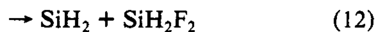
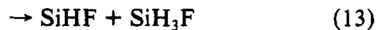
$$\rightarrow SiH_2 + SiH_3F \quad (4)$$

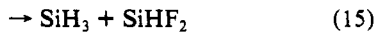
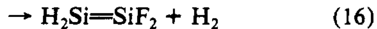
$$\rightarrow SiHF + SiH_4 \quad (5)$$

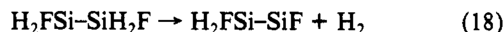
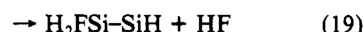
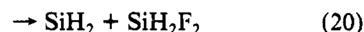
$$\rightarrow SiH_3 + SiH_2F \quad (6)$$

$$\rightarrow H_2Si{=}SiHF + H_2 \quad (7)$$

$$\rightarrow H_2Si{=}SiH_2 + HF \quad (8)$$

$$H_3Si{-}SiHF_2 \rightarrow HF_2Si{-}SiH + H_2 \quad (9)$$

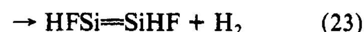
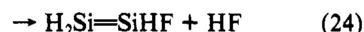
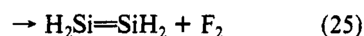
$$\rightarrow H_3Si{-}SiF + HF \quad (10)$$

$$\rightarrow H_3Si{-}SiH + F_2 \quad (11)$$

$$\rightarrow SiH_2 + SiH_2F_2 \quad (12)$$

$$\rightarrow SiHF + SiH_3F \quad (13)$$

$$\rightarrow SiF_2 + SiH_4 \quad (14)$$

$$\rightarrow SiH_3 + SiHF_2 \quad (15)$$

$$\rightarrow H_2Si{=}SiF_2 + H_2 \quad (16)$$

$$\rightarrow H_2Si{=}SiHF + HF \quad (17)$$

$$H_2FSi{-}SiH_2F \rightarrow H_2FSi{-}SiF + H_2 \quad (18)$$

$$\rightarrow H_2FSi{-}SiH + HF \quad (19)$$

$$\rightarrow SiH_2 + SiH_2F_2 \quad (20)$$

$$\rightarrow SiHF + SiH_3F \quad (21)$$

$$\rightarrow SiH_2F + SiH_2F \quad (22)$$

$$\rightarrow HFSi{=}SiHF + H_2 \quad (23)$$

$$\rightarrow H_2Si{=}SiHF + HF \quad (24)$$

$$\rightarrow H_2Si{=}SiH_2 + F_2 \quad (25)$$

Reactions 6, 15, and 22 are homolytic bond cleavage reactions and can be assumed to have little or no barrier in the reverse direction. The reverse of reactions 1, 2, 9, and 18 are insertion reactions into H_2, while the reverse of reactions 3, 10, and 19 are insertions into HF. Decomposition reactions yielding F_2 are too high in energy[5] and hence are not considered here. The other categories are insertions of SiH_2 into $SiH_{4-n}F_n$ (reactions 4, 12, and 20), insertions of SiHF into $SiH_{4-n}F_n$ (reactions 5, 13, and 21), and insertion of SiF_2 in SiH_4 (reaction 14). The 1,2-elimination of H_2 from Si_2H_6 was studied by Gordon et al.[6] and found to have a very high barrier; the 1,2-elimination of HF is expected to have a similarly high barrier. Hence 1,2-eliminations are not considered in this study.

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(1) Patai, S., Rappoport, Z., Eds. *The Chemistry of Organic Silicon Compounds*; Wiley: New York, 1989.
(2) Corey, E. R., Gaspar, P. P., Eds. *Silicon Chemistry*; Ellis Horwood: Chichester, England, 1988.
(3) Jasinski, J. M.; Meyerson, B. S.; Scott, B. A. *Annu. Rev. Phys. Chem.* **1987**, *38*, 109.
(4) Pankove, J. I., Ed. *Semiconductors and Semimetals*; Academic: New York, 1984.
(5) Ignacio, E. W.; Schlegel, H. B. *J. Phys. Chem.*, this issue. Sosa, C.; Schlegel, H. B. *J. Am. Chem. Soc.* **1984**, *106*, 5847.
(6) Gordon, M. S.; Truong, T. N.; Bonderson, E. K. *J. Am. Chem. Soc.* **1986**, *108*, 1421.
(7) Gordon, M. S.; Gano, D. R. *J. Am. Chem. Soc.* **1984**, *106*, 5421.
(8) Schlegel, H. B.; Sosa, C. *J. Phys. Chem.* **1985**, *89*, 537.
(9) Raghavachari, K.; Chandrasekhar, J.; Gordon, M. S.; Dykema, K. J. *Am. Chem. Soc.* **1984**, *106*, 5853.
(10) Trucks, G. W.; Raghavachari, K.; Higashi, G. S.; Chabal, Y. J. *Phys. Rev. Lett.* **1990**, *65*, 504; *66*, 1648.
(11) Schlegel, H. B. *J. Phys. Chem.* **1984**, *88*, 6255. Ignacio, E. W.; Schlegel, H. B. *J. Chem. Phys.* **1990**, *92*, 5404.
(12) Ho, P.; Melius, C. F. *J. Phys. Chem.* **1990**, *94*, 5120.
(13) Curtiss, L. A.; Raghavachari, K.; Deutsch, P. W.; Pople, J. A. *J. Chem. Phys.* **1991**, *95*, 2433.
(14) Sax, A. F.; Kalcher, J. *J. Phys. Chem.* **1991**, *95*, 1768.
(15) Agrawal, P. M.; Thompson, D. L.; Raff, L. M. *J. Chem. Phys.* **1990**, *92*, 1069.

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TABLE I: Total Energies[a]

molecule	3-21G HF	6-31G* HF	6-31G* MP2	6-31G* MP3	6-31G* MP4	3-21G ZPE
			Reactants			
$H_3Si-SiH_3$	−578.241 21	−581.305 09	−581.464 51	−581.497 30	−581.508 31	31.86
$H_3Si-SiH_2F$	−676.625 17	−680.225 84	−680.554 87	−680.579 93	−680.598 00	29.31
$H_3Si-SiHF_2$	−775.022 27	−779.158 11	−779.659 00	−779.676 49	−779.701 87	26.33
$H_2FSi-SiH_2F$ (anti)	−775.006 49	−779.146 25	−779.644 53	−779.661 88	−779.686 88	26.74
			Products			
$H_3Si-SiH$	−577.038 70	−580.080 05	−580.225 71	−580.257 12	−580.268 15	19.78
$H_2FSi-SiH$	−675.420 87	−679.001 50	−679.317 02	−679.340 81	−679.358 83	17.26
$HF_2Si-SiH$	−773.812 68	−777.931 67	−778.418 46	−778.434 71	−778.459 92	14.32
$H_3Si-SiF$	−675.431 27	−679.007 10	−679.328 24	−679.351 02	−679.371 15	17.26
$H_2FSi-SiF$	−773.810 90	−777.927 32	−778.417 69	−778.432 87	−778.459 84	14.65
			Transition States			
$H_3Si-SiH--H_2$	−578.127 12	−581.186 96	−581.365 64	−581.400 55	−581.412 62	29.24
$H_2FSi-SiH--H_2$	−676.513 53	−680.110 05	−680.458 75	−680.485 87	−680.504 98	26.79
$HF_2Si-SiH--H_2$	−774.908 67	−779.041 11	−779.562 33	−779.581 86	−779.608 38	23.60
$H_3Si-SiF--H_2$	−676.499 29	−680.095 73	−680.447 63	−680.474 62	−680.494 73	25.73
$H_2FSi-SiF--H_2$	−774.883 24	−779.018 21	−779.539 63	−779.559 01	−779.586 31	23.69
$H_3Si-SiH--HF$	−676.478 26	−680.054 79	−680.410 55	−680.433 26	−680.457 14	26.38
$H_2FSi-SiH--HF$	−774.861 69	−778.975 02	−779.500 73	−779.515 61	−779.546 59	23.92
$H_3Si-SiF--HF$	−774.865 56	−778.978 23	−779.507 26	−779.521 95	−779.554 04	23.05
$H_3Si-H--SiH_2$	−578.142 79	−581.211 67	−581.381 55	−581.415 53	−581.427 73	30.24
$H_2FSi-H--SiH_2$ (s)	−676.537 79	−680.143 22	−680.484 46	−680.510 19	−680.529 78	27.95
$HF_2Si-H--SiH_2$ (sg)	−774.932 42	−779.070 29	−779.583 03	−779.601 36	−779.628 28	25.08
$H_3Si-H--SiHF$	−676.520 02	−680.123 38	−680.463 86	−680.490 28	−680.510 22	27.77
$H_2FSi-H--SiHF$	−774.941 05	−779.055 31	−779.570 08	−779.585 31	−779.614 71	25.93
$H_3Si-H--SiF_2$	−774.903 08	−779.040 74	−779.551 42	−779.570 11	−779.697 69	24.66
$H_3Si-F--SiH_2$	−676.546 00	−680.127 81	−680.469 64	−680.492 87	−680.514 43	28.65
$H_2FSi-F--SiH_2$	−774.945 69	−779.063 43	−779.577 59	−779.593 23	−779.621 71	25.35
$H_3Si-F--SiHF$	−774.909 21	−779.049 05	−779.560 49	−779.578 58	−779.606 14	25.14

[a] In atomic units for total energies, kcal/mol for zero-point energies.

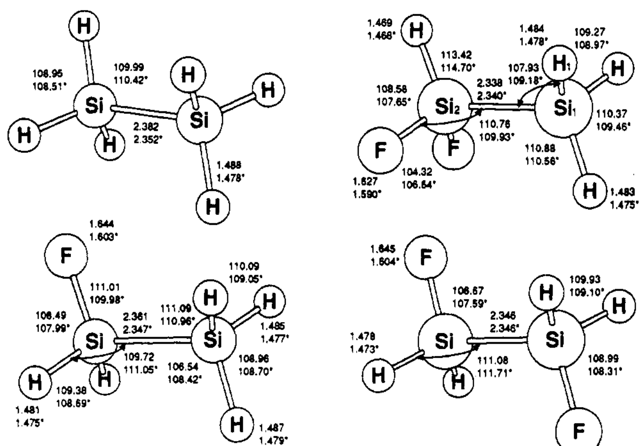


Figure 1. Optimized geometries of the fluorodisilane reactants: no superscript, HF/3-21G; asterisk, HF/6-31G*.

Computational Method

Ab initio MO calculations were carried out with GAUSSIAN 88 and GAUSSIAN 90[16] with split valence (3-21G)[17] and polarization (6-31G*)[18] basis sets. All geometries were fully optimized at the Hartree–Fock level with the 3-21G and 6-31G* basis sets using analytical gradient methods.[19] Zero-point energies were obtained at the HF/3-21G level using analytical second derivatives. The fourth-order Møller–Plesset perturbation theory[20] in the space of single, double, triple, and quadruple excitations (MP4SDTQ, frozen core) was used to estimate electron correlation energy with the 6-31G* basis set.

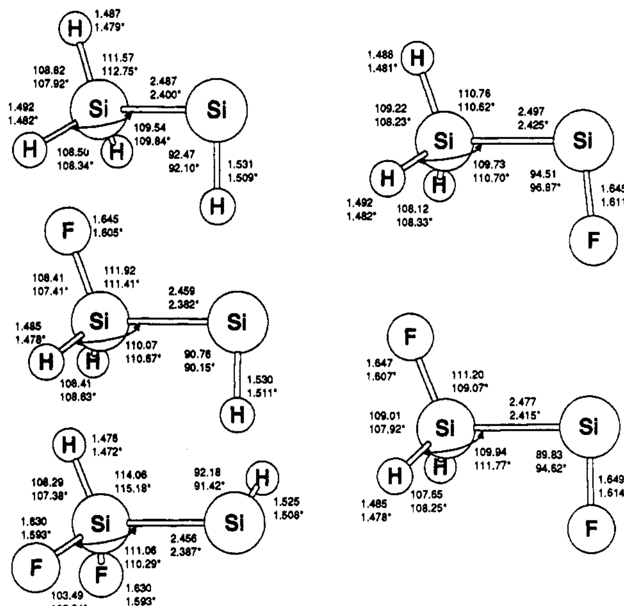


Figure 2. Optimized geometries of the fluorosilylsilylene products: no superscript, HF/3-21G; asterisk, HF/6-31G*.

Results and Discussion

Table I presents the total energies of the disilane reactants, transition states, and products. Data for the monosilanes appearing in the products of reactions 1–25 have been published previously.[5,11]

(16) Frisch, M. J.; Head-Gordon, M.; Trucks, G. W.; Foresman, J. B.; Schlegel, H. B.; Raghavachari, K.; Robb, M. A.; Binkley, J. S.; Gonzalez, C.; DeFrees, D. J.; Fox, D. J.; Whiteside, R. A.; Seeger, R.; Melius, C. F.; Baker, J.; Martin, L. R.; Kahn, L. R.; Stewart, J. J. P.; Topiol, S.; Pople, J. A. *Gaussian 90* Gaussian, Inc.: Pittsburgh, PA, 1990.

(17) Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 939. Gordon, M. S.; Binkley, J. S.; Pople, J. A.; Pietro, W. J.; Hehre, W. J. *J. Am. Chem. Soc.* **1982**, *104*, 2797.

(18) Hariharan, P. C.; Pople, J. A. *Theor. Chem. Acta* **1973**, *28*, 213. Francl, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; DeFrees, D. J.; Pople, J. A. *J. Chem. Phys.* **1982**, *77*, 3654 and references cited.

(19) Schlegel, H. B. *J. Comput. Chem.* **1982**, *3*, 214.

(20) Pople, J. A.; Krishnan, R.; Schlegel, H. B.; Binkley, J. S. *Int. J. Quantum Chem., Quantum Chem. Symp.* **1979**, *13*, 225. For a review, see: Bartlett, R. J. *Annu. Rev. Phys. Chem.* **1981**, *32*, 359.

TABLE II: Barriers for Silylene Insertion Reactions[a]

reactions	3-21G HF	6-31G* HF	6-31G* MP2	6-31G* MP3	6-31G* MP4	3-21G ΔZPE
$HSiH + H_2 \rightarrow SiH_4$[b]		21.7	11.1	11.2	12.0	3.5
$H_3Si\text{-}SiH + H_2 \rightarrow H_3Si\text{-}SiH_3$	24.5	15.3	5.4	6.5	6.8	2.8
$H_2FSi\text{-}SiH + H_2 \rightarrow H_3Si\text{-}SiH_2F$	21.9	14.4	4.4	5.5	5.8	2.9
$HF_2Si\text{-}SiH + H_2 \rightarrow HF_2Si\text{-}SiH_3$	19.6	13.2	2.6	3.6	3.8	2.6
$HSiF + H_2 \rightarrow SiH_3F$[b]		41.7	21.6	33.3	34.2	3.0
$SiH_3\text{-}SiF + H_2 \rightarrow H_3Si\text{-}SiH_2F$	36.3	25.8	17.3	17.9	18.9	1.8
$H_2FSi\text{-}SiF + H_2 \rightarrow H_2FSi\text{-}SiH_2F$	34.2	24.9	16.3	16.9	17.7	2.4
$HSiH + HF \rightarrow SiH_3F$[b]		19.4	-0.1	5.7	3.9	1.0
$H_3Si\text{-}SiH + HF \rightarrow H_3Si\text{-}SiH_2F$	13.8	18.5	-1.3	5.3	0.1	0.8
$H_2FSi\text{-}SiH + HF \rightarrow H_2FSi\text{-}SiH_2F$	12.6	19.3	-0.5	6.2	0.9	0.8
$HSiF + HF \rightarrow SiH_2F_2$[b]		22.1	3.5	9.4	7.8	0.3
$H_3Si\text{-}SiF + HF \rightarrow HF_2Si\text{-}SiH_3$	15.9	20.0	1.7	7.9	3.2	0.1
$H_3Si\text{-}H + SiH_2 \rightarrow H_3Si\text{-}SiH_3$	20.7	11.1	-1.9	-1.0	-1.2	2.5
$H_2FSi\text{-}H + SiH_2 \rightarrow H_3Si\text{-}SiH_2F$	15.2	5.4	-8.8	-7.4	-8.3	2.3
$HF_2Si\text{-}H + SiH_2 \rightarrow HF_2Si\text{-}SiH_3$	17.7	9.1	-5.1	-3.8	-4.8	2.0
$H_3Si\text{-}H + SiHF \rightarrow H_3Si\text{-}SiH_2F$	32.4	23.0	12.7	13.2	13.0	1.9
$H_2FSi\text{-}H + SiHF \rightarrow H_2FSi\text{-}SiH_2F$	30.6	21.0	9.8	10.7	9.8	1.4
$H_3Si\text{-}H + SiF_2 \rightarrow HF_2Si\text{-}SiH_3$	54.2	44.4	38.2	38.2	38.5	1.1
$H_3Si\text{-}F + SiH_2 \rightarrow H_3Si\text{-}SiH_2F$	10.8	15.8	1.2	4.2	2.1	3.0
$H_2FSi\text{-}F + SiH_2 \rightarrow H_2FSi\text{-}SiH_2F$	9.7	13.7	-1.4	1.7	-0.4	2.3
$H_3Si\text{-}F + SiHF \rightarrow HF_2Si\text{-}SiH_3$	11.4	17.9	4.5	7.2	5.2	2.2

[a] In kcal/mol with ΔZPE included. [b] From ref 5, MP4 values do not include triples.

TABLE III: Isodesmic Reactions Used To Compute the Heats of Formation of the Fluorodisilanes and Silylsilylenes[a]

reactions	3-21G HF	6-31G* HF	6-31G* MP2	6-31G* MP3	6-31G* MP4	3-21G ΔZPE	molecule, $\Delta H_f{}^\circ{}_0$
$H_3Si\text{-}SiH_2F + 2SiH_4 \rightarrow Si_2H_6 + SiH_3F + SiH_4$	-1.5	-1.2	-1.0	-1.2	-0.8	0.4	$H_3Si\text{-}SiH_2F$, -73.4
$H_3Si\text{-}SiHF_2 + 2SiH_4 \rightarrow Si_2H_6 + SiH_2F_2 + SiH_4$	-2.4	-1.4	-1.1	-1.4	-0.8	0.9	$H_3Si\text{-}SiHF_2$, -174.0
$H_2FSi\text{-}SiH_2F + 2SiH_4 \rightarrow Si_2H_6 + 2SiH_3F$	-4.7	-2.5	-2.5	-2.7	-2.0	0.9	$H_2FSi\text{-}SiH_2F$, -166.2
$H_3Si\text{-}SiH + SiH_4 \rightarrow Si_2H_6 + SiH_2$	-0.6	-0.5	0.1	0.0	0.0	-0.7	$H_3Si\text{-}SiH$, 74.8
$H_2FSi\text{-}SiH + SiH_4 \rightarrow H_2FSi\text{-}SiH_3 + SiH_2$	-1.7	-0.1	0.6	0.7	0.6	-0.7	$H_2FSi\text{-}SiH$, -19.1
$HF_2Si\text{-}SiH + SiH_4 \rightarrow HF_2Si\text{-}SiH_3 + SiH_2$	-5.1	-1.8	-1.3	-1.4	-1.4	-0.7	$HF_2Si\text{-}SiH$, -117.6
$H_3Si\text{-}SiF + SiH_4 \rightarrow Si_2H_6 + SiHF$	-2.9	-3.0	-2.1	-2.4	-1.6	-0.0	$H_3Si\text{-}SiF$, -26.4
$H_2FSi\text{-}SiF + SiH_4 \rightarrow H_2FSi\text{-}SiH_3 + SiHF$	-5.6	-3.3	-2.7	-2.8	-2.2	0.0	$H_2FSi\text{-}SiF$, -119.0

[a] In kcal/mol with ΔZPE included.

Barriers for insertion reactions are given in Table II. Table III presents the data for isodesmic reactions used to calculate the heats of formation of the fluorodisilanes and silylsilylenes; Table IV summarizes the thermal decomposition barriers.

Geometries. The structures of the disilane reactants and products are shown in Figures 1 and 2; the geometries of the monosilanes have been discussed previously.[5] The effect of fluorine substitution on disilane is relatively minor. The bonds adjacent to the fluorine are slightly shorter; the F-Si-Si and F-Si-H angles are somewhat smaller than their hydrogen analogues. For 1,2-difluorosilane, the gauche and anti conformers are equal in energy ($E_{gauche} - E_{trans}$ = -0.2 and 0.3 kcal/mol at HF/3-21G and HF/6-31G*, respectively). In the silylsilylenes, fluorine substitution on the divalent silicon opens the angle by ca. 4.5°, similar to the monosilylenes, $SiH_{2-n}F_n$. For the 2-fluoro-, 1,2-difluoro- and 2,2-diflurosilylenes, the conformers with the silylene lone pair syn to an Si-F bond are slightly favored.

The geometry of the transition state for silylsilylene insertion into H_2 (Figure 3a) is essentially the same as that of $SiH_2 + H_2$ in terms of the distances and angles between the silylene and H_2. Fluorine substitution on the silyl group has very little effect on the transition-state geometry (other rotomers may also be first-order saddle points). Similarly, the transition structures for the ipso fluorosilylsilylenes (Figure 3d,e) are close analogues of SiHF + H_2. The transition states for fluorosilylsilylene insertion into HF, Figure 4, closely resemble that of SiXY + HF[5] and can also be expected to form a cluster with HF prior to the transition state for insertion.

Figure 5 shows the transition structures for silylene insertion into an SiH bond or, correspondingly, the transition structures for disilane decomposition into a silylene and a monosilane. These structures can also be viewed as a 1,2-hydrogen shift across an Si-Si bond, followed by dissociation into a silylene and a silane. The Si-Si bond is elongated by 0.1-0.2 Å, and the migrating

TABLE IV: Thermal Decomposition Barriers of $Si_2H_{6-n}F_n$ (n = 1, 2)[a]

reaction	$\Delta H_f{}^\circ{}_0$	barrier forward	barrier reverse
$H_3Si\text{-}SiH_3$			
$\rightarrow H_3Si\text{-}SiH + H_2$	55	55	-3
$\rightarrow SiH_4 + SiH_2$	56	56	-1
$\rightarrow SiH_3 + SiH_3$	76	76	0
$\rightarrow H_2Si{=}SiH_2 + H_2$	47	86	39
$H_3Si\text{-}SiFH_2$			
$\rightarrow H_2FSi\text{-}SiH + H_2$	54	54	-4
$\rightarrow H_3Si\text{-}SiF + H_2$	47	56	9
$\rightarrow H_3Si\text{-}SiH + HF$	83	86	3
$\rightarrow SiH_3F + SiH_2$	55	55	-8, 2
$\rightarrow SiH_4 + SiHF$	47	60	13
$\rightarrow SiH_3 + SiH_2F$	78	78	0
$H_3Si\text{-}SiHF_2$			
$\rightarrow HF_2Si\text{-}SiH + H_2$	56	56	-6
$\rightarrow H_3Si\text{-}SiF + HF$	83	89	6
$\rightarrow SiH_2F_2 + SiH_2$	55	55	-5, 0
$\rightarrow SiH_3F + SiHF$	53	58	5
$\rightarrow SiH_4 + SiF_2$	32	71	39
$\rightarrow SiH_3 + SiHF_2$	81	81	0
$H_2FSi\text{-}SiH_2F$			
$\rightarrow H_2FSi\text{-}SiF + H_2$	47	54	7
$\rightarrow H_2FSi\text{-}SiH + HF$	82	86	4
$\rightarrow SiH_2F_2 + SiH_2$	48	48	0
$\rightarrow SiH_3F + SiHF$	45	50	5, 10
$\rightarrow SiH_2F + SiH_2F$	79	79	0

[a] In kcal/mol; data for $Si_2H_6 \rightarrow H_2Si{=}SiH_2 + H_2$ taken from ref 6.

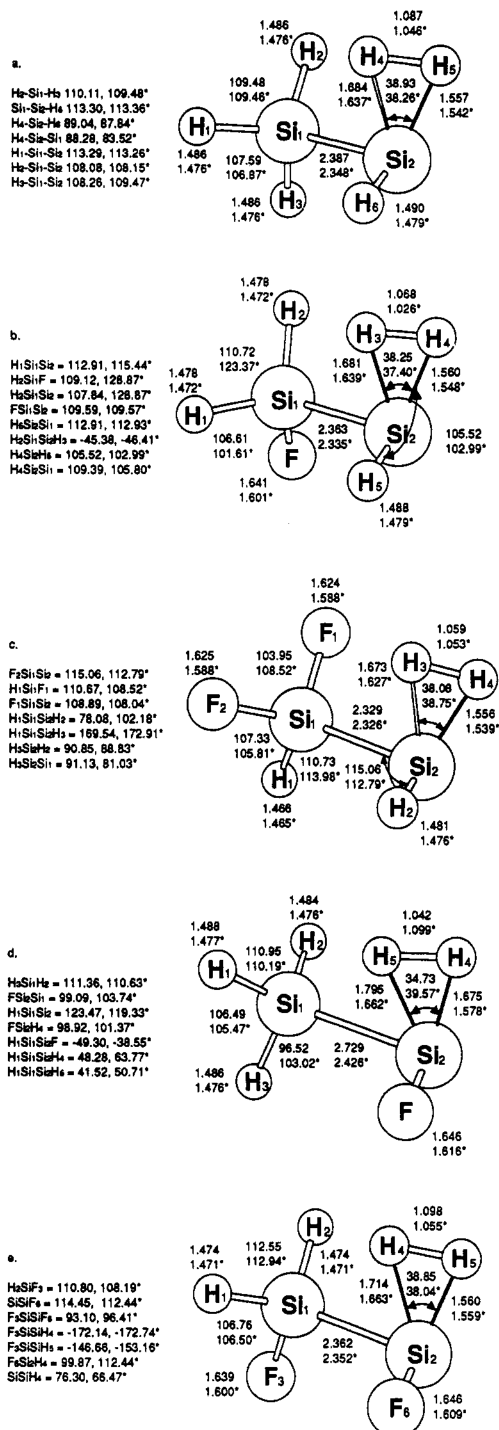


Figure 3. Optimized geometries of the transitions states for insertion into H_2: no superscript, HF/3-21G; asterisk, HF/6-31G*.

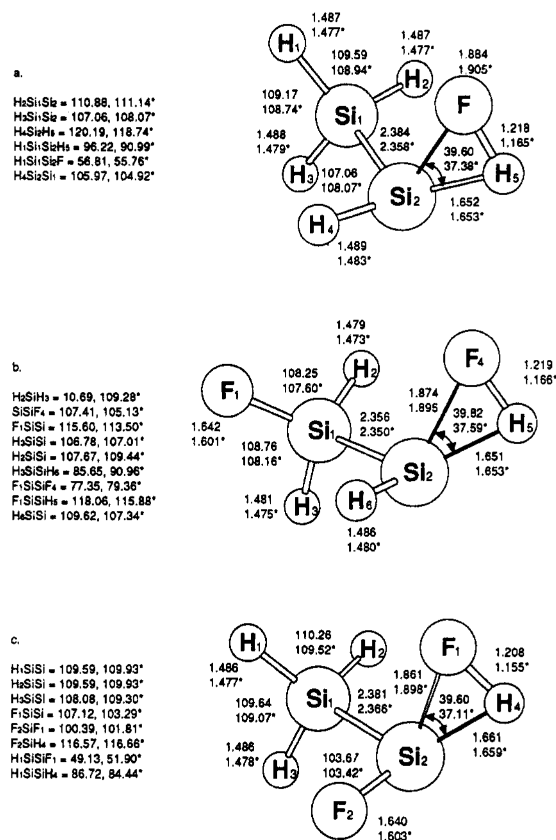
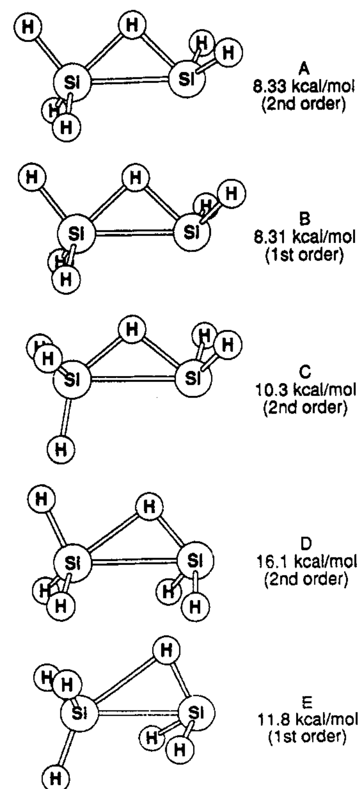


Figure 4. Optimized geometries of the transition states for insertion into HF: no superscript, HF/3-21G; asterisk, HF/6-31G*.

SCHEME I: Conformations and HF/6-31G* Barriers for SiH_2 + SiH_4 Insertion



hydrogen sits approximately above the midpoint of the bond. As shown in Scheme I, four generic conformations (A–E) can be constructed for the parent silylene insertion, $SiH_2 + SiH_4$. At the Hartree–Fock level, the insertion barrier is lower for the hydrogen migrating to the empty p_π orbital of the silylene (structures A and C) than for the hydrogen migrating to the filled lone pair (structures D and E); of the two rotomers, the syn orientation between the silyl Si–H bond and the migrating hydrogen (structure A) is lower than the anti (structure C). However, structures A, C, and D are all second-order saddle points (i.e. two imaginary frequencies) at both the HF/3-21G and HF/6-31G* levels. The lowest energy transition state at the HF level, structure B (also shown in Figure 5a), has C_1 symmetry and can be obtained from structure A by rotating 10–25° about the Si–Si bond. At the MP2 level, the $SiH_2 + SiH_4$ insertion takes place without a barrier[7] or via a transition state with an energy lower than that of the reactants (see Table II). The fluorine-substituted transition states, Figure 5b–f, are derived from structure A of Scheme I and each possesses only one imaginary frequency. Fluorine substitution has surprisingly little effect on the geometry of the transition states. The transition structures with a fluorine syn to the migrating hydrogen are more stable than

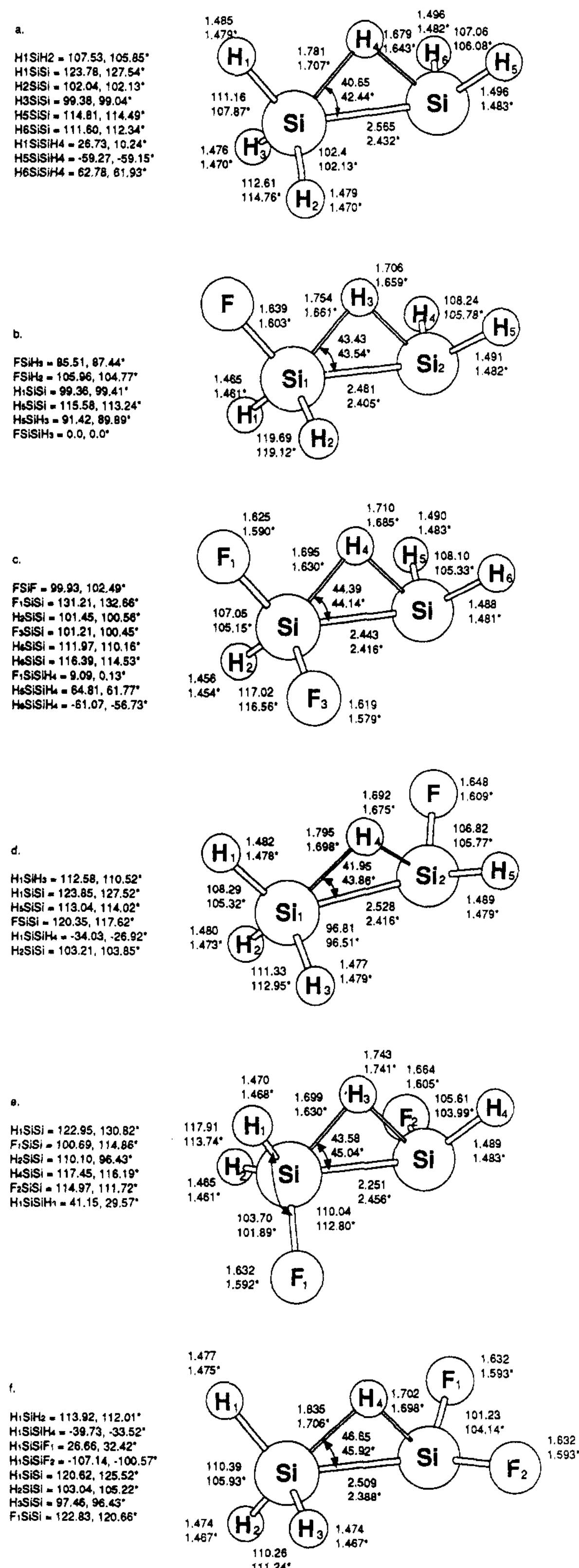


Figure 5. Optimized geometries of the transition states for insertion into Si-H bonds: no superscript, HF/3-21G; asterisk, HF/6-31G*.

the other rotomers. For H_2FSi-H + SiH_2, the syn rotomer is more stable than the gauche by 3.6 and 4.5 kcal/mol at HF/3-21G and HF/6-31G* levels, respectively; for HF_2Si-H + SiH_2, the syn,gauche structure is 4.2 and 2.9 kcal/mol more stable than the gauche,gauche at HF/3-21G and HF/6-31G* levels, respectively.

Figure 6 shows the transition states for silylene insertion into Si-F bonds. The parent reaction SiH_2 + SiH_3F has been studied previously.[7] Like the insertions into SiH bonds, these reactions

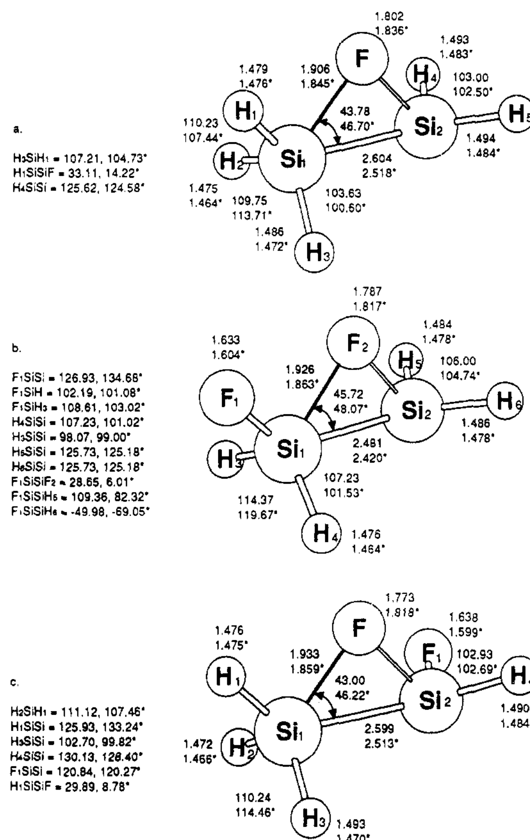
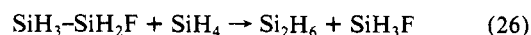


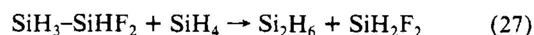
Figure 6. Optimized geometries of the transition states for insertion into Si-F bonds: no superscript, HF/3-21G; asterisk, HF/6-31G*.

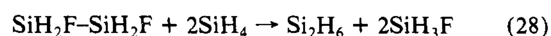
can also be described as 1,2-migrations. The fluorine is situated over the middle of the Si-Si bond approximately equidistant from the two silicons. The elongation of the Si-Si bond is similar to those of the transition states for insertion into Si-H. The effect of fluorine substitution on the transition-state geometry is small (other rotamers may also be first-order saddle points).

Insertion Barriers. The computed barriers for insertion reactions are collected in Table II. The barrier for insertion into H_2 is ca. 5 kcal/mol lower with SiH_3SiH than with SiH_2; fluorine substitution of the silyl group lowers the barrier by another 1-2 kcal/mol per fluorine. By contrast, the barrier for SiH_3SiF + H_2 insertion is 20 kcal/mol lower than that of SiHF + H_2, suggesting that the electron-donating ability of the SiH_3 group counteracts to a large extent the electron-withdrawing/barrier-raising property of the ipso fluoro substitution discussed previously.[5] By contrast, the change in the barrier for insertion into HF is relatively small (2-4 kcal/mol) when SiH_2 is replaced by SiH_3SiH or SiH_2FSiH and when SiHF is replaced by SiH_3SiF. The barriers for SiH_2 or SiHF insertion into either an Si-H bond or an Si-F bond in $SiH_{4-n}F_n$ appear to decrease with increasing fluorine substitution of the silane. When insertion into either Si-H or Si-F is possible, SiH_2 prefers the former but SiHF prefers the latter at the level of theory used in this study.

Heats of Formation. The experimental and theoretical $\Delta H_f°$ for the monosilanes were discussed in our earlier paper.[11] The heats of formation of the fluorodisilanes and silylsilylenes in the present study can be determined from the following isodesmic reactions:


$$SiH_3\text{-}SiH_2F + SiH_4 \rightarrow Si_2H_6 + SiH_3F \quad (26)$$


$$SiH_3\text{-}SiHF_2 + SiH_4 \rightarrow Si_2H_6 + SiH_2F_2 \quad (27)$$


$$SiH_2F\text{-}SiH_2F + 2SiH_4 \rightarrow Si_2H_6 + 2SiH_3F \quad (28)$$

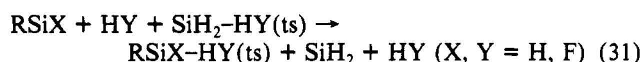
$$SiH_{3-n}F_n\text{-}SiH + SiH_4 \rightarrow SiH_{3-n}F_n\text{-}SiH_3 + SiH_2 \quad (29)$$

$$SiH_{3-n}F_n\text{-}SiF + SiH_4 \rightarrow SiH_{3-n}F_n\text{-}SiH_3 + SiHF \quad (30)$$

The heats of reaction for (26)-(30) are shown in Table III along with the heats of formation derived from these reactions. The

$\Delta H_f{}^\circ{}_0$ for Si_2H_6 computed at the G2 level of theory[13] ($\Delta H_f{}^\circ{}_0$ = 19.8 kcal/mol) has been used as a reference value. The calculated $\Delta H_f{}^\circ{}_0$ for SiH_3SiH (74.8 kcal/mol) is within 2 kcal/mol of the experimental values (73 ± 2 kcal/mol)[21-23] and the theoretical value computed at the G2 level[13] (73.7 kcal/mol). This suggests that the other heats of formation calculated from reactions 26–30 may have similar error bars.

Mechanism for Thermal Decomposition. The data pertinent to the thermal decomposition of the fluorodisilanes is collected in Table IV. The barriers for the reverse reactions were taken from Table II for the silylene insertions or were set to zero for homolytic bond cleavage. Calculations on monosilane decompositions[5] indicate that barriers for silylene insertion into H_2 are too high by 6 kcal/mol at the present level of theory; likewise, insertion barriers involving HF appear to be 4 kcal/mol too low at the present level of theory. The following isodesmic reaction was used to estimate the barriers for H_2 and HF insertions listed in Table IV



$$RSiX + HY + SiH_2\text{–}HY(ts) \rightarrow RSiX\text{–}HY(ts) + SiH_2 + HY \ (X, Y = H, F) \quad (31)$$

based on higher level calculations for $SiH_2 + H_2 \rightarrow SiH_2\text{–}H_2(ts)$ (1.7 kcal/mol[24]) and $SiH_2 + HF \rightarrow SiH_2\text{–}HF(ts)$ (6.6 kcal/mol[5]).

The energy profiles for thermal decomposition of the fluorodisilanes are shown in Figure 7. The preferred pathways for decomposition involve 1,1-elimination of H_2 and the extrusion of SiH_2 or SiHF. Homolytic cleavage of the Si–Si bond is typically 15–30 kcal/mol higher; 1,1-elimination of HF is ca. 30 kcal/mol higher. These trends are also expected to hold for more highly fluorinated disilanes.

For Si_2H_6, the barriers for decomposition into $SiH_3SiH + H_2$ and $SiH_2 + SiH_4$ are approximately equal. In Si_2H_5F, the barrier heights for $SiH_2FSiH + H_2$, $SiH_3SiF + H_2$, and $SiH_2 + SiH_3F$ (the reverse of insertion into the SiH bond) are nearly the same. The path leading to $SiHF + SiH_4$ lies ca. 5 kcal/mol higher. The 1,1-elimination barrier of HF is very high, solely due to the heat of the reaction (83 kcal/mol). Gordon et al.[6] and Curtiss et al.[13] have calculated that $SiH_2{=}SiH_2$ is 7–9 kcal/mol more stable than SiH_3SiH. Hence the ΔH_r for 1,2-elimination of HF is ca. 74–76 kcal/mol. The barrier for $SiH_2{=}SiH_2 + H_2$ 1,2-addition is ca. 40 kcal/mol; this suggests that the barrier for 1,2-elimination of HF may be 20–40 kcal/mol higher than the heat of reaction (e.g. a barrier of 95–115 kcal/mol). Thus reactions involving 1,2-elimination of H_2 or HF are not considered further.

The barrier heights for decomposition of $Si_2H_4F_2$ depend on whether the fluorine substitution is 1,1 or 1,2. As is evident from the difference in the heats of formation of the two isomers ($\Delta\Delta H_f{}^\circ$ = 7.8 kcal/mol, Table III) and from bond separation reactions such as $SiH_4 + SiH_2F_2 \rightarrow 2SiH_3F$ (ΔH_r = 6.4 kcal/mol[11]), there is a special stabilization when two fluorines are attached to the same center (for a discussion of this effect, see ref 25). For $H_3Si\text{–}SiHF_2$, the lowest energy channels lead to $HF_2Si\text{–}SiH + H_2$ and to $SiH_2 + SiH_2F_2$ with $SiHF + SiH_3F$ a few kcal/mol higher; for $H_2FSi\text{–}SiH_2F$ decomposition, the $SiH_2 + SiH_2F_2$, $H_2FSi\text{–}SiF + H_2$, and $SiHF + SiH_3F$ pathways are nearly equal.

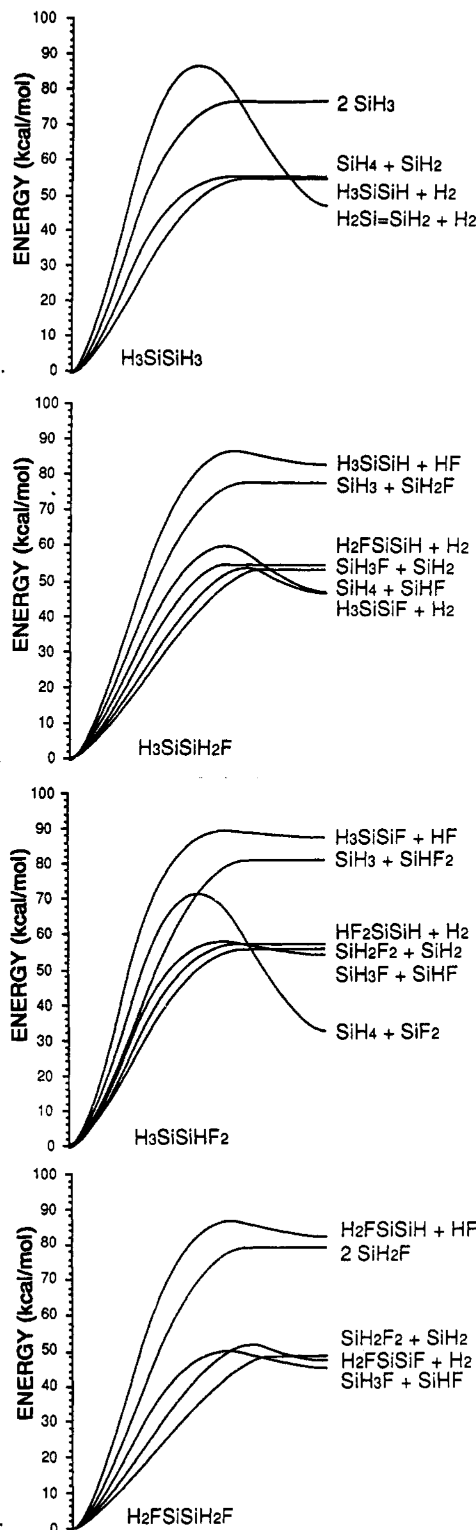


Figure 7. Energy profiles for the unimolecular decomposition of fluorodisilanes (data from Table IV).

Summary

The pathways for thermal decomposition of fluorodisilanes have been examined by ab initio molecular orbital methods. Barriers for homolytic bond cleavage have been obtained from calculated heats of formation of reactants and products. Earlier studies showed that 1,2-elimination reactions have very high barriers; hence they were not considered explicitly. The remaining pathways, 1,1-elimination of H_2 or HF and extrusion of SiXY (X, Y = H, F), are the reverse of silylene insertion reactions. The transition structures for the insertion of $SiH_{3-n}F_nSiH$ and $SiH_{3-n}F_nSiF$ into H_2 and HF closely resemble the transition structures for SiH_2 and SiHF plus H_2 and HF. The transition states for the insertion of SiXY (X,Y = H,F) into Si–H and Si–F bonds have structures that can best be described as 1,2-migration of H or F across the Si–Si bond in the product disilane. Fluorine substitution on the silyl group has a relatively small effect on the structures of the transition states for insertion reactions. Ipso fluorine substitution of silylsilylenes raises the insertion barriers but not as much as for the monosilylenes, apparently because of the electron-donating ability of the silyl group. The preferred

(21) Walsh, R. *Acc. Chem. Res.* **1981**, *14*, 246.
(22) Walsh, R. *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds. Wiley: New York, 1989; Chapter 5.
(23) Martin, G.; O'Neal, H. E.; Ring, M. A. *Int. J. Chem. Kinet.* **1990**, *22*, 613.
(24) Gordon, M. S.; Gano, D. R.; Frisch, M. J.; Binkley, J. S. *J. Am. Chem. Soc.* **1986**, *108*, 2191.
(25) Dill, J. D.; Schleyer, P. v. R.; Pople, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 1663. Ignacio, E. W.; Schlegel, H. B. *J. Phys. Chem.*, submitted for publication.

pathways for thermal decomposition of the fluorodisilanes involve 1,1-elimination of H_2 and extrusion of SiH_2 or SiHF from $RSiH_{3-n}F_n$ groups. Products with multiple fluorines on the same tetravalent center appear to be preferred over products with fluorines on different centers.

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Transition-State Properties for the Reaction of Hydroxyl Radicals with Methane

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Experimental data have been collected from a review of relevant literature regarding the temperature dependence of the rate constant for transfer of a hydrogen atom from methane to hydroxyl. Transition-state theory expressions were fitted to the data by least squares methods to determine three parameters: the mean of four low-frequency vibrational term values in the transition species, $\omega_b = 570 \pm 20$ cm^{-1}, the characteristic tunneling temperature, which was less than 200 K, and the effective height of the activation barrier, $V_b = 19 \pm 2$ kJ mol^{-1}.

Introduction

The reaction

$$OH + CH_4 \rightarrow H_2O + CH_3$$

plays a central role in the combustion of natural gas. Consequently, the reaction has been the subject of many experimental kinetic studies,[1-17] over a wide range of temperatures. The Arrhenius plot for the reaction is curved. This presents an opportunity to learn more from the temperature dependence than just the usual two Arrhenius parameters. A modified Arrhenius expression with an extra factor of T^n has previously been fitted to the data,[7,9,12,18] but the parameters determined did not have simple physical significance. An alternative, which is explored in the present article, is to fit a transition-state theory (TST) model[19] to the kinetic data.

TABLE I: Summary of Input Parameters

ω_{b1}, cm^{-1}	1306
I_{CH_4}, g Å^2 mol^{-1}	3.20
I_{OH}, g Å^2 mol^{-1}	0.89
Δ, cm^{-1}	139.7
$V_{br} - V_b$, kJ mol^{-1}	61.4
δ	4
$(I_X I_Y I_Z)_{TS}$, g^3 Å^6 mol^{-3}	1.34×10^4
I_{IR}, g Å mol^{-1}	0.67

The first two parameters obtained from this model are the effective barrier height, V_b, and the mean, transitional, vibrational term value, ω_b. To deal with the change of vibrational frequencies from reactants to transition state to products, it is assumed that several vibrational partition functions do not change significantly and that the remaining transitional vibrations may be combined in an average, low-frequency term value for the transition species. This three-parameter TST model also incorporates the notion of tunneling through the barrier with a characteristic tunneling temperature, T^*. This parameter, T^*, can be related to the second derivative of the barrier top by means of the equation

$$T^* = hc\omega^*/2\pi k_B \quad (1)$$

where h is Planck's constant, c the speed of light, k_B Boltzmann's constant, and ω^* the term value for vibration in a well created by inverting the barrier.[19]

In order to obtain these three parameters V_b, T^*, and ω_b from the TST model, several properties of the reactants and transition state must be known. Moments of inertia and vibrational frequencies of the reactants were obtained from spectroscopic sources.[20] Moments of inertia for the transition state were calculated from a semiempirical bond energy-bond order (BEBO) estimation.[16]

This method has previously been applied to several other reactions.[19,21,22] It has consistently provided transition-state

(1) Wilson, W. E.; Westenberg, A. A. *Symp. (Int.) Combust.*, [*Proc.*] **1967**, *11*, 1143-1149.
(2) Greiner, N. R. *J. Chem. Phys.* **1970**, *53*, 1070-1076.
(3) Davis, D. D.; Fisher, S.; Schiff, R. *J. Chem. Phys.* **1974**, *61*, 2213-2219.
(4) Margitan, J. J.; Kaufman, F.; Anderson, J. G. *Geophys. Res. Lett.* **1974**, *1*, 80-81.
(5) Gordon, S.; Mulac, W. A. *Int. J. Chem. Kinet., Symp.* **1975**, *1*, 289-299.
(6) Overend, R.; Paraskevopoulos, G.; Cvetanovic, R. J. *Can. J. Chem.* **1975**, *53*, 3374-3382.
(7) Zellner, R.; Steinert, W. *Int. J. Chem. Kinet.* **1976**, *8*, 397-409.
(8) Cox, R. A.; Derwent, R. G.; Holt, P. M. *J. Chem. Soc., Faraday Trans. 1* **1976**, *72*, 2031-2043.
(9) Tully, F. P.; Ravishankara, A. R. *J. Phys. Chem.* **1980**, *84*, 3126-3130.
(10) Jeong, K.-M.; Kaufman, F. *J. Phys. Chem.* **1982**, *86*, 1808-1815.
(11) Baulch, D. L.; Craven, R. J. B.; Din, M.; Drysdale, D. D.; Grant, S.; Richardson, D. J.; Walker, A.; Watling, G. *J. Chem. Soc., Faraday Trans. 1* **1983**, *79*, 689-698.
(12) Madronich, S.; Felder, W. *Symp. (Int.) Combust.*, [*Proc.*] **1984**, *20*, 703-711.
(13) Jonah, C. D.; Mulac, W. A.; Zeglinski, P. *J. Phys. Chem.* **1984**, *88*, 4100-4104.
(14) Smith, G. P.; Fairchild, P. W.; Jeffries, J. B.; Crosley, D. R. *J. Phys. Chem.* **1985**, *89*, 1269-1278.
(15) Bott, J. F.; Cohen, N. *Int. J. Chem. Kinet.* **1989**, *21*, 485-498.
(16) Ernst, J.; Wagner, H.; Zellner, R. *Ber. Bunsen-Ges. Phys. Chem.* **1978**, *82*, 409-414.
(17) Howard, C. J.; Evenson, K. M. *J. Chem. Phys.* **1976**, *64*, 197-201.
(18) Zellner, R. *J. Phys. Chem.* **1979**, *83*, 18-23.
(19) Furue, H.; Pacey, P. D. *J. Phys. Chem.* **1990**, *94*, 1419-1425.
(20) Chase, M.; Davies, C.; Downey, J.; Frurip, D.; McDonald, A.; Syverud, A. JANAF Thermochemical Tables. *J. Phys. Chem. Ref. Data, Suppl. 1* **1985**, *14*, 595, 596, 1248, 1274.

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