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Fragmentation behavior of $Si_2Cl_n^+$ cations (n = 1—6)

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Sector-field mass spectrometry was used to probe the fragmentation patterns of the cationic silicon chlorides $Si_2Cl_n^+$ (n = 1—6). For almost all $Si_2Cl_n^+$ ions, Si—Si fragmentation predominates the Si—Cl bond cleavage both in the metastable ion and collisional activation mass spectra. Analysis of the fragmentation patterns indicates that the long-lived radical cation $Si_2Cl_6^{\cdot +}$ corresponds to a complex $[SiCl_2 \cdot SiCl_4]^{\cdot +}$ rather than the intact molecular ion of hexachlorodisilane. The behavior of $Si_2Cl_5^+$ is consistent with the formation of the (trichlorosilyl)dichlorosilyl cation $Cl_3SiSiCl_2^+$. Structural aspects are also discussed for the other $Si_2Cl_n^+$ species. A semi-quantitative analysis of the fragmentation patterns in conjunction with the literature thermochemistry data was used to estimate some thermochemical properties of the $Si_2Cl_n^+$ cations.

Key words: clusters, kinetic method, mass spectrometry, silicon chlorides.

Since the isolation of the first stable disilene,[1] the chemistry of molecules containing multiple bonds to silicon received increasing attention. Theoretical studies have also predicted the existence of triple bonds to silicon, when appropriate substituents are chosen.[2,3] Chlorine substitution of silicon seems to stabilize multiple bonding,[4] and the silaalkine ClSi≡CH has recently been found in the gas phase.[5] Further, extensive theoretical studies of silicon chlorides in the context of their use as precursors for the chemical vapor deposition of epitaxial silicon have been performed.[6] Here, we report a mass spectrometric study of hexachlorodisilane Si_2Cl_6 aimed at exploring the ion chemistry of $Si_2Cl_n^+$ species (n = 1—6).

Experimental

Experiments were performed on a modified VG ZAB/HF/AMD 604 four-sector mass spectrometer with a BEBE configuration (B stands for magnetic and E for electric sector), which has been described elsewhere.[7] The $Si_2Cl_n^+$ cations (n = 1—6) were generated by electron ionization of hexachlorodisilane (Aldrich, 96%).[8] Isobaric interferences were negligible, and all the $Si_2Cl_n^+$ species (n = 1—6) showed the expected isotope patterns.** After acceleration to a kinetic energy of 8 keV, the $^{28}Si_2{}^{35}Cl_n^+$ ions of interest were mass-selected and subjected to metastable ion (MI) and collisional activation (CA) studies. MI spectra of B(1)/E(1) mass-selected $Si_2Cl_n^+$ ions were recorded by detection of the charged fragments formed unimolecularly in the field-free region between E(1) and B(2) by scanning the latter sector. CA spectra were recorded in the same manner using helium as a stationary collision gas. In order to analyze the effect of residual gas within the mass spectrometer on the metastable ion spectra, the unimolecular dissociations were also studied in the field-free regions preceding E(1) and E(2). Unless noted otherwise, the MI data reported below were corrected for signals due to the presence of residual gas.

Results and Discussion

The experiments include the metastable ion (MI) and collisional activation (CA) mass spectra of the $Si_2Cl_n^+$ ions (n = 1—6) generated by electron ionization (EI) of hexachlorodisilane. In the EI mass spectrum of Si_2Cl_6, $SiCl_n^+$ ions (n = 1—3) predominate, while the $Si_2Cl_n^+$ cations (n = 1—6) have at most 10% abundance relative to the $SiCl_2^+$ base peak; among the $Si_2Cl_n^+$ species, the $Si_2Cl_3^+$ signal is particularly weak.[8]

The ionic fragments obtained in the MI and CA mass spectra of the mass-selected $Si_2Cl_n^+$ ions are summarized in Table 1. The major dissociation channels are given in reactions (1)—(6), where it is distinguished between the Si—Cl bond cleavages affording the corresponding $Si_2Cl_{n-1}^+$ fragments and Si—Si bond cleavages generating $SiCl_n^+$ cations (n = 0—3).

$$\mathrm{Si_2Cl_6}^{\cdot +} \longrightarrow \mathrm{Si_2Cl_5}^{+} + \mathrm{Cl}^{\cdot} \tag{1a}$$

$$\mathrm{Si_2Cl_6}^{\cdot +} \longrightarrow \mathrm{SiCl_3}^{+} + \mathrm{SiCl_3}^{\cdot} \tag{1b}$$

$$\mathrm{Si_2Cl_6}^{\cdot +} \longrightarrow \mathrm{SiCl_2}^{\cdot +} + \mathrm{SiCl_4} \tag{1c}$$

$$\mathrm{Si_2Cl_5}^{+} \longrightarrow \mathrm{Si_2Cl_4}^{\cdot +} + \mathrm{Cl}^{\cdot} \tag{2a}$$

$$\mathrm{Si_2Cl_5}^{+} \longrightarrow \mathrm{SiCl_3}^{+} + \mathrm{SiCl_2} \tag{2b}$$

$$\mathrm{Si_2Cl_5}^{+} \longrightarrow \mathrm{SiCl}^{+} + \mathrm{SiCl_4} \tag{2c}$$

$$\mathrm{Si_2Cl_4}^{\cdot +} \longrightarrow \mathrm{Si_2Cl_3}^{+} + \mathrm{Cl}^{\cdot} \tag{3a}$$

$$\mathrm{Si_2Cl_4}^{\cdot +} \longrightarrow \mathrm{SiCl_3}^{+} + \mathrm{SiCl}^{\cdot} \tag{3b}$$

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Table 1. Ion intensities observed in the MI and CA mass spectra of the B(1)/E(1) mass-selected $Si_2Cl_n^+$ cations (n = 1—6)

Ion	Mass spectrum	I_{rel} (%)[a]										
		$Si_2Cl_5^+$	$Si_2Cl_4^+$	$Si_2Cl_3^+$	$Si_2Cl_2^+$	Si_2Cl^+	Si_2^+	$SiCl_4^+$	$SiCl_3^+$	$SiCl_2^+$	$SiCl^+$	Si^+
$Si_2Cl_6^+$	MI									100		
	CA	2						2	20	100	4	
$Si_2Cl_5^+$	MI	[b]	5						6		100	
	CA	[b]	100	2	3	1			75	30	40	
$Si_2Cl_4^+$	MI		[b]								100	
	CA		[b]	50	15	5	1		45	70	100	1
$Si_2Cl_3^+$	MI			[b]	2						100	
	CA			[b]	20	4	1		10	30	100	3
$Si_2Cl_2^+$	MI[c]				[b]						100	
	CA				[b]	45	3			4	100	2
Si_2Cl^+	MI[d]					[b]					100	
	CA					[b]	10				100	2

[a] Relative error ±30%, fragments <1% are omitted.
[b] Parent ion.
[c] Weak MI spectrum with a signal-to-noise ratio of ~30 for the base peak.
[d] Weak MI spectrum with a signal-to-noise ratio of ~10 for the base peak.

$$Si_2Cl_4^{\cdot+} \longrightarrow SiCl_2^{\cdot+} + SiCl_2 \qquad (3c)$$

$$Si_2Cl_4^{\cdot+} \longrightarrow SiCl^+ + SiCl_3^{\cdot} \qquad (3d)$$

$$Si_2Cl_3^+ \longrightarrow Si_2Cl_2^{\cdot+} + Cl^{\cdot} \qquad (4a)$$

$$Si_2Cl_3^+ \longrightarrow SiCl^+ + SiCl_2 \qquad (4b)$$

$$Si_2Cl_2^{\cdot+} \longrightarrow Si_2Cl^+ + Cl^{\cdot} \qquad (5a)$$

$$Si_2Cl_2^{\cdot+} \longrightarrow SiCl_2^{\cdot+} + Si \qquad (5b)$$

$$Si_2Cl_2^{\cdot+} \longrightarrow SiCl^+ + SiCl^{\cdot} \qquad (5c)$$

$$Si_2Cl_2^{\cdot+} \longrightarrow Si^{\cdot+} + SiCl_2 \qquad (5d)$$

$$Si_2Cl^+ \longrightarrow Si_2^{\cdot+} + Cl^{\cdot} \qquad (6a)$$

$$Si_2Cl^+ \longrightarrow SiCl^+ + Si \qquad (6b)$$

$$Si_2Cl^+ \longrightarrow Si^{\cdot+} + SiCl^{\cdot} \qquad (6c)$$

The only significant fragment in the MI spectrum of $Si_2Cl_6^{+\cdot}$ corresponds to ionized dichlorosilylene $SiCl_2^{+\cdot}$ concomitant with loss of neutral $SiCl_4$ (reaction (1c)). Surprisingly, the simple Si—Cl and Si—Si bond cleavages according to reactions (1a) and (1b) do not occur in the metastable ion; also upon collisional activation, the corresponding $Si_2Cl_5^+$ and $SiCl_3^+$ signals are much weaker than that of $SiCl_2^{\cdot+}$. As outlined in the discussion, the predominance of $SiCl_2^{\cdot+}$ over $SiCl_3^+$ in both spectra has some profound structural and energetic implications. As mentioned above, loss of neutral $SiCl_4$ prevails in the MI spectrum of $Si_2Cl_5^+$ (reaction (2c)), while expulsions of $Cl^{\cdot}$ and $SiCl_2$ (reactions (2a) and 2b)) are observed as minor routes (Fig. 1, *a*). Upon collisional activation, the latter channels gain much in abundance, and reaction (2a) gives rise to the base peak of the CA mass spectrum of $Si_2Cl_5^+$. Such a drastic change in the fragmentation patterns in the MI and CA spectra suggests that reaction

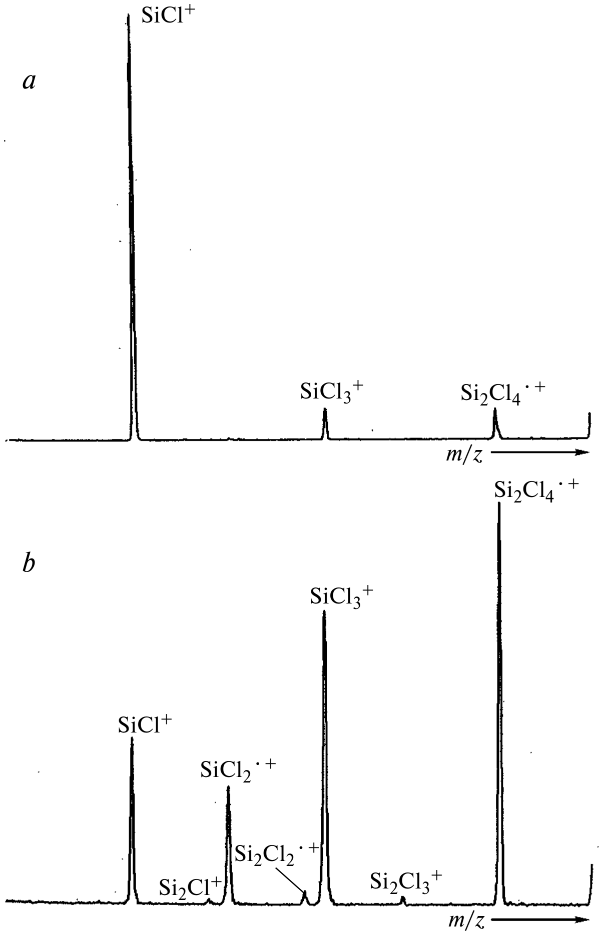


Fig. 1. Mass spectra of the $Si_2Cl_5^+$ ions generated by the dissociative electron ionization of hexachlorodisilane: *a*, MI B(1)/E(1), *b*, CA B(1)/E(1) (He as collision gas, transmission 80%).

(2c) involves a structural isomerism (see below). While loss of $SiCl_3^{\cdot}$ is exclusively observed in the MI spectrum of $Si_2Cl_4^{\cdot+}$ (reaction (3d)), the formation of $Si_2Cl_3^+$, $SiCl_3^+$ and $SiCl_2^{\cdot+}$ according to reactions (3a)—(3c) can compete effectively upon collisional activation. Similar magnitudes of these fragments in the CA spectrum may qualitatively suggest that the fragmentations of $Si_2Cl_4^{\cdot+}$ have high energy demands, and thus, the parent ion is particularly stable (see below). The opposite, *i.e.*, decreased stability, is implied by the weakness of the $Si_2Cl_3^+$ fragment upon dissociative EI of hexachlorodisilane. The same conclusion is implied by the sequence of the $Si_2Cl_n^+$ fragments upon collisional activation of $Si_2Cl_5^+$ in which $Si_2Cl_3^+$ is less abundant than $Si_2Cl_4^{\cdot+}$ as well as $Si_2Cl_2^{\cdot+}$ (Fig. 1, *b*). For metastable $Si_2Cl_3^+$, losses of neutral $Cl^{\cdot}$ and $SiCl_2$ are observed (reactions (4a) and (4b)), whereas other $SiCl_n^{\cdot+}$ fragments are only formed upon collisional activation. In the corresponding MI spectra of $Si_2Cl_2^{\cdot+}$ and Si_2Cl^+, only the $SiCl^+$ fragment forms. Moreover, the signal-to-noise ratios of the MI spectra are poor, and we can therefore not rigorously exclude that the signals observed are to some extent due to collisional activation with residual gas present in the mass spectrometer. The weakness of the MI spectra for $n = 1$ and 2 is indeed not unexpected, because the densities of states, which support metastable states having lifetimes in the order of microseconds decrease dramatically on going from polyatomic molecules to tetra-, tri-, or even diatomic species. Interestingly, collisional activation of $Si_2Cl_2^{\cdot+}$ affords mainly Si_2Cl^+ and $SiCl^+$ according to reactions (5a) and (5c), whereas the reactions (5b) and (5d) yielding $SiCl_2^{\cdot+}$ and $Si^{\cdot+}$, respectively, are barely observed. Finally, note that the prevalence of $SiCl^+$ as ionic fragment in the MI spectra of almost all $Si_2Cl_n^+$ species can simply be attributed to the particularly low ionization energy of the $SiCl^{\cdot}$ radical (E_i = 6.79 eV [9]); $Si_2Cl_6^{\cdot+}$ is an exception in this respect because unimolecular formation of $SiCl^+$ would require co-generation of neutral $SiCl_5^{\cdot}$ which lacks stability.

As we have outlined recently,[10] the elucidation of energetic and structural aspects of binary A_mB_n clusters can very much be assisted by thermochemical considerations of the fragmentation channels observed in mass spectrometric experiments, provided that their energy demands are known with sufficient accuracy.[11] The present analysis is largely based on the thermochemistry of silicon chlorides evaluated in Ref. 9 along with some complementary literature data of Si_mCl_n species (Table 2).[8]

Table 2. Heats of formation of neutral ($\Delta H^{\circ}_{f,n}$) and ionic ($\Delta H^{\circ}_{f,ion}$) $Si_mCl_n^{0/+}$ species (m = 1, 2; n = 0—6) at 298 K and ionization energies (E_i) used in the data analysis

Species	$\Delta H^{\circ}_{f,n}$	$\Delta H^{\circ}_{f,ion}$	E_i /eV
	kcal mol^{-1}		
Si	107.6±1.9 [9]	297.1±1.9 [9]	8.1517 [a]
SiCl	46±5 [b,9]	203.9±2.5 [9]	6.79±0.24 [9]
$SiCl_2$	−40.3±0.8 [9]	187.3±2.2 [9]	9.81±0.10 [9]
$SiCl_3$	−78±3 [9]; −93.3 [8]	99.8±1.6 [9]	7.65±0.15 [9]
$SiCl_4$	−158.4±0.3 [9]	115.0±1.3	11.79±0.01
Si_2Cl_4	−102.8 [c,d]		
Si_2Cl_6	−233.9 [c]	6 [e]	10.4 [8]
Cl	28.99 [9]		
Si_2	141 [8]	323 [e]	7.9 [8]

[a] See http://physics/nist/gov/atomic.

[b] *Ab initio* calculations give a significantly lower value of 36.5 kcal mol^{-1}, see Ref. 12.

[c] For theoretical estimate, see Ref. 13.

[d] Refers to the $Cl_3SiSiCl$ isomer; tetrachlorodisilene $Cl_2Si{=}SiCl_2$ is less stable (by 8.5 kcal mol^{-1}).

[e] Value derived from $\Delta H^{\circ}_{f,n}$ and E_i.

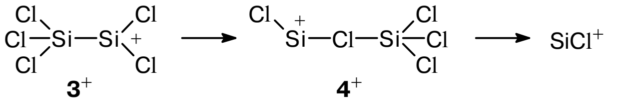
Structural aspects. Let us begin with $Si_2Cl_6^{\cdot+}$, formally corresponding to the molecular ion of hexachlorodisilane. In the experiment, $SiCl_2^{\cdot+}$ formed in reaction (1c) predominates the fragmentation patterns both in MI and CA. The heats of formation (ΔH°_f) compiled in Table 2 suggest that their sum for reaction (1c) is $\Sigma\Delta H_f(1c) = 28.9 \pm 2.2$ kcal mol^{-1}. Interestingly, however, the thermochemical data given in Ref. 9 predict formation of $SiCl_3^+$ as ionic fragment to be even more favorable, *i.e.*, $\Sigma\Delta H_f(1b) = 21.8 \pm 3.4$ kcal mol^{-1}. Yet, this channel is not observed at all in the MI spectrum and also much weaker than the $SiCl_2^{\cdot+}$ fragment upon CA. Note that the usage of $\Delta H_f(SiCl_3^{\cdot})$ = 93.3 kcal mol^{-1} given in Ref. 8 makes the situation even worse.[12] This experimental result has two implications. At first, the predominance of $SiCl_2^{\cdot+}$ in the MI and CA spectra suggests that long-lived $Si_2Cl_6^{\cdot+}$ does not anymore possess the structure of the neutral precursor, but has rearranged to a structure in which the $SiCl_2$ unit is already preformed, *e.g.*, $\mathbf{1}^{\cdot+} \rightarrow \mathbf{2}^{\cdot+}$ (Scheme 1). If instead the molecular ion $\mathbf{1}^{\cdot+}$ constitutes the long-lived ion, one would expect the predominance of reaction (1b) at least upon collisional activation at keV energies in which direct bond cleavages are favored. The second implication relies on the theory of unimolecular dissociation in general and the kinetic method in particular.[14] Thus, provided that long-lived $Si_2Cl_6^{\cdot+}$ behaves as a statistical ensemble with respect to the distribution of internal energy in the metastable ion, there exist no reason why either $\mathbf{1}^{\cdot+}$ or $\mathbf{2}^{\cdot+}$ should not undergo reaction (1b), if the energy demand of this route is indeed lower than that of reaction (1c) or comparable to it. Further, there are no obvious arguments in favor of kinetic hindrances of reaction (1b) occurring from either $\mathbf{1}^{\cdot+}$ or $\mathbf{2}^{\cdot+}$. Hence, the thermochemical properties of the $SiCl_n^{0/+}$ species given in Table 2 appear questionable. Specifically, the predominance of reaction (1c)

Scheme 1

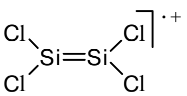
suggests that either the heats of formation of $SiCl_3{}^{\cdot}$ and $SiCl_3{}^{+}$ are too low and/or that of $\Delta H_f(SiCl_2{}^{\cdot+})$ is too large; $\Delta H_f(SiCl_4)$ is assumed to be settled.

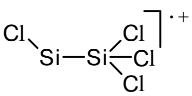
In the case of $Si_2Cl_5{}^{+}$, the preference of $SiCl^{+}$ in the MI spectrum is consistent with the literature thermochemistry, *i.e.*, $\Sigma\Delta H_f(2c) = 45.5\pm2.5$ kcal mol^{-1} is significantly lower than $\Sigma\Delta H_f(2b) = 59.5\pm1.8$ kcal mol^{-1}. Nevertheless, the fact that reactions (2a) and (2b) can compete in the MI and govern the CA spectrum suggests that reaction (2c) is associated with a structural rearrangement, *i.e.*, the chlorine migration from the (trichlorosilyl)dichlorosilyl cation $\mathbf{3}^{+}$ to the ion/neutral complex $\mathbf{4}^{+}$ (Scheme 2). We shall return to this aspect further below.

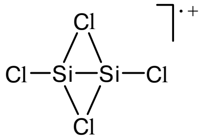
Scheme 2



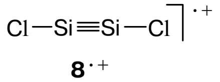
For $Si_2Cl_4{}^{\cdot+}$, three topological structures are conceivable: tetrachlorodisilene $\mathbf{5}^{\cdot+}$, silylidene $\mathbf{6}^{\cdot+}$, and bridged structures such as $\mathbf{7}^{\cdot+}$. The experimental data are insufficient to deduce the connectivity of the ion. Thus, the $SiCl^{+}$ and $SiCl_3{}^{+}$ fragments observed in the CA spectrum are in favor of structure $\mathbf{6}^{\cdot+}$, while the significant amount of $SiCl_2{}^{\cdot+}$ is assumed to be characteristic of $\mathbf{5}^{\cdot+}$. *Ab initio* calculations[15] of the neutral Si_2Cl_4 isomers predict a preference for the silylene, *i.e.*, neutral **6** is computed to be 8.5 kcal mol^{-1} more stable than **5**. Note that the preference for reaction (3b) and its charge-permuted variant (3d) cannot be attributed to mere thermochemistry, *i.e.*, while $\Sigma\Delta H_f(3d) = 125.9\pm3.9$ kcal mol^{-1} is significantly lower than $\Sigma\Delta H_f(3c) = 147.0\pm2.3$ kcal mol^{-1}, $\Sigma\Delta H_f(3d) = 145.8\pm5.2$ kcal mol^{-1} is similar to the latter. Resuming these arguments, it seems most likely that dissociative ionization of Si_2Cl_6 gives rise to a mixture of $Si_2Cl_4{}^{\cdot+}$ isomers.

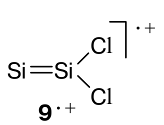

$\mathbf{5}^{\cdot+}$


$\mathbf{6}^{\cdot+}$


$\mathbf{7}^{\cdot+}$

The fragmentation pattern of the $Si_2Cl_3{}^{+}$ cation is non-specific, and no stringent structural conclusions can be drawn. Prevalence of $SiCl^{+}$ in the MI spectrum can simply be assigned to a favorable thermochemistry of this channel, and upon collisional activation, all conceivable $SiCl_n{}^{+}$ fragments (n = 0—3) are formed in competition. Thus, the structures $Cl_2SiSiCl^{+}$ and Cl_3SiSi^{+} are equally conceivable. More instructive is the CA spectrum of $Si_2Cl_2{}^{\cdot+}$, in which the symmetrical cleavage reaction (5c) is much more abundant than (5b) and (5d) in both MI and CA, although $\Sigma\Delta H_f(5c) = 249.9\pm5.6$ kcal mol^{-1} is comparable to $\Sigma\Delta H_f(5d) = 256.8\pm2.1$ kcal mol^{-1}; $\Sigma\Delta H_f(5b) = 294.9\pm2.9$ kcal mol^{-1} is significantly higher in energy because $E_i(SiCl_2) \gg E_i(Si)$. Hence, the preference of reaction (5c) suggests that $Si_2Cl_2{}^{\cdot+}$ corresponds to ionized dichlorodisilyne $\mathbf{8}^{\cdot+}$ rather than silylidene $\mathbf{9}^{\cdot+}$. Finally, the $SiCl^{+}$ fragment also governs the spectra of Si_2Cl^{+}, which can be attributed to a favorable thermochemistry, *i.e.*, $\Sigma\Delta H_f(6a) = 310.5\pm3.1$ kcal mol^{-1} versus $\Sigma\Delta H_f(6b) = 352$ kcal mol^{-1} and $\Sigma\Delta H_f(6c) = 343.1\pm5.3$ kcal mol^{-1}.


$\mathbf{8}^{\cdot+}$


$\mathbf{9}^{\cdot+}$

Thermokinetic aspects. Let us now analyze the data by using the assumption that the kinetic method can be applied to the metastable ion fragmentation of the $Si_2Cl_n{}^{+}$ species. In particular, the absence or presence of losses of chlorine atoms from the metastable $Si_2Cl_n{}^{+}$ ions are used to derive some estimates of the thermochemistry of the $Si_2Cl_{n-1}{}^{+}$ species formed.[10] The central assumption of the kinetic method is that the branching ratio for ion dissociation into two competing channels A and B is determined by the difference of the free energies ($\Delta\Delta G$) of the two routes according to the expressions $\Delta\Delta G(T_{eff}) = RT_{eff}\ln(I_A/I_B)$, where T_{eff} is an effective ion temperature and I_A and I_B are the relative intensities of the fragments.[14] By definition, the kinetic method can only provide relative energies, and anchoring to reference values is required when absolute quantities are to be derived. While there is an ongoing debate in the literature about the theoretical foundations of the kinetic method,[16—19] it has found several, quite valuable applications.[14] Unfortunately, however, the ambiguity of the thermochemical reference data for the $SiCl_n$ species (see above) as well as the possible formation of isomeric mixtures (see below) preclude a rigorous quantitative analysis of the present metastable ion data. Instead, a semi-quantitative approach is applied here, in which we use the source temperature of 473 K as an estimate of the effective temperature in ion dissociation, neglect corrections for mass discrimination and entropic effects,[10] and assign a general error margin of ±10 kcal mol^{-1} to all values. Thus, the absence (<0.1%) of $Si_2Cl_5{}^{+}$ upon dissociation of metastable $Si_2Cl_6{}^{\cdot+}$ implies $\Sigma\Delta H_f(1a) > 31$ kcal mol^{-1}, where we use the average of reactions (1b) and (1c) as reference, and accordingly derive a lower bound of $\Delta H_f(Si_2Cl_5{}^{+}) > 12$ kcal mol^{-1} for the cationic fragment. While unimolecular loss of atomic chlorine is indeed detected in the MI spectrum of $Si_2Cl_5{}^{+}$, yet another obstacle is encountered in applying the kinetic method to metastable ion dissociation. Thus, using the reference data given in Table 2, the competition of reactions (2b) and (2c) would require T_{eff} = 2700 K for metastable $Si_2Cl_5{}^{+}$, a value which is not unphysical but appears unreasonably large for a molecule of this size. Instead, the competition finds a rationale, if we assume that $Si_2Cl_5{}^{+}$ formed upon dissociative EI of hexachlorodisilane corresponds to a mixture of 3^+ and 4^+ of which the former undergoes reaction (2b) while the latter affords the energetically more favorable $SiCl^+$ fragment. Loss of Cl can, however, occur from either structure, and hence we arrive at $\Sigma\Delta H_f(2a) = 50$ or 60 kcal mol^{-1}, depending on the choice of the reference system, which leads to $\Delta H_f(Si_2Cl_4^{\cdot +}) = 26\pm15$ kcal mol^{-1}, where the increased error bar reflects the particular uncertainty in anchoring. Further, also note that the connectivity of the $Si_2Cl_4^{\cdot +}$ species formed in reaction (2a) is unknown. The absence of $Cl^{\cdot}$ loss from metastable $Si_2Cl_4^+$ implies $\Sigma\Delta H_f(3a) > 132$ kcal mol^{-1}, and hence $\Delta H_f(Si_2Cl_3^+) > 103$ kcal mol^{-1}. Likewise, the occurrence of $Cl^{\cdot}$ loss from metastable $Si_2Cl_3^+$ suggests $\Sigma\Delta H_f(4a) = 167$ kcal mol^{-1} or $\Delta H_f(Si_2Cl_2^{\cdot +}) = 138\pm10$ kcal mol^{-1}. Finally, the absence of reactions (5a) and (6a) yields lower bounds of $\Delta H_f(Si_2Cl^+) > 226$ kcal mol^{-1} and $\Delta H_f(Si_2^+) > 284$ kcal mol^{-1}; the latter bound is in keeping with the literature value of $\Delta H_f(Si_2^+) = 323$ kcal mol^{-1} (see Table 2).

Despite numerous uncertainties in the reference data as well as in the assignment of the ion structures, the experimental data can be used to provide a rough survey about the bond strengths of the $Si_2Cl_n^+$ species (Table 3). A qualitative confirmation for the suitability of this approach is that both the Si—Cl and Si—Si bond strengths of $Si_2Cl_3^+$ are particularly low, being consistent with the low abundance of this ion upon dissociative ionization of hexachlorodisilane. For a more elaborate evaluation, however, a re-examination of the thermochemistry of the $SiCl_n^{0/+}$ species as well as adequate computational studies of $Si_mCl_n^+$ species are indicated.[12] For example, combination of $\Delta H_f(Si_2Cl_4^{\cdot +}) = 26\pm15$ kcal mol^{-1} derived here with the computed $\Delta H_f(\mathbf{6}^{\cdot +}) = -102.8$ kcal mol^{-1} for the most stable neutral isomer[15] implies $E_i(Si_2Cl_4) = 5.6\pm0.7$ eV. This value is lower than that expected intuitively and thus may indicate that either $\Delta H_f(\mathbf{6}^{\cdot +})$ is too large or $\Delta H_f(Si_2Cl_4^{\cdot +})$ is too low. Some doubt on the computed value of the neutral silylidene is put forward by consideration of the hypothetical dechlorination reactions (7) and (8) to the corresponding silylidenes.

$$SiCl_4 \longrightarrow SiCl_2 + Cl_2 \quad (7)$$

$$Si_2Cl_6 \longrightarrow Cl_3SiSiCl + Cl_2 \quad (8)$$

Thus, compared to a value of $\Delta H_f(7) = 118$ kcal mol^{-1} for the formation of dichlorosilylidene from tetrachlorosilane, the data in Table 2 predict a larger endothermicity for the generation of the more substituted silylidene $\mathbf{6}^{\cdot +}$, *i.e.*, $\Delta H_f(8) = 131$ kcal mol^{-1}.

In addition to these energetic aspects, some of the ions examined here are worth reconsideration in more detailed experimental and theoretical studies, the putative silyne cation $Si_2Cl_2^{\cdot +}$ in particular.

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Table 3. Summarized estimates for the heats of formation (ΔH_f) of the $Si_2Cl_n^+$ cations and bond dissociation energies derived therefrom (E_d)[a]

Cation	ΔH_f	E_d(Si—Cl)[b]	E_d(Si—Si)[c]
	kcal mol^{-1}		
Si_2Cl^+	>226	<127	<86
$Si_2Cl_2^+$	138	>117	112
$Si_2Cl_3^+$	>103	<64	<61
$Si_2Cl_4^+$	26	>106	100
$Si_2Cl_5^+$	>12	<43	<48
$Si_2Cl_6^+$	6	>35	>16

[a] For error bars, see text.

[b] Losses of $Cl^{\cdot}$ to afford fragments with unknown structures.

[c] Given relative to the respective $SiCl_{n-m}^+/SiCl_m$ asymptotes of lowest energy demands.

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