in the formation of NH(A) from hydrazine. In methylamine the values predicted from type (c) are in close agreement with the observed, whereas those predicted from type (a) are inconsistent with the observed. It is likely that the umbrella inversion motion of $CH_3(X)$ is selectively enhanced in dissociation process 8.

The ajusted E_{av} values for the formation of NH(A) from hydrazine and methylamine are 1.3–1.9 eV. These fairly large available energies suggest that the conformation of the precursor states forming NH(A) is very different from that of the ground state of each parent molecule, and that higher vibrational levels of the precursor state are formed according to the Franck–Condon principle. Thus, these NH(A) formations are probably due to excitation into a pure repuslive precursor state. The rotational

energy distribution of the NH(A) state seems to be enhanced when the products depart from each other on a repulsive surface. In the formation of NH(c) from hydrazine, by use of energy disposal of types (a) and (b), E_{av} of 0.4 eV for process (6) is obtained on comparison of the observed T_r of NH(c) with the predicted value. This E_{av} value is considerably lower than that for the formation of NH(A). This, together with the fairly good agreement between the onset and ΔH for NH(c) formation from hydrazine, indicates that NH(c) formation is probably ascribed to excitation into the repulsive wall of a bound precursor state.

Heats of Formation of Fluorine-Substituted Silylenes, Silyl Radicals, and Silanes

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The experimental heats of formation are known quite accurately for SiH_4 and SiF_4 and somewhat less accurately for SiH_2, SiF_2, and SiH_3. There is some disagreement over the heat of formation of SiF_3 and similar experiments on SiH_3F, SiH_2F_2, and $SiHF_3$ may also be unreliable. The heats of formation of SiHF, SiH_2F, and $SiHF_2$ have not been determined experimentally. Ab initio molecular orbital calculations have been carried out at the MP4SDQ/6-31G**//HF/6-31G* level and a series of isodesmic reactions has been used in conjunction with the experimental values for SiH_2, SiF_2, SiH_3, SiH_4, and SiF_4 to estimate the following heats of formation (298 K, ideal gas): SiHF, -132 ± 6; SiH_2F, -178 ± 6; $SiHF_2$, -586 ± 6; SiF_3, -1000 ± 5; SiH_3F, -355 ± 2; SiH_2F_2, -772 ± 2; and $SiHF_3$, -1201 ± 2 kJ mol^{-1}.

Introduction

The kinetics and reactivity of small silicon-containing molecules are attracting considerable interest. Silicon is not simply a second-row analogue of carbon, and reaction mechanisms can be quite different from the first row.[1] For example, pyrolysis of silanes yields silylenes rather than silyl radicals, whereas photolysis produces silyl radicals.[1] Both silylenes and silyl radicals with various degrees of fluorination are though to be important intermediates in chemical vapor deposition[2,3] and glow discharge deposition[4] of amorphous silicon films from SiH_4 and SiF_4, as well as in plasma etching of silicon surfaces[5] by CF_4, but the mechanisms of these processes are not well understood.

Fundamental to the understanding of the kinetics and mechanisms of reactions involving these silicon compounds is a reliable set of heats of formation. For a few of the stable compounds accurate experimental ΔH_f° are available[6] (SiH_4,[7] SiF_4[8]), while reasonable values exist for some of the reactive species (SiH_2,[9,10] SiF_2,[11] SiH_3[12]). There is a bit of controversy over the ΔH°_f for SiF_3.[11,13,14] Farber and Srivastava[11] have obtained a value from the high-temperature equilibration of Si and SiF_4, but this underestimates the SiH dissociation energy in $SiHF_3$ which was measured directly by Doncaster and Walsh.[13] High-temperature equilibration measurements[15] have also been carried out for SiF_4 and H_2, yielding heats of formation for SiH_3F, SiH_2F_2, and $SiHF_3$. However, these may be subject to similar difficulties, since differences in the ΔH_f° show trends opposite to the first-row analogues.[16,17] For the remainder (SiHF, SiH_2F, and $SiHF_2$) no measurements of the heats of formation are available. Thus, there appears to be considerable uncertainty in the heats of formation for at least half of the compounds, particularly for the partially fluorinated structures.

We became aware of this gap in the thermochemistry of small silicon compounds during a quantum chemical study of fluorosilylene insertion reactions.[18] In the present paper, we use ab

initio molecular orbital calculations at the MP4/6-31G** level to examine a series of isodesmic reactions and to estimate the heats of formation of fluorine substituted silylenes, silyl radicals, and silanes.

Method

Ab initio molecular orbital calculations were performed with the GAUSSIAN 80 and 82 systems[19] using split-valence[20] (3-21G)

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TABLE I: Total Energies[a]

| | 3-21G | 6-31G* | | | | 6-31G** | | | | | | |
	$-E$(HF)	$-E$(HF)	$-E2$	$-E3$	$-E$4SDQ	$-E$(HF)	$-E2$	$-E3$	$-E$4SDQ	$-E$4T	ZPE	thermal
SiH$_2$	288.48429	289.99978	0.06728	0.01707	0.00491	290.00263	0.08075	0.01820	0.00464	0.00109	31.4	7.5
SiHF	386.88166	388.93190	0.24222	0.00871	0.00895	388.93341	0.24912	0.00936	0.00889	0.00526	23.5	7.7
SiF$_2$	485.30063	487.88467	0.41879	0.00030	0.01255	487.88467	0.41879	0.00030	0.01255	0.00961	13.8	8.5
SiH$_3$	289.08054	290.60612	0.06833	0.01607	0.00422	290.61058	0.08766	0.01782	0.00380	0.00116	57.5	7.9
SiH$_2$F	387.45897	389.52283	0.23841	0.00811	0.00763	389.52590	0.25148	0.00942	0.00750	0.00469	48.9	8.1
SiHF$_2$	485.84972	488.45082	0.41030	0.00036	0.01103	488.45237	0.41673	0.00104	0.01101		37.6	9.1
SiF$_3$	584.24278	587.38123	0.58160	-0.00697	0.01401	587.38123	0.58160	-0.00697	0.01401		24.2	10.7
SiH$_4$	289.68698	291.22513	0.08189	0.01838	0.00470	291.23084	0.10815	0.02100	0.00426	0.00135	84.7	7.9
SiH$_3$F	388.07406	390.14840	0.25130	0.01083	0.00777	390.15284	0.27135	0.01304	0.00768	0.00469	75.8	8.2
SiH$_2$F$_2$	486.47324	489.08181	0.42288	0.00357	0.01094	498.53723	0.43626	0.00514	0.01099		65.2	9.2
SiHF$_3$	584.87584	588.01833	0.59458	-0.00317	0.01387	588.01985	0.60115	-0.00236	0.01393		51.8	10.8
SiF$_4$	683.27208	686.94984	0.76461	-0.00917	0.01637	686.94984	0.76461	-0.00917	0.01637		36.0	12.7

[a] Total energies in au; E(MP2) = E(HF) + $E2$, E(MP3) = E(HF) + $E2$ + $E3$. E(MP4SDTQ) = E(HF) + $E2$ + $E3$ + E4SDQ + E4T; zero point energies and thermal contributions in kJ mol^{-1}, 1 au = 2625.5 kJ mol^{-1}; total energies for hydrogen atom: E(HF) = -0.49620 at 3-21G and -0.49824 at 6-31G*; total energies for fluorine atom: E(HF) = -98.84501 for 3-21G and E(HF) = -99.36496, E(MP2) = -99.48727, E(MP3) = -99.49569, E(MP4SDQ) = -99.49745, E(MP4SDTQ) = -99.49865 for 6-31G*.

TABLE II: Molecular Geometries[a]

molecule	symmetry	parameter	HF/ 3-21G	HF/ 6-31G*	exptl
SiH$_2$	C_{2v}	R(SiH)	1.530	1.508	1.521
		∠HSiH	93.7	93.3	92.1
SiHF	C_s	R(SiF)	1.637	1.602	
		R(SiH)	1.534	1.516	
		∠HSiF	97.7	97.3	
SiF$_2$	C_{2v}	R(SiF)	1.625	1.592	1.591
		∠FSiF	96.6	99.9	101.0
SiH$_3$	C_{3v}	R(SiH)	1.486	1.476	
		∠HSiH	107.2	108.0	
SiH$_2$F	C_s	R(SiF)	1.640	1.598	
		R(SiH)	1.483	1.476	
		∠HSiF	109.9	108.8	
		∠HSiH	110.7	110.4	
SiHF$_2$	C_s	R(SiF)	1.625	1.586	
		R(SiH)	1.480	1.475	
		∠FSiF	104.8	107.1	
		∠HSiF	109.8	108.6	
SiF$_3$	C_{3v}	R(SiF)	1.610	1.575	1.56
		∠FSiF	112.3	111.2	109.5
SiH$_4$	T_d	R(SiH)	1.486	1.475	1.481
SiH$_3$F	C_{3v}	R(SiF)	1.635	1.594	1.593
		R(SiH)	1.478	1.470	1.486
		∠HSiF	109.2	108.8	108.4
SiH$_2$F$_2$	C_{2v}	R(SiF)	1.619	1.581	1.577
		R(SiH)	1.464	1.461	1.471
		∠FSiF	105.4	107.6	107.9
		∠HSiH	113.2	113.4	112.0
SiHF$_3$	C_{3v}	R(SiF)	1.601	1.569	1.562
		R(SiH)	1.445	1.449	1.447
		∠HSiF	112.1	110.9	110.6
SiF$_4$	T_d	R(SiF)	1.584	1.557	1.552

[a] Bond lengths in Å, angles in degrees; experimental geometries refer to r_0 structures quoted in the most recent JANAF tables[6] (SiH$_2$ from ref 28).

and polarization[21] (6-31G* and 6-31G**) basis sets. The 6-31G* basis contains a set of six Cartesian d functions on each of the heavy atoms; the 6-31G** basis augments the 6-31G* basis with a set of three p functions on each hydrogen. All equilibrium geometries were fully optimized with analytical gradient methods[22] at the HF/3-21G and HF/6-31G* levels. Electron correlation energy was estimated with Møller–Plesset perturbation theory[23]

TABLE III: Vibrational Frequencies[a]

molecule	frequencies, cm^{-1}	ref
SiH$_2$	1107, 2063, 2078, (1005, , 2022)	30
SiHF	920, 965, 2046 (834, 859, 1913)	31
SiF$_2$	377, 958, 973 (345, 885, 872)	32
SiH$_3$	784, 989′, 2275, 2292′	
SiH$_2$F	775, 863, 935, 1005, 2293, 2312	
SiHF$_2$	328, 838, 847, 940, 1030, 2296	
SiF$_3$	229′, 415, 905, 1062′ (290′, 406, 832, 954′)	33
SiH$_4$	973″, 1046′, 2286″, 2295 (913″, 972′, 2186″, 2189)	34
SiH$_3$F	800′, 943, 990′, 1132, 2338′, 2352 (728′, 875, 961′, 2209′, 2206)	35
SiH$_2$F$_2$	341, 782, 805, 934, 996, 1041, 1127, 2429, 2435 (322, 730, 730, 869, 903, 981, 982, 2225, 2246)	36
SiHF$_3$	315′, 430, 922, 946′, 1119′, 2556 (305′, 425, 844′, 859, 999′, 2315)	37
SiF$_4$	270′, 392″, 845, 1156″ (264′, 389″, 801, 1030″)	38

[a] Calculated harmonic frequencies at the HF/3-21G level; experimental anharmonic frequencies in parentheses; doubly degenerate modes indicated with a single prime, triply degenerate with a double prime.

up to fourth order, including all single, double, and quadruple excitations (MP4SDQ, frozen core). For some of the smaller molecules triple substitutions could also be included. Vibrational frequencies and zero point energies were obtained from analytical second derivatives[24] calculated at the HF/3-21G level. Thermal contributions include $^1/_2 RT$ for each translational and rotational degree of freedom, plus changes in the vibrational energy due to thermal population of the excited vibrational modes.[25] The enthalpy difference for a reaction is the energy difference (electronic + zero point + thermal) plus the change in PV (ΔPV = 0 for isodesmic reactions). Ideal gas entropies were calculated by standard statistical mechanical methods.[25]

Results and Discussion

Total energies, molecular geometries, and vibrational frequencies are listed in Tables I, II, and III respectively for SiH$_2$, SiHF, SiF$_2$, SiH$_3$, SiH$_2$F, SiHF$_2$, SiF$_3$, SiH$_4$, SiH$_3$F, SiH$_2$F$_2$, SiHF$_3$, and SiF$_4$. Data for some of these compounds have been published previously[18,26,27] but are collected here for convenience. Table IV and V present Si–F and Si–H dissociation energies; selected isodesmic reactions are given in Table VI. Theoretical estimates and experimental values for the heats of formation are summarized in Table VII.

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TABLE IV: Si–H Dissociation Energies[a]

level	SiH$_3$	SiH$_2$F	SiHF$_2$	SiH$_4$	SiH$_3$F	SiH$_2$F$_2$	SiHF$_3$
HF/3-21G	262.7	213.0	138.9	289.4	312.1	334.3	359.3
HF/6-31G*	238.8	243.4	178.3	317.1	334.3	348.5	364.6
MP2/6-31G*	286.6	233.3	156.0	352.7	368.2	381.5	398.6
MP3/6-31G*	283.9	231.8	156.2	358.8	375.3	390.0	408.6
MP4SDQ/6-31G*	282.1	228.3	152.2	360.0	375.6	389.8	408.3
HF/6-31G*	288.0	247.5	182.4	320.4	337.9	352.4	368.6
MP2/6-31G**	306.2	253.7	177.0	374.2	390.1	403.7	419.9
MP3/6-31G**	305.2	253.8	179.0	382.5	399.6	414.5	432.0
MP4SDQ/6-31G**	303.0	250.2	174.9	383.7	400.1	414.4	431.8
MP4SDTQ/6-31G**	303.2	248.7		384.2	400.1		
ΔZPE[b]	−24.3	−23.5	−22.1	−25.3	−25.0	−25.7	−25.7
theor[c]	278.7	226.7	152.8	358.4	375.1	388.7	406.1
exptl	260[d]			372[f]			418[g]
	280[e]						351[g]

[a] In kJ mol^{-1}. [b] HF/3-21G ΔZPE's scaled by 0.93. [c] MP4SDQ/6-31G** + ΔZPE. [d] Using $\Delta H_f°(SiH_2)$ recommended by Bell et al.[10] [e] Using $\Delta H_f°(SiH_2)$ calculated by Pople et al.[41] [f] Doncaster and Walsh.[2,13] [g] Farber and Srivastava.[11,15]

TABLE V: Si–F Dissociation Energies [a]

level	SiH$_2$F	SiHF$_2$	SiF$_3$	SiH$_3$F	SiH$_2$F$_2$	SiHF$_3$	SiF$_4$
HF/3-21G	340.5	323.1	255.1	389.9	444.4	475.5	483.9
HF/6-31G*	415.1	404.2	345.5	465.6	509.4	531.8	534.7
MP2/6-31G*	543.2	524.4	451.8	624.8	672.6	694.5	694.1
MP3/6-31G*	497.6	480.3	410.7	588.9	638.5	663.1	666.2
MP4SDQ/6-31G*	500.1	481.2	409.7	593.7	642.6	665.9	667.7
HF/6-31G**	415.6	404.3	345.5	465.5	509.3	531.7	534.7
MP2/6-31G**	542.8	523.3	451.8	626.7	673.3	694.8	694.1
MP3/6-31G**	497.6	479.3	410.7	592.0	639.9	663.7	666.2
MP4SDQ/6-31G**	500.5	480.2	409.7	597.6	644.5	666.8	667.7
MP4SDTQ/6-31G**	506.8			603.7			
ΔZPE[b]	−16.3	−13.1	−9.7	−17.0	−15.2	−13.2	−11.0
theor[c]	484.2	467.1	400.0	580.6	629.3	653.6	656.7
exptl			484[d]	643[e]			686[d]
			570[e]				600[e]

[a] In kJ mol^{-1}. [b] HF/3-21G ΔZPE's scaled by 0.93. [c] MP4SDQ/6-31G** + ΔZPE. [d] Doncaster and Walsh.[12,13] [e] Farber and Srivastava.[11,15]

TABLE VI: Isodesmic Reactions[a]

level	SiHF$_3$ + SiH$_3$ → SiH$_4$ + SiF$_3$	$^1/_2$SiH$_2$ + $^1/_2$SiF$_2$ → SiH$_2$F	$^2/_3$SiH$_3$ + $^1/_3$SiF$_3$ → SiH$_2$F	$^1/_3$SiH$_3$ + $^2/_3$SiF$_3$ → SiHF$_2$	$^3/_4$SiH$_4$ + $^1/_4$SiF$_4$ → SiH$_3$F	$^1/_2$SiH$_4$ + $^1/_2$SiF$_4$ → SiH$_2$F$_2$	$^1/_4$SiH$_4$ + $^3/_4$SiF$_4$ → SiHF$_3$
HF/3-21G	69.9	28.4	23.6	14.8	24.1	16.5	−0.1
HF/6-31G*	47.5	27.1	21.9	14.1	20.8	14.9	0.9
MP2/6-31G*	45.9	29.2	24.5	14.7	24.1	15.9	−0.8
MP3/6-31G*	49.8	29.2	25.2	15.6	25.9	18.6	1.5
MP4/6-31G*	48.3	28.6	24.8	14.8	25.5	17.5	0.4
HF/6-31G**	48.2	26.9	21.6	13.9	20.3	14.5	0.6
MP2/6-31G**	45.7	28.6	23.8	14.5	22.8	14.8	−1.1
MP3/6-31G**	49.5	28.3	24.1	15.2	23.9	16.8	0.9
MP4/6-31G**	48.1	27.5	23.4	14.1	22.8	15.0	−0.7
ΔZPE[b]	−0.4	0.8	2.3	2.1	3.1	4.6	3.3
thermal	−0.1	−0.3	−0.7	−0.7	−0.9	−1.1	−0.7
theor[c]							
$\Delta H°$(0 K)	47.7 ± 4	28.3 ± 2	25.7 ± 2	16.2 ± 2	23.9 ± 2	19.6 ± 2	2.6 ± 2
$\Delta H°$(298 K)	47.6 ± 4	28.0 ± 2	25.0 ± 2	15.5 ± 2	23.0 ± 2	18.5 ± 2	1.9 ± 2
exptl							
$\Delta H°$(298 K)	41 ± 5[d]				−38 ± 8[e]	−13 ± 8[e]	−23 ± 8[e]
	−21 ± 8[e]						

[a] In kJ mol^{-1}. [b] HF/3-21G ΔZPE's scaled by 0.93. [c] MP4SDQ/6-31G** + ΔZPE + thermal. [d] Doncaster and Walsh.[12,13] [e] Farber and Srivastava.[11,15]

Geometry. The HF/6-31G* optimized geometries in Table II are in good agreement with experiment. As already established,[20] the HF/3-21G level underestimated Si–F bond lengths. The most clearly discernible trend is a decrease in the Si–F bond length with increasing fluorine substitution (ΔR_{SiF} = ca. 0.1 Å per fluorine). A similar trend is seen for the Si–H bonds in the silanes and to a lesser extent in the silyl radicals. Although systematic changes in the bond angles should also be expected (e.g., increasing pyramidality of the radicals with fluorine substitution), no clear trends are found.

Frequencies. The experimental anharmonic vibrational frequencies are compared with the theoretical harmonic frequencies in Table III and in Figure 1. The theoretical frequencies are relatively uniformly 7.4% higher than the observed, primarily due to the neglect of vibrational anharmonicity and electron correlation. A scale factor of 0.93 has been applied to all zero point energy differences used below to correct for this overestimation. For the first row, HF/3-21G calculations yield frequencies that are 12% too high.[29] The apparently better performance for the second row probably can be traced to the overestimation of the SiF bond length at the HF/3-21G level which, in turn, lowers the frequency

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TABLE VII: Heats of Formation and Entropies[a]

molecule	calcd			exptl			
	$\Delta H_f°$(0 K)	$\Delta H_f°$(298 K)	S(298 K)	$\Delta H_f°$(0 K)	$\Delta H_f°$(298 K)	S(298 K)	ref
SiH$_2$			207	250 ± 6	248 ± 6		9, 10
					268		41
SiHF	-141 ± 6	-142 ± 6	239	-172 ± 20	-173 ± 20		c
	-131 ± 6[b]	-132 ± 6[b]			-163[b]		c
SiF$_2$			256	-587 ± 1	-588 ± 1	256	6, 11
SiH$_3$			217	200 ± 6	195 ± 6		12
SiH$_2$F	-173 ± 6	-178 ± 6	249	-199 ± 20	-203 ± 20		c
SiHF$_2$	-583 ± 6	-586 ± 6	270	-598 ± 20	-602 ± 20		c
SiF$_3$	-989 ± 4	-992 ± 4		-997 ± 5	-1000 ± 5	282	13
			282	-1082 ± 8	-1085 ± 8		11
SiH$_4$			204	44 ± 2	34 ± 2	205	6
SiH$_3$F	-345 ± 2	-355 ± 2	238	-369 ± 20	-378 ± 20	238	6
				-408 ± 8	-416 ± 8		15
SiH$_2$F$_2$	-763 ± 2	-772 ± 2	261	-782 ± 20	-791 ± 20	262	6
				-795 ± 8	-804 ± 8		15
SiHF$_3$	-1193 ± 2	-1201 ± 2	276	-1196 ± 20	-1203 ± 20	277	6
				-1217 ± 8	-1226 ± 8		15
SiF$_4$			282	-1609 ± 1	-1615 ± 1	283	6

[a] Heats of formation in kJ mol^{-1}, entropies in J K^{-1} mol^{-1}. [b] Using $\Delta H_f°$(SiH$_2$) calculated by Pople et al.[41] [c] Estimated by linear interpolation.
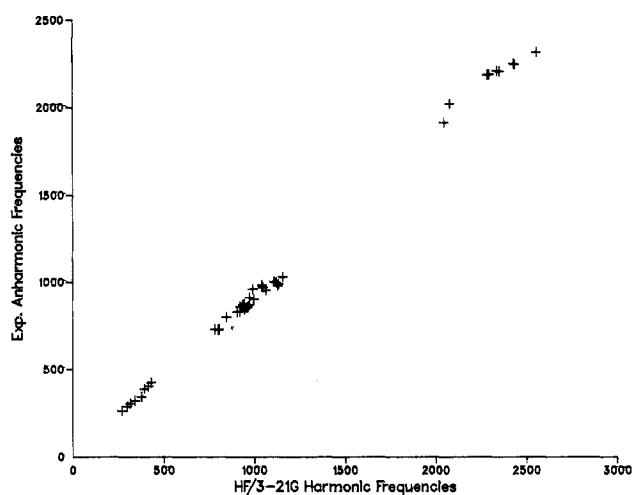

Figure 1. Experimental anharmonic vibrational frequencies vs. calculated harmonic frequencies for SiH$_2$, SiHF, SiF$_2$, SiF$_3$, SiH$_4$, SiH$_3$F, SiH$_2$F$_2$, SiHF$_3$, and SiF$_4$.

and improves the agreement. The calculated SiH stretching frequencies increase more rapidly with fluorine substitution than the observed frequencies. This is because the changes in the SiH bond lengths with fluorine substitution are somewhat too large at the 3-21G level.

Bond Dissociation Energies. The calculated SiH dissociation energies are compared with experiment in Table IV. In general, the basis set and correlation effects are relatively large. Nevertheless, the D_0(Si–H) for SiH$_4$ is only 14 kJ mol^{-1} from the experimental value.[12] A similar agreement is found for CH$_4$ with the same level of calculation.[39] For SiHF$_3$ the calculated value
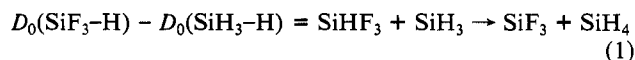
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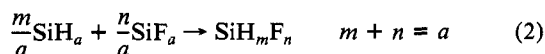(34) Kattenberg, H. W.; Oskam, A. *J. Mol. Spectrosc.* **1974**, *49*, 52.
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is in agreement with Doncaster and Walsh[13] (12 kJ mol^{-1}) but not with the D_0(SiH) obtained by using the $\Delta H_f°$ of Farber and Srivastava.[11,15] The SiH dissociation energies for the other silanes vary smoothly between D_0(SiH$_3$–H) and D_0(SiF$_3$–H), suggesting that these calculated values are also uniformly 10–15 kJ mol^{-1} too low.

The calculated SiH dissociation energies in the radicals are not as good as the silanes (errors of -1, (-31), and (-61) kJ mol^{-1} for SiH$_3$, SiH$_2$F, and SiHF$_2$, respectively, based on the experimental (and theoretical) heats of formation in Table VII). The change in the error is more disconcerting than the magnitude. MCSCF calculations by Schaefer[26] have shown that the ground-state wave function contains a large contribution (~0.2) from the low-lying excited singlet configuration. This suggests that triple substitutions may be important for an MP4 calculation based on a single reference determinant. However, at the MP4SDTQ/6-31G** level, the SiH dissociation energies are essentially unchanged.

Table V lists the calculated and experimental SiF dissociation energies. The basis set and correlation effects are larger than for SiH dissociations, as are the absolute errors in the dissociation energies (30 kJ mol^{-1} for SiF$_4$). For the silanes, the bond strengths increase with fluorine substitution. This is in contrast to the experimental values based on data by Farber and Srivastava.[11,15] The calculated SiF dissociation energies in the radicals are affected by the same computational difficulties in the silylenes discussed above.

Isodesmic Reactions. If the reactants and products contain the same numbers of the same types of bonds, the reaction is said to be isodesmic. Errors due to basis set and correlation energy nearly cancel; zero point energy changes and differences in the temperature dependence of the enthalpy are also small. Table VI lists the set of isodesmic reactions that are appropriate for the estimation of the heats of formation for SiH$_n$F$_m$.

Bond dissociations are not isodesmic reactions, but differences in dissociations are isodesmic. In particular, consider:

$$D_0(\text{SiF}_3\text{–H}) - D_0(\text{SiH}_3\text{–H}) = \text{SiHF}_3 + \text{SiH}_3 \rightarrow \text{SiF}_3 + \text{SiH}_4 \quad (1)$$

Although the SiH dissociation energies change by 65 kJ mol^{-1} in going from the HF/6-31G* level to MP4/6-31G**, the differences in D_0(SiH) vary by only ±2 kJ mol^{-1}; hence, considerable confidence can be placed in the estimated $\Delta H°$(298) for this reaction. The calculation results (48 kJ mol^{-1}) are in good agreement with Doncaster and Walsh[12] (41 kJ mol^{-1}) but not Farber and Srivastava[11,15] (-21 kJ mol^{-1}).

The other isodesmic reactions in Table VI correspond to an interpolation between the unsubstituted and the perfluoro compounds.

$$\frac{m}{a}\mathrm{SiH}_a + \frac{n}{a}\mathrm{SiF}_a \rightarrow \mathrm{SiH}_m\mathrm{F}_n \qquad m + n = a \qquad (2)$$

Linear interpolation of the $\Delta H°_f$ amounts to assuming $\Delta H° = 0$ for these reactions. The calculations indicate sizeable deviations from linearity in the same direction as the fluoromethanes.[16,17] The interpolation reactions seem to be even less sensitive to basis set and correlation effects than (1), with the HF/3-21G values being within 1–2 kJ mol^{-1} of the MP4/6-31G** results. Hence, the estimated $\Delta H°(298)$'s should be quite reliable. The calculations for the fluorosilanes disagree in sign and magnitude with Farber and Srivastava (further discussion below).

The heat of reaction for $^1/_2\mathrm{SiH}_2 + {}^1/_2\mathrm{SiF}_2 \rightarrow \mathrm{SiHF}$ is ca. 27 kJ mol^{-1} at the HF level, and ca. 28 kJ mol^{-1} at the MP2, MP3, and MP4 levels based on a single reference configuration. This is in good agreement with the DZ+P, two-configuration SCF (TCSCF) calculations of Schaefer et al.[26,40] (25 kJ mol^{-1}). To test the importance of higher excitations, we repeated our MP4 calculations with triple substitutions (MP4SDTQ/6-31G**) and found a change of only 0.3 kJ mol^{-1}. This suggests that basis set effects could be more significant than higher excitations.

Experimental Heats of Reaction. Table VII summarizes the measured $\Delta H_f°$ for various fluorine substituted silylenes, silyl radicals, and silanes. The $\Delta H_f°$ for SiH$_4$ has been obtained from the decomposition of silane to amorphous silicon and hydrogen;[7] $\Delta H_f°$ for SiF$_4$ has been determined by direct combination of the elements.[8] Purnell et al.[9] have studied the kinetics of silane and disilane pyrolysis, obtaining a value for $\Delta H_f°(\mathrm{SiH}_2)$. Bell, Perkins, and Perkins[10] have reviewed the literature and recommend $\Delta H_f° = 248$ kJ mol^{-1} for SiH$_2$. Extensive calculations by Pople et al.[41] indicate $\Delta H_f° = 268$ kJ mol^{-1} for SiH$_2$ and suggest the kinetic data for SiH$_2$ insertions be reinterpreted. The high-temperature equilibration of Si and SiF$_4$ has yielded $\Delta H_f°$ for SiF$_2$.[11] Doncaster and Walsh have measured the SiH bond dissociation energy in SiH$_4$[12] and SiHF$_3$,[13] permitting the calculation of the heat of formation of SiH$_3$ and SiF$_3$ (given $\Delta H_f°$ for SiHF$_3$). Farber and Srivastava[11] have also obtained a value for SiF$_3$ from SiF$_4$ + SiF$_2$ → 2 SiF$_3$, a side reaction in Si + SiF$_4$ → 2SiF$_2$. However, Walsh[14] has questioned this result, since it leads to an unusually low value for $D_0(\mathrm{SiH})$ in SiHF$_3$. The heats of formation for SiH$_3$F, SiH$_2$F$_2$, and SiHF$_3$ reported in the JANAF tables[6] were derived by linear interpolation. For the carbon analogues,[16,17] this leads to errors of 50 kJ mol^{-1}. Farber and Srivastava[15] have obtained $\Delta H_f°$ for SiH$_3$F, SiH$_2$F$_2$, and SiHF$_3$ from the reaction of SiF$_4$ and H$_2$ at high temperatures. These do show strong deviations from a linear interpolation, but in a sense opposite to the carbon analogues.[16,17] Thus these values should be used with caution. There are no experimental data for SiHF, SiH$_2$F, and SiHF$_2$. Approximate values can be obtained by linear interpolation, keeping in mind

that sizeable errors could result.

Theoretical Estimates of $\Delta H_f°$. The calculated $\Delta H°$ for reactions in Table VI can be combined with the experimental $\Delta H_f°$ in Table VII to estimate the heats of formation of the partially fluorinated compounds. For the silanes, the linear interpolated values quoted in the JANAF tables[6] are in error by up to 25 kJ mol^{-1}. This discrepancy is less than for the fluorocarbons, indicating that the nonadditive interactions in the fluorosilanes are smaller. The theoretical $\Delta H_f°$ for SiH$_3$F, SiH$_3$F, SiH$_2$F$_2$, and SiHF$_3$ disagree with the values of Farber and Srivastava[15] by up to 60 kJ mol^{-1}. Since the calculated $\Delta H°$ for the isodesmic reactions used to determine these $\Delta H_f°$ are constant over two orders of magnitude of change in the complexity of the wave function, the theoretical results are probably more reliable than the $\Delta H_f°$ determined by Farber and Srivastava.[15]

The measured $D_0(\mathrm{SiF}_3\mathrm{-H})$[13] can be combined with the calculated $\Delta H_f°$ for SiHF$_3$ to give $\Delta H_f° = -1000 \pm 5$ kJ mol^{-1} for SiF$_3$. Alternatively, the calculated $\Delta H°$ for SiHF$_3$ + SiH$_3$ → SiF$_3$ + SiH$_4$ can be combining with the heats of formation SiH$_3$, SiH$_4$, and SiHF$_3$ to yield $\Delta H_f°(\mathrm{SiF}_3) = -992 \pm 4$ kJ mol^{-1}, in good agreement with the value based on $D_0(\mathrm{SiF}_3\mathrm{-H})$. Since the isodesmic reactions 2 seem to be less sensitive to the calculational level than reaction 1, $\Delta H_f° = -1000 \pm 5$ kJ mol^{-1} is probably a better estimate. This value is used along with the isodesmic reactions in Table VI to obtain $\Delta H_f°$ for SiH$_2$F and SiHF$_2$. An analogous interpolation for the silylenes yields $\Delta H_f°(\mathrm{SiHF}) = -132 \pm 6$ kJ mol^{-1} from the present calculations and -135 ± 6 kJ mol^{-1} from Schaefer's data.[26]

Entropies. Ideal gas entropies are also listed in Table VII. The present values are based on the theoretical vibrational frequencies and molecular geometries. This gives rise to a ca. 1 J K^{-1} mol^{-1} difference when compared to the ideal gas values calculated in the JANAF tables.[6]

Conclusions

Good agreement with experiment is found for the theoretical optimized geometries and vibrational frequencies of fluorine-substituted silylenes, silyl radicals, and silanes. The $\Delta H°$ for a series of isodesmic reactions have been calculated at levels up to MP4SDQ/6-31G**. Since heats of reaction are not very sensitive to the calculational level, they have been used to estimate the $\Delta H_f°$ for SiHF, SiH$_2$F, SiHF$_2$, SiF$_3$, SiH$_3$F, SiH$_2$F$_2$, and SiHF$_3$. The results are in agreement with the $D_0(\mathrm{SiH}_3\mathrm{-H})$ and $D_0(\mathrm{SiF}_3\mathrm{-H})$ measured by Doncaster and Walsh[12,13] but disagree with the $\Delta H_f°$ obtained by Farber and Srivastava.[11,15]

(40) Size consistency corrections are required before the TCSCF + CISD energies in ref 26 can be used in this reaction.

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