

Ab Initio Study of the Reaction Pathways for $\text{Si}^+ + \text{SiX}_4$ ($\text{X} = \text{F}, \text{Cl}$)

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The reaction pathways of $\text{Si}^+ + \text{SiF}_4$ and $\text{Si}^+ + \text{SiCl}_4$ have been studied by ab initio molecular orbital methods. Equilibrium geometries and transition structures were fully optimized at the Hartree–Fock level with the 3-21G and 6-31G* basis sets. Barrier heights have been computed with fourth-order Møller–Plesset perturbation theory, with and without annihilation of spin contamination. Direct attack of Si^+ on X in SiX_4 forms a cluster $\text{X}_3\text{Si–X–Si}^+$, which has a substantial barrier for rearrangement to $\text{X}_3\text{Si–SiX}^+$. Both clusters can dissociate into $\text{SiX}_3 + \text{SiX}^+$ or $\text{SiX}_3^+ + \text{SiX}$; the second cluster can rearrange further to yield $\text{X}_2\text{Si–SiX}_2^+$, which can dissociate to $\text{SiX}_2 + \text{SiX}_2^+$. The calculated thresholds agree well with the observed values for $\text{SiF}^+ + \text{SiF}_3$, $\text{SiCl}^+ + \text{SiCl}_3$, $\text{SiCl}_3^+ + \text{SiCl}$ and $\text{SiCl}_2^+ + \text{SiCl}_2$; however, the observed thresholds for $\text{SiF}_3^+ + \text{SiF}$ and $\text{SiF}_2^+ + \text{SiF}_2$ are considerable higher than the calculated values, suggesting an activation barrier or a dynamic bottleneck.

Introduction

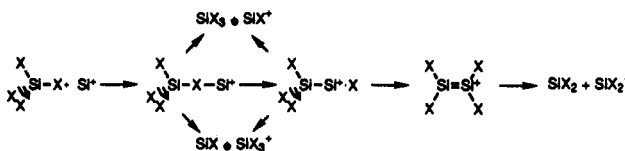
The thermodynamics and reactivity of halogen-substituted silicon compounds are important to the understanding of processes such as chemical vapor deposition^{1–3} and plasma etching of silicon.^{4,5} However, reliable data for these systems are often difficult to obtain. The thermochemistry of silicon hydrides has been studied extensively, both experimentally and theoretically (for recent reviews see refs 6 and 7). Curtiss et al.^{8,9} have used the G-1 and G-2 approaches to calculate enthalpies of formation for SiH_n and Si_2H_n neutrals and cations and find very good agreement with experiment.^{10,11} The heats of formation of SiF_4 ¹² and SiCl_4 ¹³ are firmly established, but the experimental thermochemistry of some of the subhalides is not as well-known (see refs 6 and 7 for discussions). The heats of formation of SiF_n^+ and SiCl_n^+ have recently been studied experimentally by Armentrout et al.^{15–18} Melius et al.^{19,20} have used the BAC-MP4 approach to obtain theoretical estimates of the heats of formation of SiH_mF_n and SiH_mCl_n ($m + n = 1–4$). Ignacio and Schlegel^{21,22} have calculated heats of formation for SiH_mF_n and SiH_mF_n^+ ($n + m = 1–4$) using isodesmic reactions. Similar quality calculations on heats of formation of SiCl_n^+ are not yet available in the literature.

Armentrout et al.^{14–16} and Mandich et al.²³ have reported experimental studies on the mechanisms and energetics of $\text{Si}^+ + \text{SiX}_4$ for $\text{X} = \text{H}, \text{F},$ and Cl (Scheme I). Raghavachari²⁴ has made a detailed theoretical study of the reaction pathway of $\text{Si}^+ + \text{SiH}_4$ and obtained excellent agreement with the experimental studies of Mandich et al.²³ For the silicon fluorine system, the heats of formation calculated by Ignacio and Schlegel^{21,22} are in good agreement with the experimental thresholds¹⁵ for $\text{Si}^+ + \text{SiF}_4 \rightarrow \text{SiF}^+ + \text{SiF}_3$; however, the experimental thresholds¹⁵ for the $\text{SiF}_3^+ + \text{SiF}$ and $\text{SiF}_2^+ + \text{SiF}_2$ channels are higher than the calculated heats of reaction by 0.55 and 0.86 eV, respectively.²² For $\text{Si}^+ + \text{SiCl}_4$, no direct comparison between high-level theory and experiment is available in the literature. In the present investigation, the reaction pathways of $\text{Si}^+ + \text{SiF}_4$ and $\text{Si}^+ + \text{SiCl}_4$ have been studied and the relative enthalpies and barrier heights have been computed for the structures shown in Scheme I.

Method

Ab initio molecular orbital calculations were performed with the GAUSSIAN 90 system of programs²⁵ using split-valence²⁶ and polarization basis sets²⁷ (3-21G and 6-31G*). Geometries

SCHEME I



were fully optimized by using analytical gradient methods²⁸ at the Hartree–Fock level with the 3-21G and 6-31G* basis sets. Electron correlation energy was estimated with Møller–Plesset perturbation theory²⁹ up to fourth order, including all single, double, triple, and quadruple excitations (MP4SDTQ, frozen core). Vibrational frequencies and zero point energies were obtained from analytical second derivatives³⁰ calculated at the HF/6-31G* level. Thermal contributions to the enthalpy include $1/2RT$ for each translational and rotational degree of freedom, plus changes in the vibrational energy due to thermal population of the excited vibrational modes.³¹

Results and Discussion

The calculated total energies for Si_2F_4^+ and Si_2Cl_4^+ along with the zero point energy and thermal corrections are listed in Table I; vibrational frequencies are presented in Table II. Molecular geometries are collected in Figures 1–5. Relative enthalpies for the various transition states and equilibrium geometries are presented in Table III, Figures 6–8. Estimates of the heats of formation of SiCl_n and SiCl_n^+ are listed in Table IV; the corresponding data for SiF_n and SiF_n^+ have been published previously.^{21,22}

Electronic Structure and Equilibrium Geometries. It is known for the hydrogen analogue²⁴ that the lowest energy reaction proceeds on the doublet potential energy surface and that the quartet surface leads to structures that are higher in energy. Therefore, only the doublet surface was explored for Si^+ reacting with SiF_4 and SiCl_4 . As shown in Scheme I, the interaction of Si^+ with SiX_4 leads to an ion–molecule complex of C_2 symmetry. The $^2A'$ electronic state is lower in energy than the $^2A''$ state for both $\text{X} = \text{F}$ and $\text{X} = \text{Cl}$. For the structure shown in Figure 1, $\text{SiF}_4\text{–Si}^+$, the complex is almost linear (179.1° at HF/3-21G and 176.9° at HF/6-31G*) but there is a significant elongation of the interacting Si–F bond (1.641 Å compared to 1.557 Å in SiF_4 at HF/6-31G*). An even greater elongation is seen for $\text{SiCl}_4\text{–Si}^+$ (2.173 Å compared to 2.029 Å in SiCl_4 at HF/6-31G*). In contrast to the fluorine case, the $\text{SiCl}_4\text{–Si}^+$ is bent at a higher basis level rather than linear (119.1° at HF/6-31G* compared to 177.0° at HF/3-21G).

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TABLE I: Total Energies^a

molecule		UHF/ 3-21G	UHF/ 6-31G*	UMP2/ 6-31G*	UMP3/ 6-31G*	UMP4/ 6-31G*	PMP4/ 6-31G*	ZPE/ 6-31G*	thermal
minima									
F ₃ Si-F-Si ⁺	C-1	-970.371 50	-975.520 69	-976.327 72	-976.327 82	-976.365 83	-976.366 78	8.5	4.6
F ₃ Si-SiF ⁺	C-2	-970.278 71	-975.495 01	-976.312 25	-976.305 58	-976.349 39	-976.350 59	8.8	4.6
F ₂ Si-SiF ₂ ⁺	C-3	-970.266 25	-975.480 68	-976.300 39	-976.291 67	-976.336 76	-976.338 20	8.7	4.6
Cl ₃ Si-Cl-Si ⁺	C-4	-2403.823 38	-2415.618 18	-2416.258 04	-2416.314 12	-2416.339 12	-2416.338 26	5.2	5.4
Cl ₃ Si-SiCl ⁺	C-5	-2403.788 40	-2415.623 29	-2416.271 63	-2416.325 17	-2416.352 52	-2416.353 21	5.5	5.3
Cl ₂ Si-SiCl ₂ ⁺	C-6	-2403.783 14	-2415.621 99	-2416.272 22	-2416.325 34	-2416.352 83	-2416.354 90	5.6	5.3
transition structures									
F ₃ Si-F-Si ⁺ → F ₃ Si-SiF ⁺	TS-1	-970.263 13	-975.452 83	-976.280 06	-976.274 32	-976.319 69	-976.321 53	8.2	4.1
F ₃ Si-SiF ⁺ → F ₂ Si-SiF ₂ ⁺	TS-2	-970.256 30	-975.459 79	-976.288 69	-976.278 37	-976.325 27	-976.326 45	8.4	4.1
Cl ₃ Si-Cl-Si ⁺ → Cl ₃ Si-SiCl ⁺	TS-3	-2403.760 66	-2415.573 75	-2416.219 21	-2416.275 12	-2416.302 68	-2416.304 46	4.8	5.3
Cl ₃ Si-SiCl ⁺ → Cl ₂ Si-SiCl ₂ ⁺	TS-4	-2403.769 90	-2415.605 44	-2416.260 66	-2416.312 39	-2416.340 20	-2416.340 77	5.5	4.8
reactants and products									
Si ⁺ + SiCl ₄		-2403.802 92	-2415.598 18	-2415.225 25	-2416.282 90	-2416.305 84	-2416.306 38	4.9	4.8
SiCl ⁺ + SiCl ₃		-2403.790 20	-2415.596 15	-2416.232 76	-2416.290 34	-2416.316 35	-2416.316 68	4.4	4.7
SiCl ₃ ⁺ + SiCl		-2403.738 63	-2415.565 40	-2416.205 21	-2416.261 79	-2416.288 42	-2416.289 33	4.6	4.6
SiCl ₂ ⁺ + SiCl ₂		-2403.753 07	-2415.561 25	-2416.201 04	-2416.257 90	-2416.285 12	-2416.285 79	4.0	4.6

^a Total energies in au, zero point energies (unscaled), and thermal contributions in kcal/mol.

TABLE II: Vibrational Frequencies

molecule	frequencies ^a
minima	
C-1	29, 38, 155, 254, 263, 387, 390, 425, 755, 940, 1170, 1173
C-2	18, 106, 132, 201, 289, 326, 334, 474, 901, 1076, 1153, 1154
C-3	33, 91, 118, 194, 206, 329, 362, 444, 973, 1041, 1115, 1168
C-4	15, 60, 131, 153, 190, 225, 240, 261, 402, 525, 695, 715
C-5	18, 69, 98, 142, 195, 197, 228, 335, 503, 678, 690, 698
C-6	31, 64, 66, 139, 161, 208, 262, 331, 566, 666, 690, 731
transition structures	
TS-1	375i, 38, 176, 213, 250, 331, 352, 396, 760, 893, 1146, 1191
TS-2	226i, 105, 122, 204, 251, 302, 317, 490, 788, 1028, 1080, 1170
TS-3	142i, 19, 53, 65, 77, 198, 201, 222, 478, 502, 769, 774
TS-4	146i, 67, 95, 154, 179, 198, 224, 401, 476, 620, 710, 729

^a In cm⁻¹, unscaled.

The next step in the reaction involves the insertion of Si⁺ into SiX₄ to form SiX₃-SiX⁺ via the transition state shown in Figure 2. The transition state has C₁ symmetry and is approximately anti (dihedral angle 180.0° at 3-21G and 164.4° at 6-31G*). The transition state is relatively late, with the Si₁-F₃ bond very much elongated (2.034 Å versus 1.641 Å in C-1) and the Si-Si bond nearly fully formed (2.665 Å versus 2.458 Å in C-2). The product shown in Figure 3 is effectively a free rotor (rotational barrier of only 0.05 kcal/mol at 3-21G level) with an anti minimum at the HF/6-31G* level (the 3-21G minimum is syn, probably reflecting basis set deficiencies). For the transition state with X = Cl, TS-3, the Si-Si bond length is rather elongated at the HF/3-21G level (3.252 Å) and even more elongated at the HF/6-31G* level (3.932 Å). This structure is internally UHF stable and Mulliken population analysis shows that 90% of the charge is on the SiCl₃ group. Despite the long Si-Si bond, this structure is 5 kcal/mol lower than the separated products SiCl₃⁺ + SiCl at the HF/6-31G* level and 9 kcal/mol lower at the PMP4/6-31G** level. The reaction path was followed at the HF/3-21G level and leads down from the transition state TS-3 to both C-4 and C-5 minima.

The products of Si⁺ insertion into SiX₄ (X = F, Cl), C-2 and C-5, have C_s symmetry with ²A' electronic ground states. The structures are anti at HF/6-31G*, similar to X = H. The SiSiF

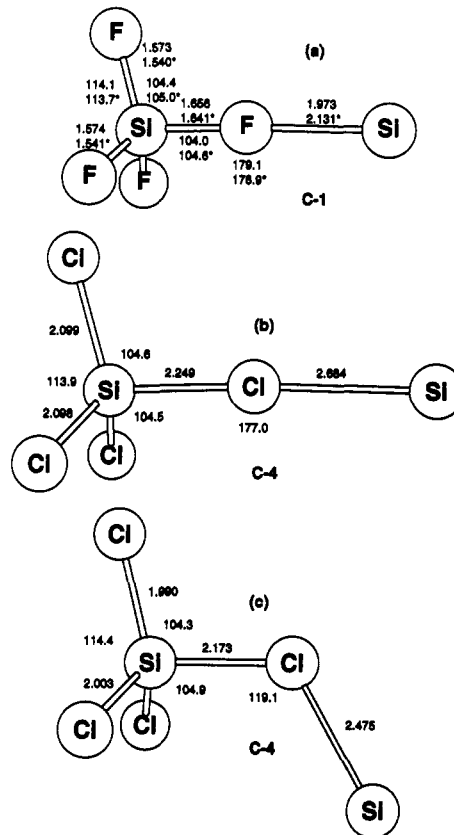


Figure 1. (a) Optimized geometries at HF/3-21G (no superscript) and HF/6-31G* (asterisk) for F₃Si-F-Si⁺ (C_s symmetry), (b) optimized geometry at HF/3-21G for Cl₃Si-Cl-Si⁺ (C_s symmetry), and (c) optimized geometry at HF/6-31G* for Cl₃Si-SiCl⁺ (C_s symmetry).

and SiSiCl angles are both somewhat smaller than the SiSiH angle (112.6° and 115.6° versus 122.0°, respectively).

The transition state corresponding to the 1,2-X atom migration leading to X₂Si-SiX₂⁺ has C₁ symmetry and is shown in Figure 4. For the fluorine case, TS-2, the transition state is relatively late, with the Si₂-F₃ bond almost fully formed (1.684 Å versus 1.555 Å in C-3) and the Si-Si bond shorter than products (2.291 Å versus 2.432 Å in C-3). For X = Cl, transition state TS-4 exhibits similar characteristics, with Si₂-Cl₃ nearly fully formed (2.162 Å versus 2.005 Å in C-6) and a short Si-Si bond (2.298 Å versus 2.381 Å in C-6).

The products of the 1,2-migration are shown in Figure 5. Unlike the disilene ion H₂Si-SiH₂⁺, which has a planar D_{2h} ethylene type structure, F₂Si-SiF₂⁺ and Cl₂Si-SiCl₂⁺ are nonplanar with

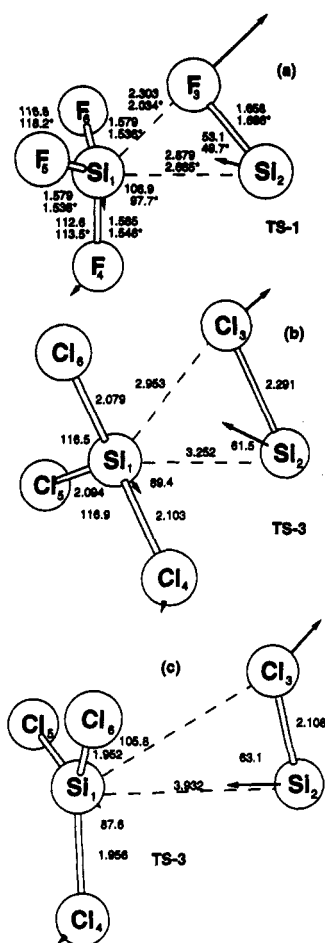


Figure 2. Transition states optimized at HF/3-21G (no superscript) and HF/6-31G* (asterisk) for (a) $F_3Si-SiF^+$ ($\angle F_3Si_1F_4Si_2 = 112.7, 103.2^*$, $\angle F_6Si_1F_4Si_2 = -112.7, -121.4^*$) and (b, c) for $Cl_3Si-SiCl^+$ ($\angle Cl_5Si_1Cl_4Si_2 = -120.2, -85.8^*$ and $\angle Cl_6Si_1Cl_4Si_2 = 116.9, 106.8^*$).

C_s symmetry. These ions are unsymmetrically trans-bent with angles between the plane of the halogens and the Si-Si bond of 117.9° and 161.5° for the fluorine case, C-3, and 128.2° and 159.8° for the chlorine case, C-6. Mulliken population analysis indicates that the more pyramidal center has 42% of the positive charge for C-3 and 40% for C-6. At HF/3-21G, the $F_2Si-SiF_2^+$ structure has one imaginary frequency and is 27.7 kcal/mol above the unsymmetrically trans-bent structure. By contrast to singlet $F_2Si-SiF_2$,³² both $F_2Si-SiF_2^+$ and $Cl_2Si-SiCl_2^+$ are stable with respect to Si-Si bond dissociation.

Heats of Formation. The experimental and theoretical heats of formation of SiF_n and SiF_n^+ have been discussed previously.^{6,7,15,19,21,22} The experimental heat of formation of $SiCl_4$ is well established¹³ and has been used as a standard reference value for the calculations discussed below. Gross et al.³³ obtained $\Delta H_f^\circ_{298}(SiCl_4) = -158.4 \pm 0.3$ kcal/mol from the direct chlorination of silicon in a bomb calorimeter. The value of $\Delta H_f^\circ_{298}(SiCl_3) = -93.3$ kcal/mol is adopted by JANAF for trichlorosilyl radical on the mass spectroscopy-effusion data of Farber and Srivastava.³⁴ This value is in disagreement with Walsh et al.³⁵ whose value of -80.1 ± 2.2 kcal/mol is based on the measured bond dissociation energy of $SiCl_3-H$. The value adopted by JANAF¹³ for dichlorosilylene, -40.3 ± 0.8 kcal/mol, is the average of four studies based on the $Si/SiCl_4$ equilibrium whose values agree to within ± 0.4 kcal/mol. Two studies were based on a flow technique^{36,37} and one on a static technique³⁸ of the reaction $Si(cr) + SiCl_4(g) = 2 SiCl_2(g)$. The fourth study³⁴ involved the mass spectroscopy-effusion study of $Si(g) + SiCl_4(g) = 2SiCl_2(g)$. The value adopted by JANAF¹³ for chlorosilylydine, $\Delta H_f^\circ_{298}(SiCl) = 47.4 \pm 1.6$ kcal/mol, is based on the third-law analysis

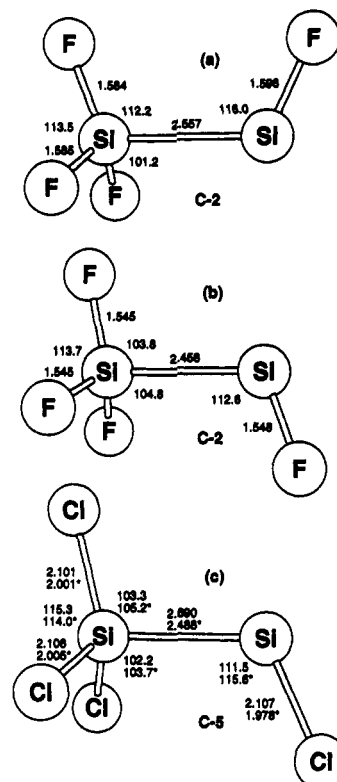


Figure 3. Optimized geometries: (a) syn at HF/3-21G for $F_3Si-SiF^+$, (b) anti at HF/6-31G* for $F_3Si-SiF^+$, and (c) HF/3-21G (no superscript) and HF/6-31G* (asterisk) for $Cl_3Si-SiCl^+$.

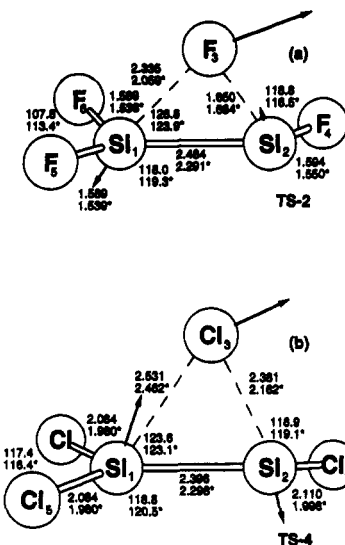
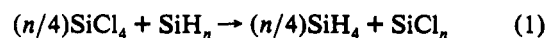


Figure 4. (a) Transition states optimized at HF/3-21G (no superscript) and HF/6-31G* (asterisk) for $F_2Si-SiF_2^+$ ($\angle F_4Si_2Si_1F_3 = 97.8, 96.8^*$, $\angle F_3Si_1Si_2F_3 = 78.4, 81.7^*$, $\angle F_6Si_1Si_2F_3 = -67.8, -76.2^*$) and (b) $Cl_2Si-SiCl_2^+$ ($\angle Cl_4Si_2Si_1Cl_3 = 99.4, 103.6^*$, $\angle Cl_5Si_1Si_2Cl_3 = 92.0, 90.1^*$, $\angle Cl_6Si_1Si_2Cl_3 = -91.2, -88.9^*$).

of the mass spectroscopy-effusion data of Farber and Srivastava³⁴ and may be subject to the same problems as $\Delta H_f^\circ_{298}(SiCl_3)$ discussed above. Walsh³⁵ recommends using 37 ± 10 kcal/mol with caution, whereas Armentrout et al.^{16,17} obtain 46 ± 5 kcal/mol.

The theoretical heats of formation of $SiCl_n$ ($n = 1-3$) have been calculated by Ho, Coltrin, Melius, and Binkley using the bond additivity method.^{19,20} Another estimate of the heats of formation can be obtained by using the following set of isodesmic reactions



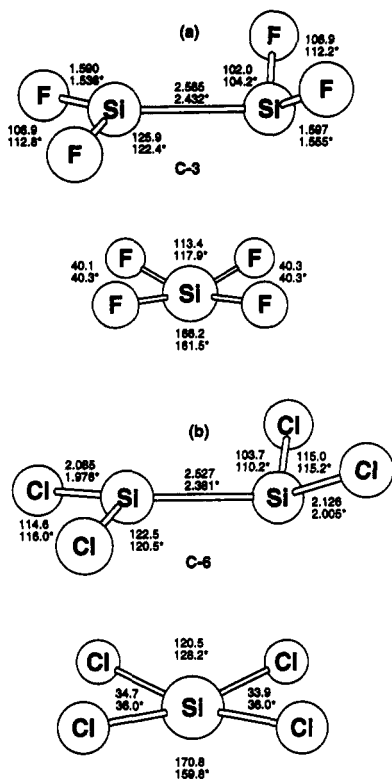


Figure 5. Optimized geometries at HF/3-21G (no superscript) and HF/6-31G* (asterisk) for $F_2Si-SiF_2^+$ and $Cl_2Si-SiCl_2^+$ along with the Newman projection.

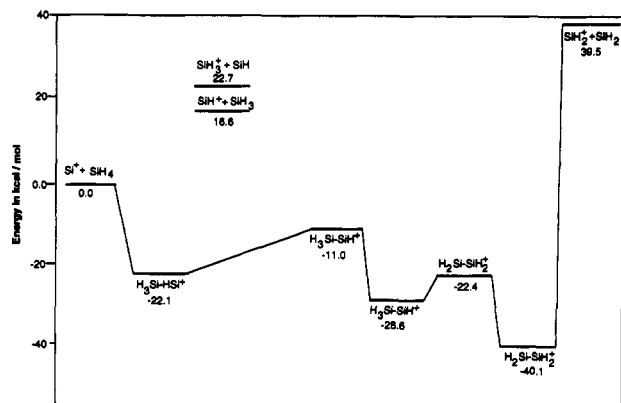


Figure 6. Theoretical estimates of the relative energies at PMP4/6-31G* for the $Si^+ + SiH_4$ system.

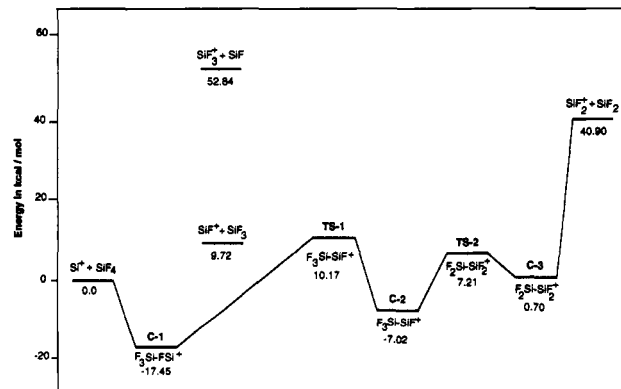
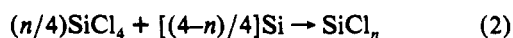


Figure 7. Theoretical estimates of the relative enthalpies at PMP4/6-31G* for the $Si^+ + SiF_4$ system.



Theoretical estimates for the heats of formation of $SiCl_n^+$ can be obtained by combining the calculated heats of reaction with the

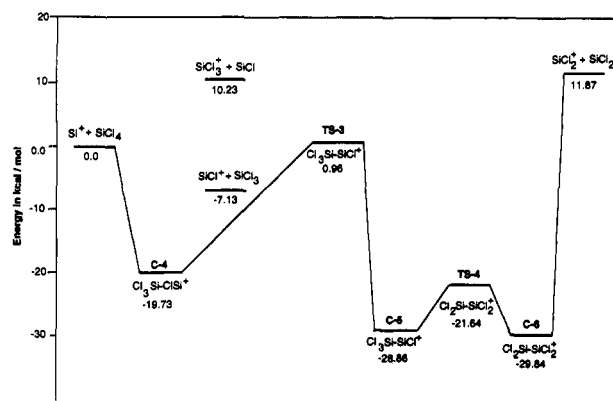
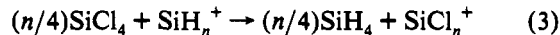


Figure 8. Theoretical estimates of the relative enthalpies at PMP4/6-31G* for the $Si^+ + SiCl_4$ system.

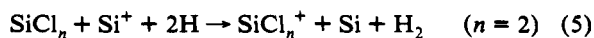
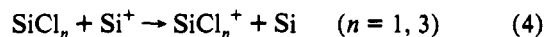
following experimental values: $\Delta H_f^\circ(298)(Si) = 107.6 \pm 2$,¹³ $\Delta H_f^\circ(298)(SiH) = 89.6 \pm 1.2$,¹⁰ $\Delta H_f^\circ(298)(SiH_2) = 65.5 \pm 1.0$,³⁹ $\Delta H_f^\circ(298)(SiH_3) = 47.9 \pm 0.6$,⁴⁰ $\Delta H_f^\circ(298)(SiH_4) = 8.2 \pm 0.5$,¹³ $\Delta H_f^\circ(298)(SiCl_4) = -158.4 \pm 0.3$ kcal/mol.¹³ The heat of formation for $SiCl_3^+$ from eqs 1 and 2 gives an average value of -76.4 kcal/mol. This value is in excellent agreement with the value obtained by Ho et al.²⁰ using the bond additivity method (-76.5 kcal/mol). The calculations are in good agreement with the experimental values obtained by Walsh³⁵ (-80.1 kcal/mol) but do not support the measurements of Farber and Srivastava³⁴ (-93.3 kcal/mol). The average value for the heat of formation of $SiCl_2^+$ obtained from eqs 1 and 2 is -38.8 kcal/mol. This value is in good agreement with the previous calculations (-37.6 kcal/mol)²⁰ and the experimental value (-40.3 ± 0.8 kcal/mol).¹³ The value calculated for $SiCl$ is $\Delta H_f^\circ(298) = 36.6$ kcal/mol, in good agreement with computations of Ho et al.²⁰ (37.9 kcal/mol). Both agree with the recommendation of Walsh³⁵ (37 ± 10 kcal/mol), but are 8–11 kcal/mol lower than the measurements of Farber et al.³⁴ and Armentrout et al.¹⁷ (47.4 ± 1.6 and 46 ± 5 kcal/mol, respectively). Considering these discrepancies, a new and independent determination of the experimental $\Delta H_f^\circ(SiCl)$ would be desirable.

New values for the heats of formation of $SiCl_n^+$ have recently been obtained by Fisher and Armentrout¹⁷ using guided ion beam mass spectrometry to study the reaction of O_2^+ , Ar^+ , Ne^+ , and He^+ with $SiCl_4$. The recommended values are $\Delta H_f^\circ(298)(SiCl^+) = 203.9 \pm 2.5$, $\Delta H_f^\circ(298)(SiCl_2^+) = 187.3 \pm 2.2$, and $\Delta H_f^\circ(298)(SiCl_3^+) = 99.8 \pm 1.6$ kcal/mol (thermal electron convention).

The heats of formation of $SiCl_n^+$ ($n = 1-3$) can be calculated from the theoretical heats of reaction for



combined with the following experimental data: $\Delta H_f^\circ(298)(SiH^+) = 272 \pm 1.2$,¹⁰ $\Delta H_f^\circ(298)(SiH_2^+) = 276.6 \pm 0.6$,¹⁰ $\Delta H_f^\circ(298)(SiH_3^+) = 232.4 \pm 1.4$ ¹⁰ or 237.0 ± 0.7 ,⁴⁷ kcal/mol. A second set of isodesmic reactions that can be used to obtain the heats of formation of $SiCl_n^+$ compares the ionization potential of $SiCl_n$ to Si by using the $\Delta H_f^\circ(298)(Si^+) = 297.1$ ⁴¹ kcal/mol.



For $SiCl_2^+$, an isogyric reaction is used to circumvent problems arising from changes in the number of unpaired electrons⁴⁵ (experimental $\Delta H_f^\circ(298)(H) = 52.10$ kcal/mol¹³).

The bond additivity correction (BAC) method^{19,20} can also be used to calculate the heat of formation of a compound from the theoretical heat of atomization by correcting the error in the dissociation energy of each type of bond. As in the fluorine case,²² the tricoordinated cation is used to calculate the BAC:

TABLE III: Relative Enthalpies^a

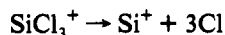
molecule		HF/3-21G	HF/6-31G*	MP2/6-31G*	MP3/6-31G*	MP4/6-31G*	PMP4/6-31G*
minima							
F ₃ Si-F-Si ⁺	C-1	-23.30	-12.14	-17.15	-15.81	-17.19	-17.45
F ₃ Si-SiF ⁺	C-2	35.21	4.24	-7.18	-1.58	-6.61	-7.02
F ₂ Si-SiF ₂ ⁺	C-3	42.98	13.18	0.21	7.10	1.27	0.70
Cl ₃ Si-Cl-Si ⁺	C-4	-12.57	-12.28	-20.31	-19.32	-20.61	-19.73
Cl ₃ Si-SiCl ⁺	C-5	9.63	-15.24	-28.58	-26.00	-28.77	-28.86
Cl ₂ Si-SiCl ₂ ⁺	C-6	13.02	-14.33	-28.86	-26.02	-28.87	-29.84
transition structures							
F ₃ Si-F-Si ⁺ → F ₃ Si-SiF ⁺	TS-1	43.95	29.67	11.98	16.99	10.99	10.17
F ₃ Si-SiF ⁺ → F ₂ Si-SiF ₂ ⁺	TS-2	48.35	25.43	6.69	14.57	7.61	7.21
Cl ₃ Si-Cl-Si ⁺ → Cl ₃ Si-SiCl ⁺	TS-3	26.28	15.09	3.54	4.64	1.74	0.96
Cl ₃ Si-SiCl ⁺ → Cl ₂ Si-SiCl ₂ ⁺	TS-4	20.66	-4.61	-22.28	-18.56	-21.62	-21.64
reactants and products							
Si ⁺ + SiF ₄		0.00	0.00	0.00	0.00	0.00	0.00
SiF ⁺ + SiF ₃		29.59	18.71	10.08	13.78	9.52	9.72
SiF ₃ ⁺ + SiF		83.69	63.75	53.22	58.34	53.06	52.84
SiF ₂ ⁺ + SiF ₂		65.87	52.61	40.85	46.86	40.78	40.90
Si ⁺ + SiCl ₄		0.00	0.00	0.00	0.00	0.00	0.00
SiCl ⁺ + SiCl ₃		7.31	0.61	-5.38	-5.33	-7.26	-7.13
SiCl ₃ ⁺ + SiCl		39.87	20.09	12.10	12.77	10.46	10.23
SiCl ₂ ⁺ + SiCl ₂		30.22	22.12	14.13	14.63	11.95	11.87

^a Relative energies in kcal/mol with zero-point (unscaled) and thermal contributions (298 K, 1 atm).

TABLE IV: Theoretical Heats of Formation (kcal/mol, Thermal Electron Convention)

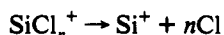
	theoretical ΔH_f° ₂₉₈				exptl ΔH_f° ₂₉₈
	isodesmic	using IP	BAC	best est	
SiCl	36.6		37.9 ^a	37.2	47.4 ± 1.6, ^b 46 ± 5, ^d 37 ± 10 ⁱ
SiCl ₂	-38.9		-37.6 ^a	-38.2	-40.3 ± 0.8, ^b 39.4 ± 3.4 ^k
SiCl ₃	-76.4		-76.5 ^a	-76.4	-80.1 ± 2.2, ⁱ -93.3 ^l
SiCl ₄	-158.4 ^j		-158.4 ^j		-158.4 ± 1.3 ^b
SiCl ⁺	205.0	206.8	205.3	205.7	203.9 ± 2.5, ^d 217 ± 7, ^e 202 ± 5/ ^f 204 ± 5/ ^g 202 ^h
SiCl ₂ ⁺	187.1	189.0	183.1	186.4	187.3 ± 2.2, ^d 188 ± 3, ^e 190 ± 6, ^e 191.9 ± 2.6 ^h
SiCl ₃ ⁺	106.2, 110.8	106.5	103.8 ^j	107.8	103.8 ± 2, ^m 99.8 ± 1.6, ^d 102 ± 3 ^e

^a Reference 20. ^b Reference 13. ^c Reference 16. ^d Reference 17. ^e Reference 16. ^f Reference 43. ^g Reference 44. ^h Reference 42. ⁱ Reference 35. ^j Reference value. ^k Reference 18. ^l Reference 34. ^m Reference 17, assuming SiCl₃⁺ + ClO₂ as products.



$$\text{BAC}(\text{Si-Cl}^+) = \frac{1}{3}(\text{experimental } \Delta H_f - \text{calculated } \Delta H_f) = 14.20 \text{ kcal/mol (6)}$$

based on ΔH_f calculated at MP4/6-31G** with ΔZPE scaled by 0.93 and thermal corrections to 298 K calculated at HF/6-31G*. There are two choices for ΔH_f° ₂₉₈(SiCl₃⁺). Weber and Armentrout find 102 ± 3 kcal/mol based on thresholds for Si⁺ + SiCl₄ → SiCl₃⁺ + SiCl. Fisher and Armentrout obtain 99.8 kcal/mol from O₂⁺ + SiCl₄ → SiCl₃⁺ + O₂ + Cl. However, there is some doubt concerning the products of this reaction. If the products are ClO₂ (ΔH_f° ₂₉₈(ClO₂ → Cl + O₂) = 4.76 ± 0.49 kcal/mol⁴⁸), the heat of formation for SiCl₃⁺ becomes 103.8 kcal/mol. Calculations based on isodesmic reactions support this higher value. The BAC is based on ΔH_f° ₂₉₈(SiH₃⁺) = 103.8 kcal/mol. For comparison, the bond additivity corrections for the fluorosilane cations is BAC(SiF⁺) = 11.54 kcal/mol (MP4/6-31G** at 298 K).²² The heat of formation of SiCl_n⁺ can be calculated in the following way:



$$\Delta H_f^\circ = \text{calculated } \Delta H_f^\circ + n\text{BAC}(\text{SiCl}^+)$$

$$\Delta H_f^\circ(\text{SiCl}_n^+) = \Delta H_f^\circ(\text{Si}^+) + n\Delta H_f^\circ(\text{Cl}) - \Delta H_f^\circ \quad (7)$$

The theoretical estimates of the heats of formation are summarized in Table IV. Similar calculations on neutral species appear to have error bars of ca. 3 kcal/mol. The average calculated value for SiCl⁺ from eqs 3, 4, and 7 is 205.7 kcal/mol; for SiCl₂⁺, eqs

TABLE V: Calculated and Observed Thresholds for Si⁺ + SiX₄ (eV)

Si ⁺ + SiX ₄ →	SiX ⁺ + SiX ₃	SiX ₃ ⁺ + SiX	SiX ₂ ⁺ + SiX ₂
X = H			
PMP4/6-31G** ^a	0.72	0.98	1.71
best theor est ^b	0.58	0.79	1.49
observed ^c	0.74	0.91	1.72
X = F			
PMP4/6-31G**	0.42	2.29	1.77
best theor est ^d	0.11	1.93	1.48
observed ^e	0.10	2.48	2.35
X = Cl			
PMP4/6-31G**	-0.31	0.44	0.51
best theor est ^f	-0.41	0.27	0.41
observed ^g	≤ 0	0.3	0.4

^a Reference 24. ^b Reference 9. ^c Reference 14. ^d Reference 22. ^e Reference 15. ^f Present work. ^g Reference 16.

3, 5, and 7 yield an average of 186.4 kcal/mol. Both are in good agreement with the experimental values¹⁷ (203.9 and 187.3 kcal/mol, respectively). For SiCl₃⁺, the average value calculated from eqs 3 and 4, 106.4 kcal/mol, agrees with an earlier determination of ΔH_f° ₂₉₈(SiCl₃⁺) = 102 ± 3 kcal/mol¹⁶ and recent measurements based on thresholds for SiCl₃⁺ from O₂⁺ + SiCl₄,¹⁷ provided ClO₂ is assumed to be the product (ΔH_f° ₂₉₈(SiCl₃⁺) = 103.8 ± 2 kcal/mol) rather than Cl + O₂ (99.8 kcal/mol). The present calculations also yield an adiabatic ionization potential for SiCl₃, 7.92 eV, that is in excellent agreement with recent experiments of Hudgens et al.⁴⁷ (7.93 ± 0.05 eV).

Energetics. Table V compares the calculated thresholds for Si⁺ + SiX₄ with the observed values. Two sets of calculated values are given. The first is obtained directly from the PMP4/6-31G** calculation. The second is based on the best theoretical estimates of the heats of formation (from the present and previous

calculations) for the species involved. For SiH_n, the G-2 values of Curtiss et al.⁹ were used; the theoretical heats of formation of SiF_n^{21,22} and SiCl_n are based on isodesmic reactions, as discussed above. Except for two reactions, all of the calculated thresholds in Table V were within ±0.2 eV of the observed values, and the best theoretical estimates are equal to or slightly lower than the observed thresholds. For Si⁺ + SiF₄ → SiF₃⁺ + SiF and SiF₂⁺ + SiF₂, the best theoretical thresholds are considerably lower than observed, indicating an activation barrier or a dynamic bottleneck. The PMP4/6-31G** calculations are 0.1–0.3 eV (3–10 kcal/mol) higher than the best estimates; this suggests similar error bounds on the relative energies and barrier heights within each reaction scheme.

Reaction Mechanism. The calculated reaction profiles for SiX₄ + Si⁺ (X = H, F, and Cl) are shown in Figures 6–8. The experimental data suggest that SiX⁺ + SiX₃ and SiX₃⁺ + SiX are formed by a direct mechanism, i.e., without going through a stable intermediate. The present calculations do not preclude such a mechanism. However, both the calculations of Raghavachari²⁴ and the present work show that there are tightly bound clusters of the form X₃Si–X–Si⁺ with well depths of 17–22 kcal/mol. These clusters can dissociate to SiX⁺ + SiX₃ or SiX₃⁺ + SiX or can rearrange to X₃Si–Si–X⁺. For X = H, this rearrangement to form H₃Si–Si–H⁺ has a barrier of only 11 kcal/mol. For X = F and Cl, the barrier for rearrangement is considerably higher, 27 and 21 kcal/mol, respectively. More significantly, the barrier for X = F is 10 kcal/mol above the reactants, whereas for X = Cl and H, the barrier is equal to (±1 kcal/mol) or lower than reactants; this may be the source of the dynamic bottleneck that elevates the observed threshold for the production of SiF₂⁺ + SiF₂.

The second cluster, X₃Si–Si–X⁺, can dissociate via homolytic cleavage to SiX⁺ + SiX₃ or by heterolytic cleavage to SiX₃⁺ + SiX or can rearrange to X₂SiSiX₂⁺. For X = H and Cl, this rearrangement is quite facile (6–7 kcal/mol barrier) and provides a mechanism for the scrambling of isotopically labeled Si that is seen experimentally.^{14,16,23} The barrier for X = F is considerably higher (14 kcal/mol above F₃Si–Si–F⁺ and 7 kcal/mol above reactants) and this suggests that isotopic scrambling should be less efficient for X = F, especially at lower energies.

Disilicon species are observed for Si⁺ + SiH₄^{14,23} but not for SiF₄¹⁵ and SiCl₄.¹⁶ In part, this may be due to the higher barrier for Si⁺ insertion into an SiF or SiCl bond, TS-1 or TS-3. Second, the Si–Si bond in X₂SiSiX₂⁺ is considerably weaker for X = F and Cl (ca. 40 kcal/mol) than for X = H (ca. 80 kcal/mol), making the fragmentation of X₂SiSiX₂⁺ more likely for X = F and Cl. For X = H, larger clusters are formed via H₂ elimination to form H₂SiSi⁺, which can continue to insert into SiH₄. Comparison with the thermal decomposition of SiH_{4–n}F_n⁴⁶ suggests that elimination of X₂ from X₂SiSiX₂⁺ and X₃SiSiX⁺ should be much more difficult for X = F and Cl than for X = H. This would block further cluster growth via the same mechanism as in silane and would favor fragmentation into stable monosilane species.

Conclusions

Structures and energetics have been calculated for the clusters and transition states in the reaction Si⁺ + SiX₄ → X₃Si–X–Si⁺ → X₃Si–Si–X⁺ → X₂SiSiX₂⁺ and for fragmentation into SiX⁺ + SiX₃, SiX₃⁺ + SiX, and SiX₂⁺ + SiX₂ for X = F and Cl. Theoretical estimates of heats of formation have been obtained for SiCl_n and SiCl_n⁺. The calculated thresholds for production of SiX⁺ + SiX₃, SiX₃⁺ + SiX, and SiX₂⁺ + SiX₂ are in good agreement with experiment, except for SiF₃⁺ + SiF and SiF₂⁺ + SiF₂. For these two, the theoretical thresholds are lower than experiment, suggesting an activation barrier or dynamical bottleneck. The energy profiles for the reactions are in agreement with other qualitative features of the experiments, such as isotopic scrambling.

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