Thermochemistry of Hydrochlorofluorosilanes: A Gaussian-3 Study

Siu-Hung Chien, Wai-Kee Li,* and N. L. Ma*

Department of Chemistry, The Chinese University of Hong Kong, Shatin, N.T., Hong Kong, and Chemical Application Division, Institute of High Performance Computing, 89C Science Park Drive, #02-11/12 The Rutherford, Singapore 118261

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A high-level theoretical study on the thermochemistry of hydrochlorofluorosilanes has been carried out using the Gaussian-3 (G3), and its computationally less expensive variant G3(MP2), methods. In this paper, we report the heats of formation of 15 silanes, their adiabatic ionization energies (IEs), electron affinities (EAs), and proton affinities (PAs), as well as the acidities of 10 hydrosilanes. Good to excellent agreement with the available experimental data is found for essentially all calculated quantities. The only exceptions are those involving the SiF_4^+ cation, such as the IE and PA of SF_4. The origin of this failure is not immediately clear, even though this failure is not confined to the G3 methods. Because many of the thermochemical data for the industrially important silanes are not available in the literature, the results reported here may be taken as reliable estimates.

Introduction

Silicon is the fundamental building block of microelectronic and other advanced materials. Its interaction with halogen atoms and their ions is of particular interest in chemical vapor decomposition and the fabrication of wafers. Although the chemistry of hydrochlorofluorosilanes (HCFSi) has attracted numerous experimental and theoretical studies, there is very little experimental thermochemical information on the anions, proton affinities, and acidities of these silanes. In terms of theoretical results, various groups have investigated HCFSi and their related species.[1−5] However, these studies involve different levels of theory for different systems and, hence, direct comparison among the results is difficult. Consequently, a self-consistent set of thermochemical data for these silanes is clearly desirable.

For the smaller analogues of HCFSi, that is, the hydrochlorofluoromethanes (HCFM), we have recently carried out high-level computational studies at the Gaussian-3 (G3) level of theory.[6] For these substituted methanes, experimental thermochemical data are available for 46 of the 55 quantities studied. Good overall agreement between G3 and experimental values is obtained.[7] But major discrepancies are found for five experimental values: the proton affinities of CH_2F_2, CHF_3, and CF_3Cl, as well as the acidities of CH_2F_2 and CHF_2Cl. For all these cases, we find evidence that the experimental values may need to be revised.[7] Ignoring these five quantities, the agreement between the G3 results and the experimental data (in terms of absolute mean deviation) are within 4 kJ mol^{-1} for 15 heats of formation (ΔH_f), 0.11 eV for 15 ionization energies (IEs), 1 kJ mol^{-1} for four proton affinities (PAs), and 8 kJ mol^{-1} for seven acidities.

Motivated by this success for the HCFM systems, and the lack of experimental data for the silanes, we have performed a parallel theoretical study at the G3 level of theory for HCFSi. In this paper, we report the ΔH_f values of 15 neutral HCFSi, their radical cations (HCFSi$^{\bullet+}$) and anions (HCFSi$^{\bullet-}$), as well as their protonated (HCFSi + H$^+$) and deprotonated (HCFSi − H$^-$) species. From these values, the IEs, electronic affinities (EAs), PAs, and acidities of the silanes can then be determined. Our calculated thermochemical values will then be compared with available experimental data and other theoretical results.

In this paper, apart from applying the G3 method, we have also performed the G3(MP2) calculations[8] on the same silane systems. Although the G3(MP2) method is a computationally less expensive variant of the G3 protocol, the two methods have a number of differences. The major difference lies in the core size used in the electron correlation treatment. In the G3 level of theory, the effect of core correlation is estimated at the MP2 level using the “G3large” basis set with a “full core.” On the other hand, the frozen core assumption is used in all electron correlations in the G3(MP2) method. It is not clear how this difference in core size affects the calculated thermochemical properties at the two different levels. Hence, in this paper, on the basis of the results obtained on the HCFSi systems, we will make a brief comparison between the G3 and the G3(MP2) models.

Methods of Calculation

All calculations were carried out on DEC 500au, DEC 600au, COMPAQ XP900, COMPAQ XP1000, and SGI10000 workstations as well as on SGI Origin 2000 high performance server, using the Gaussian 98 package of programs.[9]

The computational methods we used were the aforementioned G3 and G3(MP2) levels of theory. In the G3 method, the structure of a species is optimized at the MP2(full)/6-31G(d) level. On the basis of this optimized structure, single-point calculations at the levels of QCISD(T)/6-31G(d), MP4/6-31G(d), MP4/6-31+G(d), MP4/6-31G(2df,p), and MP2(full)/G3large are carried out. In addition, the model requires higher-level correction (HLC) in the calculation of the G3 total electronic energy (E_e). The MP2(full)/6-31G(d) vibrational frequencies, scaled by 0.9661, are applied for the zero-point vibrational energy (ZPVE) correction at 0 K ($E_0 = E_e +$ ZPVE).

In the G3(MP2) method, on the basis of the geometry optimized at the MP2(full)/6-31G(d) level, frozen-core single-point calculations at the QCISD(T)/6-31G(d) and MP2/G3MP2large levels are carried out. In addition, HLC and ZPVE corrections are also applied.

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TABLE 1: G3 and G3(MP2) Heats of Formation[a] (ΔH_{f0} and ΔH_{f298}, in kJ mol^{-1}) of Hydrochlorofluorosilanes as Well as Their Cations and Anions at 0 and 298 K[b]

	netural		cation		anion	
neutral silane	ΔH_{f0}	ΔH_{f298}	ΔH_{f0}	ΔH_{f298}	ΔH_{f0}	ΔH_{f298}
SiH_4	**43.7**	**35.3**	**1109.2**	**1102.5**	**181.3**	**172.9**
	43.4	*34.8*	*1103.0*	*1096.3*	*179.5*	*171.1*
	(46)	(35)	(1170)	[1105.4][c]		
				(1159)		
SiH_3F	**−342.4**	**−350.9**	**775.1**	**769.7**	**−253.4**	**−260.0**
	−341.4	*−349.6*	*771.3*	*765.9*	*−251.9*	*−258.5*
	(−367.2 ± 21)[d]	(−367.2 ± 21)[d]		(752)		
SiH_3Cl	**−124.4**	**−132.3**	**940.5**	**935.6**	**−65.6**	**−70.8**
	−126.0	*−134.0*	*934.7*	*929.8*	*−72.3*	*−77.5*
	(−132 ± 8)[d]	[−135.6 ± 10.5]		(899)		
		(−141.8 ± 8)[d]				
SiH_2F_2	**−759.6**	**−766.6**	**396.3**	**391.9**	**−674.7**	**−680.5**
	−757.3	*−764.4*	*392.4*	*388.1*	*−670.9*	*−676.8*
	(−782 ± 21)	(−791 ± 21)	(395)	(386)		
SiH_2FCl	**−528.1**	**−534.8**	**568.2**	**564.4**	**−462.1**	**−467.8**
	−528.1	*−534.8*	*563.2*	*559.4*	*−463.8*	*−469.5*
SiH_2Cl_2	**−302.4**	**−308.7**	**767.7**	**764.5**	**−327.9**	**−331.8**
	−305.5	*−311.8*	*760.5*	*757.2*	*−334.3*	*−338.3*
	(−313 ± 13)[d]	[−315.1 ± 8.3][e]		(765)		
		(−320.5 ± 13)[d]				
$SiHF_3$	**−1187.7**	**−1193.1**	**26.4**	**23.9**	**−1084.7**	**−1087.9**
	−1184.5	*−1189.8*	*22.9*	*20.4*	*−1080.9*	*−1084.2*
	(−1194 ± 21)	(−1201 ± 21)	(157)	(150)		
$SiHF_2Cl$	**−948.6**	**−953.5**	**193.3**	**191.5**	**−898.3**	**−901.8**
	−947.0	*−951.8*	*189.0*	*187.3*	*−896.8*	*−900.3*
$SiHFCl_2$	**−713.6**	**−717.9**	**391.8**	**390.6**	**−734.6**	**−737.0**
	−714.5	*−718.8*	*385.8*	*384.6*	*−738.5*	*−740.9*
$SiHCl_3$	**−483.5**	**−487.2**	**591.8**	**591.1**	**−510.4**	**−511.4**
	−487.3	*−491.0*	*583.5*	*582.8*	*−518.0*	*−519.0*
	[−491.2 ± 4.2][e]	[−496.2 ± 4.2][e]	(652)	(647)		
	(−477)	(−482)				
SiF_4	**−1603.7**	**−1607.1**	**−94.1**	**−95.2**	**−1559.1**	**−1561.5**
	−1599.5	*−1602.9*	*−92.1*	*−93.2*	*−1555.0*	*−1557.4*
	(−1609 ± 1)	(−1615 ± 1)	(−94)	(−100)		
			[−133.7 ± 8.7][f]	[−139.7±8.7][f]		
			(−143.4)[g]	(−149.4)[g]		
				(−150.2 ± 0.5)[h]		
SiF_3Cl	**−1364.2**	**−1367.0**	**−136.4**	**−137.8**	**−1366.4**	**−1367.5**
	−1360.9	*−1363.7*	*−134.1*	*−135.5*	*−1365.7*	*−1366.9*
	(−1314 ± 63)[d]	(−1318 ± 63)[d]				
SiF_2Cl_2	**−1126.4**	**−1128.6**	**62.6**	**61.7**	**−1164.4**	**−1164.6**
	−1125.4	*−1127.5*	*63.4*	*62.4*	*−1165.8*	*−1165.9*
$SiFCl_3$	**−891.4**	**−892.9**	**268.6**	**268.5**	**−941.2**	**−940.6**
	−892.7	*−894.2*	*267.5*	*267.4*	*−945.9*	*−945.3*
	(−838.8 ± 63)[d]	(−841 ± 62.8)[d]				
$SiCl_4$	**−660.1**	**−660.9**	**464.5**	**463.4**	**−719.0**	**−717.6**
	−664.8	*−665.6*	*460.1*	*458.9*	*−727.7*	*−726.2*
	[−660.6 ± 1.3][d]	[−662.8 ± 1.3][d]	(520)	[481.2 ± 12.6][i]		
	(−618)	(−610)		(528)		

[a] The G3 results are shown in bold font, and the G3(MP2) values are shown in italic font. [b] All experimental heats of formation, given in brackets, are taken from ref 11, unless otherwise stated. For those species with multiple experimental entries, the preferred value is given in square brackets. [c] Ref 14. [d] Ref 10. [e] Ref 15. [f] Ref 12. [g] Ref 16. [h] Ref 17. [i] Ref 18.

The G3/G3(MP2) heats of formation at temperature T (ΔH_{fT}) in this work were calculated in the following manner. For molecule AB, its G3/G3(MP2) ΔH_{fT} was calculated from the G3/G3(MP2) heat of reaction ΔH_{rT} ($A + B \rightarrow AB$) and the respective experimental $\Delta H_{fT}(A)$ and $\Delta H_{fT}(B)$ for elements A and B. In the calculations for anions, the ΔH_{fT} for a free electron was set to be zero.

Results and Discussion

The G3 and G3(MP2) heats of formation for the studied silanes and their cations and anions are listed in Table 1, whereas those for the protonated and deprotonated species are given in Table 2. On the basis of these results, the IEs, EAs, PAs, and acidities of the silanes can be calculated, and these quantities are summarized in Table 3.

Heats of Formation. Let us first consider the series SiH_mF_n, with m, $n = 0, 1, 2, ...$, and $m + n = 4$. From Table 1, it is seen that the calculated results for SiH_4 and SiF_4 are in excellent agreement with experimental data. For the other three members of the series, the available "experimental data" are not direct measurements.[10] Rather, they were obtained by linear interpolation between the experimental values of SiH_4 and SiF_4. In any event, the calculated values are within the error range of these "experimental data." Hence, the G3/G3(MP2) results for SiH_3F, SiH_2F_2, and $SiHF_3$ may be taken as reliable estimates.

Next we consider the series SiF_4, SiF_3Cl, ..., $SiCl_4$. Once again, the calculated results for SiF_4 and $SiCl_4$ are in very good accord with the experimental data. In addition, for $SiCl_4$, on the basis of the G3 result, we are able to conclude which of the two rather disparate experimental values should be more accurate (see Table 1). For SiF_2Cl_2, no experimental result is available for comparison. The ΔH_f values of SiF_3Cl and $SiFCl_3$ have error ranges of ±63 kJ mol^{-1} and these results were reported in 1960.[10] Clearly, they deserve reexamination.

Now we consider the series SiH_4, SiH_3Cl, ..., $SiCl_4$. Aside from SiH_4 and $SiCl_4$, which have been examined already, the

TABLE 2: G3 and G3(MP2) Heats of Formation[a] (ΔH_{f0} and ΔH_{f298}, in kJ mol^{-1}) of Protonated and Deprotonated Hydrochlorofluorosilanes at 0 and 298 K[b]

neutral silane	protonated species			deprotonated species		
	cation	ΔH_{f0}	ΔH_{f298}	anion	ΔH_{f0}	ΔH_{f298}
SiH_4	$H_2{\cdot}SiH_3^+$	**940.6**	**930.8**	SiH_3^-	**66.9**	**62.3**
		938.0	*928.2*		*65.8*	*61.2*
			(917)			(63 ± 10)
SiH_3F	$HF{\cdot}SiH_3^+$	**600.2**	**591.1**	SiH_2F^-	**−318.5**	**−322.6**
		600.7	*591.4*		*−315.7*	*−319.9*
SiH_3Cl	$HCl{\cdot}SiH_3^+$	**770.0**	**760.6**	SiH_2Cl^-	**−148.4**	**−152.1**
		767.9	*758.6*		*−152.0*	*−155.7*
SiH_2F_2	$HF{\cdot}SiH_2F^+$	**216.8**	**208.5**	$SiHF_2^-$	**−750.9**	**−753.8**
		217.5	*209.2*		*−747.3*	*−750.2*
SiH_2FCl	$HF{\cdot}SiH_2Cl^+$	**427.1**	**419.7**			
		426.1	*418.7*	$SiHFCl^-$	**−562.9**	**−565.1**
	$HCl{\cdot}SiH_2F^+$	**398.5**	**391.0**			
		397.1	*389.6*		*−563.9*	*−566.1*
SiH_2Cl_2	$HCl{\cdot}SiH_2Cl^+$	**603.2**	**595.6**	$SiHCl_2^-$	**−374.5**	**−376.2**
		600.0	*592.3*		*−380.2*	*−381.9*
$SiHF_3$	$HF{\cdot}SiHF_2^+$	**−174.9**	**−181.3**	SiF_3^-	**−1227.4**	**−1228.2**
		−173.3	*−179.6*		*−1223.0*	*−1223.9*
						(−1230 ± 46)[c]
						(−1284 ± 35)
$SiHF_2Cl$	$HF{\cdot}SiHFCl^+$	**38.2**	**32.0**			
		38.6	*32.4*	SiF_2Cl^-	**−1023.4**	**−1023.3**
	$HCl{\cdot}SiHF_2^+$	**5.0**	**−0.7**		*−1022.4*	*−1022.3*
		5.4	*−0.3*			
$SiHFCl_2$	$HF{\cdot}SiHCl_2^+$	**251.7**	**252.3**			
		249.9	*244.9*	$SiFCl_2^-$	**−815.9**	**−815.1**
	$HCl{\cdot}SiHFCl^+$	**219.3**	**213.8**		*−819.0*	*−818.3*
		217.6	*212.1*			
$SiHCl_3$	$HCl{\cdot}SiHCl_2^+$	**429.9**	**425.0**	$SiCl_3^-$	**−608.9**	**−607.5**
		425.6	*420.6*		*−616.5*	*−615.1*
						(−589 ± 21)
SiF_4	$HF{\cdot}SiF_3^+$	**−546.1**	**−550.6**			
		−543.6	*−548.1*			
			(−588)			
SiF_3Cl	$HF{\cdot}SiF_2Cl^+$	**−340.8**	**−344.8**			
		−339.1	*−343.1*			
	$HCl{\cdot}SiF_3^+$	**−374.9**	**−378.9**			
		−373.1	*−377.1*			
SiF_2Cl_2	$HF{\cdot}SiFCl_2^+$	**−130.3**	**−133.9**			
		−130.2	*−133.7*			
	$HCl{\cdot}SiF_2Cl^+$	**−166.2**	**−169.6**			
		−165.8	*−169.1*			
$SiFCl_3$	$HF{\cdot}SiCl_3^+$	**82.8**	**80.7**			
		80.7	*78.6*			
	$HCl{\cdot}SiFCl_2^+$	**48.2**	**45.3**			
		46.4	*43.5*			
$SiCl_4$	$HCl{\cdot}SiCl_3^+$	**259.2**	**257.1**			
		254.7	*252.6*			

[a] The G3 results are shown in bold font, and the G3(MP2) values are shown in italic font. [b] All experimental heats of formation, shown in brackets, are taken from ref 11, unless otherwise stated. [c] Ref 13.

TABLE 3: G3 and G3(MP2) Ionization Energies (IE, in eV) and Electron Affinities (EA, in eV) at 0 K, Proton Affinities (PA, in kJ mol^{-1}) and Acidity (in kJ mol^{-1}) at 298 K of Hydrochlorofluorosalines[a,b]

species	IE	EA	PA[c]	acidity
SiH_4	**11.05**	**−1.43**	**631.5**	**1554.4**
	10.98	*−1.41*	*636.0*	*1555.7*
	[11.00 ± 0.02][d]		[639.7][e]	(1558 ± 8)
	(11.65)		(648)	
SiH_3F	**11.59**	**−0.92**	**585.3**	**1555.5**
	11.53	*−0.93*	*588.4*	*1559.0*
	(11.7)[f]			
SiH_3Cl	**11.03**	**−0.61**	**634.3**	**1507.3**
	10.99	*−0.56*	*636.8*	*1507.6*
	(11.4)[f]			
SiH_2F_2	**11.98**	**−0.88**	**552.1**	**1540.0**
	11.92	*−0.90*	*555.8*	*1543.5*
	[12.2]			
	(12.85)[g,h]			
SiH_2FCl	**11.36**	**−0.68**	**572.7*/601.9**	**1496.9**
	11.31	*−0.67*	*575.9*/605.0*	*1498.1*
SiH_2Cl_2	**11.09**	**0.26**	**622.9**	**1459.6**
	11.05	*0.30*	*625.3*	*1459.3*
	[11.4][f]			
	(11.70)[g,h]			
$SiHF_3$	**12.58**	**−1.07**	**515.4**	**1492.0**
	12.51	*−1.07*	*519.2*	*1495.3*
	(14.0)[f]			[1493 ± 46][i]
				(1446 ± 14)
$SiHF_2Cl$	**11.84**	**−0.52**	**541.7*/574.5**	**1457.3**
	11.77	*−0.52*	*545.1*/577.8*	*1458.9*
$SiHFCl_2$	**11.46**	**0.22**	**562.6*/595.4**	**1430.1**
	11.40	*0.25*	*565.7*/598.5*	*1429.9*
$SiHCl_3$	**11.15**	**0.28**	**614.9**	**1406.9**
	11.10	*0.32*	*617.7*	*1405.4*
	(11.7)[f]			(<1501)
SiF_4	**15.65**	**−0.46**	**470.7**	—
	15.62	*−0.46*	*474.6*	
	[15.29 ± 0.08][j]		(502.9)[d]	
	(15.7)[f]			
	(15.19)[k]			
SiF_3Cl	**12.73**	**0.02**	**505.0*/539.1**	—
	12.72	*0.05*	*508.8*/542.8*	
	(13.44)[g,l]			
SiF_2Cl_2	**12.32**	**0.39**	**532.5*/568.2**	—
	12.32	*0.42*	*535.6*/571.0*	
$SiFCl_3$	**12.02**	**0.52**	**553.6*/591.8**	—
	12.02	*0.55*	*556.6*/591.7*	
$SiCl_4$	**11.66**	**0.61**	**609.1**	—
	11.66	*0.65*	*611.1*	
	(11.79 ± 0.1)			

[a] The G3 values are shown in bold font, and the G3(MP2) values are shown in italic font. [b] All experimental data, given in bracket, are taken from ref 11, unless otherwise specified. For those species with multiple experimental entries, the preferred value is given in square brackets. [c] For silanes with both chloro- and fluoro-substituents, the PA value for protonation occurring at a fluorine atom is indicated with an asterisk. [d] Ref 14. [e] Ref 20. [f] IE taken to be the onset of the photoelectron band. [g] Vertical ionization energies. [h] Ref 21. [i] See text. [j] Ref 12. [k] Ref 16. [l] Ref 22.

calculated ΔH_f values for the remaining three members are all in excellent agreement with the experimental data. For the remaining three silanes not discussed so far, SiH_2FCl, $SiHF_2Cl$, and $SiHFCl_2$, no experimental results are available for comparison.

To briefly conclude at this point, both the G3 and G3(MP2) methods yield accurate ΔH_f values for the neutral silanes. This conclusion lends support for the calculated results for the silane cations and anions, for which very little experimental information is available. Actually, for silane anions, there are no experimental heats of formation at all in the literature. Anyway, we will consider the calculated ΔH_f results for the silane cations and anions when we discuss the IEs and EAs of the neutral silanes.

Before leaving this section, we briefly compare the G3/G3(MP2) results with those obtained with other theoretical methods. Table 4 compares our results with those obtained with bond additive corrections (BAC)[1,2] and isodesmic reaction schemes[3,4] at the MP4-correlated level with a variety of basis sets. Examining the results in this table, it is seen that the G3/G3(MP2) results for the chlorinated species are in better agreement with the BAC and isodesmic results (absolute mean deviation is 2.1 kJ mol^{-1} for BAC and 2.4 kJ mol^{-1} for isodesmic) than the fluorinated species (absolute mean deviation is 10.6 kJ mol^{-1} for BAC and 10.3 kJ mol^{-1} for isodesmic). Since the accepted error range for the G3/G3(MP2) methods is about ±10 kJ mol^{-1}, it may be argued that the four theoretical methods compared in Table 4 yield results with overlapping error ranges.

TABLE 4: Calculated Standard Heats of Formation at 298 K ($\Delta H_{f298}{}^0$) for Hydrochlorofluorosilanes Using a Variety of Methods

species	G3	G3(MP2)	BAC-MP4	isodesmic	experiment
SiH_4	35.1	34.8	34.3[a]	34.3[b]	35[c]
SiH_3F	−350.9	−349.6	−357 ± 5.1[a]	−357.7[b]	−376.6 ± 21[d]
SiH_3Cl	−132.3	−134.0	−133.9[a,e]	−134.7[f]	−135.6±10.5[g]
SiH_2F_2	−766.6	−764.4	−779.8 ± 6.2 [a]	−779.5[b]	−791 ± 2[c]
SiH_2Cl_2	−308.7	−311.8	−311.3 [a,e]	−311.3[f]	−315.1 ± 8.3[g]
SiH_2FCl	−534.8	−534.8			
$SiHF_3$	−1193.1	−1189.8	−1207.6 ± 5.6[a]	−1205.8[b]	−1201 ± 21[c]
$SiHF_2Cl$	−953.5	−951.8			
$SiHFCl_2$	−717.9	−718.8			
$SiHCl_3$	−487.2	−491.0	−489.5[a,e]	−489.5[f]	−496.2 ± 4.2[d]
SiF_4	−1607.1	−1602.9	−1615.0 ± 4.2[a,e]	1615.8[b]	−1615 ± 1[c]
$SiClF_3$	−1367.0	−1363.7		−1378.6[f]	−1318 ± 63[d]
$SiCl_2F_2$	−1128.6	−1127.5		−1141.8[f]	
$SiCl_3F$	−892.9	−894.2		−902.9[f]	−841 ± 62[d]
$SiCl_4$	−660.9	−665.6	−662.7[a,e]		−662.8 ± 1.3[d]

[a] Ref 1. [b] Ref 3. [c] Ref 11. [d] Ref 10. [e] Ref 2. [f] Ref 4. [g] Ref 15.

Ionization Energies. Because of Jahn−Teller effect, neutral chlorofluorosilanes with high symmetries such as T_d (SiF_4 and $SiCl_4$) and C_{3v} (SiF_3Cl and $SiFCl_3$) tend to distort to lower symmetries upon ionization. Similar distortion has been reported for the methane analogues.[7] The hydrogen-containing HCFSi cations may be described as complexes between HX (X is either F or Cl) and the remaining part of the cation. Additionally, at the HF/6-31G(d) level, the expectation values of the S^2 operator ($\langle S^2 \rangle$) for all cations are between 0.75 and 0.78, suggesting that spin contamination is not a problem in this case.

Examining the IEs listed in Table 3, the G3 and G3(MP2) methods tend to yield IEs lower than the experimental data found in the literature. However, it should be noted that many of the quoted experimental IEs (such as those of SiH_2F_2, SiH_2Cl_2, and SiF_3Cl) in Table 3 are vertical IEs. They should not be compared with the calculated adiabatic IEs; they are listed here for reference only. Also, many of the reported values (such as those of SiH_3F, SiH_3Cl, SiH_2F_2, SiH_2Cl_2, $SiHF_3$, $SiHCl_3$, and SiF_4) are of doubtful accuracy, according to the compilers of the data book.[11] In short, only the experimental IEs of SiH_4, SiF_4, and $SiCl_4$ are of sufficient accuracy for comparison with the G3/G3(MP2) results. Among these sets of quantities, there is excellent agreement for the SiH_4 results, whereas those for $SiCl_4$ are in fair accord.

For SiF_4, three fairly different experimental IEs are found in the literature. Among them, the one reported by Armentrout and co-workers[12] (15.29 ± 0.08 eV) appears to be the most accurate. However, our calculated G3/G3(MP2) IEs (15.65 and 15.62 eV) are about 0.35 eV off this value. Furthermore, calculating at the MP4/6-31G(d,p) level with an isogyric scheme, Edgar and Schlegel[5] obtained an IE of 15.34 eV for SiF_4, in good agreement with experiment. To resolve the difference between the computed results, we have calculated the IE of SiF_4 at a variety of levels with both direct subtraction and Edgar and Schlegel's isogyric scheme. The results are summarized in Table 5. Examining these results, it is seen that the direct subtraction method in general yields lower IEs (by 0.5 eV or more) than the isogyric scheme. More importantly, the various methods fail to arrive at a consistent value for this IE. It appears that the agreement between Edgar and Schlegel's result and the experimental value may be fortuitous, because larger basis sets and higher correlation levels [such as QCISD(T,full)/G3large] fail to yield similar results. Although it is difficult to pin down the reason for theory's failure to yield an accurate IE for SiF_4, it is clear the problem lies with SiF_4^+ (recall that the G3 ΔH_f of SiF_4 is in very good agreement with the experimental value).

TABLE 5: Ionization Energies of SiF_4 Calculated at a Variety of Levels

	level of theory		IE (eV)	
entry[a]	basis set	CI	isogyric scheme	direct subtraction
1[b]	6-31G(d,p)	MP4SDTQ	15.34	14.80
2	6-31G(d)	MP4SDTQ	15.72	14.80
3		QCISD(T)	15.70	14.79
4	6-31G(d,p)	MP4SDTQ	15.35	14.80
5		QCISD(T)	15.34	14.79
6	6-31G(2df,2p)	MP4SDTQ	15.26	15.01
7	6-311G(d,p)	MP4SDTQ	15.52	14.99
8		QCISD(T)	15.50	14.97
9	6-311+G(d,p)	MP4SDTQ	15.71	15.17
10	6-311G(2df,p)	MP4SDTQ	15.49	15.26
11	6-311+G(3df,2p)	MP2	16.06	15.62
12	Aug-CC-PVDZ	MP4SDTQ	15.53	15.14
13		QCISD(T)	15.49	15.10
14	CC-PVTZ	MP4SDTQ	15.39	15.28
15	G3large	MP2(Full)	16.10	15.76
16		QCISD(T,Full)	15.69	15.48
17		G3	15.66	15.65
	experiment		15.29 ± 0.08[c]	

[a] Geometry optimization for entry 1 is done at the HF/6-31G(d) level. Those for the remaining entries are carried out at the MP2(full)/6-31G(d) level. [b] Ref 5. [c] Ref 12.

Finally, it is noted that successive fluorine substitutions increase the IE from 11.04 eV (for SiH_4) to 12.58 eV ($SiHF_3$). This steady increase is also found in the HCFMs. In contrast, chlorine substitutions appear to have little effect on the IEs of the silanes, which suggests that the highest occupied molecular orbitals for the chlorinated silanes are essentially nonbonding orbitals mainly localized on the chlorine atoms.

Electron Affinities. Upon attaching an extra electron to form an anion, the structure of silane undergoes distortion. This distortion is relatively minor, compared with that arising from ionization of a silane to form a cation. In other words, unlike the structure of a silane cation, the structure of a silane anion does not resemble a complex. At the HF/6-31G(d) level, the expectation values $\langle S^2 \rangle$ for all anions range from 0.75 to 0.76, suggesting very little spin contamination.

As mentioned previously, we have not been able to find any experimental EAs for the silanes in the literature. Therefore, all the calculated EAs given in Table 3 await experimental confirmation. The EAs of many silanes (such as SiH_4, SiH_3F, SiH_3Cl, SiH_2F_2, SiH_2FCl, $SiHF_3$, $SiHF_2Cl$, and SiF_4) are calculated to be negative, implying that the corresponding anions are unstable. Such a result is not entirely unexpected, as the extra electron will be occupying high-lying antibonding orbitals. Take SiH_3Cl as an example: the Si−Cl bond in the neutral species measures 2.058 Å, whereas the corresponding bond length is 2.893 Å in SiH_3Cl^-.

Proton Affinities. Because the experimental PAs for the silanes found in the literature are quantities determined at 298 K, the G3/G3(MP2) PAs given in Table 3 are calculated using enthalpies (H_{298}) instead of absolute energies (E_0). Similar to the protonated species of HCFMs, protonation of a silane occurs at the halogen atom, except for SiH_4. For silanes with both fluorine and chlorine substituents, protonation at either F or Cl is possible; both PAs are reported in Table 3. A protonated silane cation may be described as a complex between HX and the remaining three-coordinated dehalogenated portion of the cation.

For the HCFMs, protonation occurs preferentially at the fluorine atom, rather than at the chlorine atom.[7] For the silanes, the opposite trend is observed. As an example, when a proton is attached to SiH_2FCl, the formation of $HCl{\cdot}SiH_2F^+$ is preferred over HF•CH_2Cl^+. Furthermore, the X...Si distance in the protonated species ranges from 1.82 Å (in $F_3Si...FH^+$) to 2.33 Å (in $Cl_3Si...ClH^+$). These X...Si distances are shorter than the X...C distances in the protonated methanes. These results indicate that the protonated silane cations are much stronger complexes than the corresponding methane cations.

Of 15 silanes studied, only two experimental PAs are found in the literature: 639.7 kJ mol^{-1} for SiH_4 and 502 kJ mol^{-1} for SiF_4. Our G3 PA for SiH_4 is 631.4 kJ mol^{-1}, in good agreement with experiment. On the other hand, the G3 PA for SiF_4 is 470.8 kJ mol^{-1}, in poor accord with experiment. This failure may be related to the poor G3 IE obtained for SiF_4.

Acidities. As expected, the deprotonated silanes have a pyramidal structure. Examining the results reported in Table 3, it is found that the acidity of silanes decreases with increasing halogen substitution. This may be the result of the withdrawing of negative charge from the Si atom by the electronegative halogen(s).

Of the 10 silanes studied, two experimental acidity values and one upper bound are found in the literature. The G3/G3(MP2) acidities of SiH_4 (1554.4 and 1555.7 kJ mol^{-1}) are in excellent agreement with experiment (1558 ± 8 kJ mol^{-1}). Meanwhile, the G3/G3(MP2) acidity for $SiHF_3$ (1492.0 and 1495.3 kJ mol^{-1}) is in poor accord with the value (1446 ±14 kJ mol^{-1}) listed in Lias et al.'s compendium.[11] However, on the basis of the experimental ΔH_f values for H^+ (1528.0 kJ mol^{-1}), and SiHF3 (1201 ± 21 kJ mol^{-1}) found in the same data book,[11] as well as the experimental ΔH_f for SiF_3^- (1230 ± 46 kJ mol^{-1}) reported by Kawamata et al.,[13] we can arrive at an acidity value of 1493 ± 46 kJ mol^{-1} for $SiHF_3$, which is in excellent agreement with the G3 result.

Finally, an experimental acidity upper bound (<1501 kJ mol^{-1}) is reported[11] for $SiHCl_3$. Our G3/G3(MP2) results, 1406.9 and 1405.4 kJ mol^{-1}, are well below this upper bound.

G3 versus G3(MP2). There are 76 independent quantities reported in this work, namely, 15 ΔH_f values, 15 IEs, 15 EAs, 21 PAs, and 10 acidities. The average absolute deviations between the G3 and G3(MP2) results are 2.2 kJ mol^{-1} for the heats of formation, 0.04 eV (or 3.86 kJ mol^{-1}) for IEs, 0.02 eV (1.93 kJ mol^{-1}) for EAs, 3.2 kJ mol^{-1} for PAs, and 1.7 kJ mol^{-1} for acidities. The overall average absolute deviation for all 76 quantities is 2.7 kJ mol^{-1}. From this simple statistical analysis, it may be concluded that the G3 and G3(MP2) methods yield very similar results for the silanes, even though, as mentioned previously, these methods have slightly different theoretical bases (such as full core versus frozen core, the G3large basis against G3MP2large basis, MP4 versus MP2 correlation, etc.). So, at least for the silanes and their ions, the G3(MP2) method is practically as good as the computationally more expensive G3 method.

Conclusion

We have applied the G3 and G3(MP2) methods to investigate the thermochemistry of 15 hydrochlorofluorosilanes: 15 heats of formation, 15 IEs, 15 EAs, 21 PAs, and 10 acidities have been calculated. It is found that the calculated ΔH_f values for the silanes are in good to excellent agreement with the available experimental data. In the literature, only three accurate IEs for silanes are available. Upon comparing the G3/G3(MP2) IEs with experiment, it is found that there is very good agreement for SiH_4 and for $SiCl_4$, but not for SiF_4. The origin of the failure for the IE of SiF_4 is not clear, even though this failure is not confined to the G3 methods. In the literature there are no experimental EAs for the silanes to compare with our calculated results. As far as the PAs are concerned, only two experimental data are found in the literature; one (that of SiH_4) is in very good agreement with the G3 results, whereas the other one (that of SiF_4) is about 30 kJ mol^{-1} off. This shortcoming may be related to the aforementioned failure for the IE of SiF_4. Among the 10 acidities calculated, only two (those of SiH_4 and $SiHF_3$) may be compared with experiment, and the agreement is excellent in both instances.

In summary, essentially all of the G3/G3(MP2) results obtained in this work are in good to excellent agreement with experiment. The only exceptions are those quantities involving SiF_4^+. Because thermochemical data for the silanes are relatively scarce, the results reported here may be taken as reliable estimates.

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