boring molecules and will hence lower the coupling constants. The occurrence of temperature-dependent intermolecular bonding may account for the positive coefficients. Intermolecular bonding of this form has been observed to exist in $BiCl_3$.[10] In such a case a decrease of intermolecular bonding with increasing temperature compensates or overbalances the normal temperature effect. Such an effect is strongly suggested by the observed data for the dimethyl, dipropyl, and dibutyl compounds. The variation in the magnitude of the temperature coefficients where multiple crystalline sites occur indicates that some sites are more favorably situated for intermolecular bonding than others. The fact that only negative coefficients are observed for the phenyl compounds where large organic groups would tend to prevent close association of a tin atom and a chlorine atom from another molecule tends to substantiate this reasoning also. The crystal structures of the investigated compounds are not known, but these observed temperature effects indicate that the most probable location for a tin atom is in a distorted octahedral site, surrounded by its four singly bonded groups and one or more partial intermolecular bonds to chlorines in neighboring molecules. It is the lowering of the order of these latter bonds with increasing temperatures that would lead to an increase in the asymmetry at the chlorine sites and hence the observed increase in coupling constant with temperature.

From this work it can be concluded that there is both ionic and π character involved in addition to the σ character of the Sn–Cl bond. The occurrence of positive temperature coefficients indicates intermolecular bonding in the solid. While evidence to date tends to favor explaining the changes in the observed coupling constants as being due to changes in π bonding with substituent, the asymmetry parameter and principal axis system for the electric field gradient at the chlorine atoms must be determined in order to settle the issue.

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[10] H. G. Robinson, *Phys. Rev.*, **100**, 1731 (1955).

Mass Spectra of Silazanes

J. Silbiger,[1a] C. Lifshitz,[1b] J. Fuchs,[1a] and A. Mandelbaum[1c]

Contribution from the Department of Inorganic and Analytical Chemistry and the Department of Physical Chemistry, The Hebrew University, Jerusalem, Israel, and the Department of Chemistry, Israel Institute of Technology, Haifa, Israel.

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Abstract: The 70-v mass spectra of some silazanes and chloro- and methoxysilazanes are presented. The compounds studied include cyclic tri- and tetradimethylsilazanes and newly synthesized linear methoxy- and chlorodisilazanes. Expulsion of stable molecules, such as ammonia, methane, HCl (from the chlorosilazanes), and CH_2O (from the methoxy compound), has been observed. These fragmentations are usually accompanied by metastable transitions.

The information concerning mass spectra of silicon compounds is limited.[2-4] The only silazane which has been studied is hexamethyldisilazane.[5] As mass spectrometry is becoming increasingly important in the analytical determination of chemical compounds, we have studied the spectra of some silazanes: hexamethylcyclotrisilazane (I), octamethylcyclotetrasilazane (I), pentamethylmonochlorodisilazane (III), 1,3-dichlorotetramethyldisilazane (IV), 1,3-dimethoxytetramethyldisilazane (V), and 1,3-bis(dimethylchlorosilyl)-tetramethylcyclodisilazane (VI).

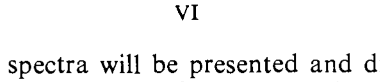
$[(CH_3)_2SiNH]_3$
I

$[(CH_3)_2SiNH]_4$
II

$(CH_3)_3SiNHSi(CH_3)_2Cl$
III

$Cl(CH_3)_2SiNHSi(CH_3)_2Cl$
IV

$CH_3O(CH_3)_2SiNHSi(CH_3)_2OCH_3$
V



$Cl(CH_3)_2SiN{-}Si(CH_3)_2{-}NSi(CH_3)_2Cl$, with $Si(CH_3)_2$ above bridging the two N atoms

VI

The mass spectra will be presented and discussed in terms of the structures of the respective molecules. We were able to assign plausible structures to the major peaks in each spectrum. The structures were in some cases verified by comparing the computed and observed relative abundance of isotopic species of the same fragment ion. The origin of certain fragment ions could be established unambiguously with the aid of metastable ions.

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[1] (a) Department of Inorganic and Analytical Chemistry, The Hebrew University; part of this work is taken from a Ph.D. thesis to be submitted to the Senate of the Hebrew University by J. F.; (b) Department of Physical Chemistry, The Hebrew University; (c) Israel Institute of Technology.

[2] G. G. Hess, F. W. Lampe, and L. S. Sommer, *J. Am. Chem. Soc.*, 87, 5327 (1965).

[3] B. G. Hobrock and R. W. Kiser, *J. Phys. Chem.*, **66**, 155 (1962).

[4] F. E. Saalfeld and H. J. Svec, *Inorg. Chem.*, **2**, 46 (1963).

[5] A. G. Sharkey, Jr., R. A. Friedel, and S. H. Langer, *Anal. Chem.*, **29**, 770 (1957).

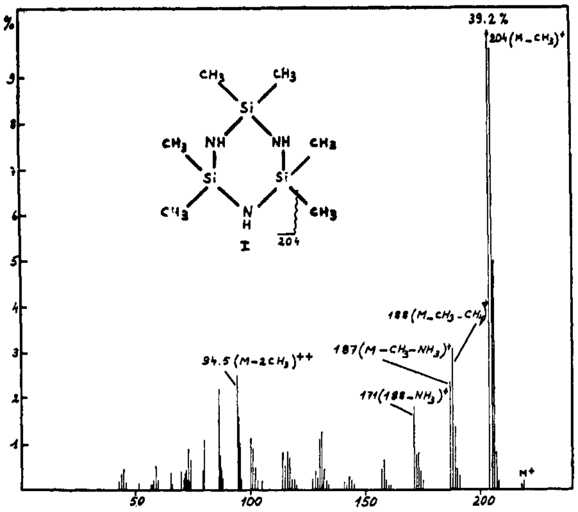

Figure 1. Mass spectrum of hexamethylcyclotrisilazane (I).

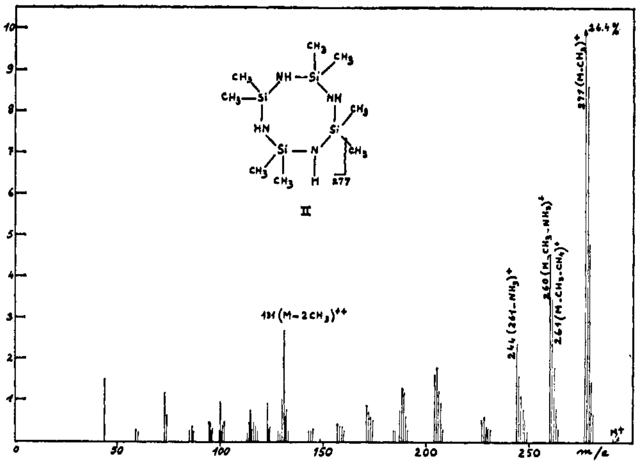

Figure 2. Mass spectrum of octamethylcyclotetrasilazane (II).

Experimental Section

Measurements were made with an Atlas CH4 8-in. radius of curvature, 60° sector-field mass spectrometer. A 3000-v ion accelerating voltage and magnetic scanning were used to obtain mass spectra. The AN4 ion source was operated at 70-v nominal electron energy and at 20- or 40-μa ionizing electron current. The temperature of the source was regulated at 250 ± 0.1°. Source and collector slit widths were externally adjustable; with narrow slits (0.03- and 0.07-mm source and collector, respectively) the resolution (1% adjacent peak-height contribution) was $M/\Delta M = 1900$. Wider slits (0.1 and 0.3 mm) were used at times (with a resolution of 600) to get more information about metastable ions. From our experience in working with metastable ions, using the Atlas CH4 mass spectrometer, this latter slit combination gives the correct metastable ion intensity without too much loss in resolution, so that most of the metastables can still be resolved from the normal ions in the spectrum. The pressure dependence of the metastable ions was not determined. However, the operating conditions under which the spectra were taken were normal, *i.e.*, the analyzer tube pressures were lower than 5×10^{-7} mm.

The samples were introduced into the ion source through the all-metal, molecular flow, inlet system of the mass spectrometer, which was kept at room temperature.

Ion current measurements were made by means of a secondary electron multiplier and recording potentiometer or photographed with the Honeywell Visicorder. The gain of the electron multiplier, as a function of mass, was determined and found to be lowered by not more than a factor of 1.5 from *m/e* 50 to 350.

Compounds I and II were prepared by treating dimethyldichlorosilane with ammonia.[6]

The methods used for the preparation of compounds III–VI have recently been described.[7,8] Pentamethylmonochlorodisilazane (III) contained trimethylchlorosilane as a minor impurity. Its contribution to the mass spectrum was small and only at low *m/e* values.

Results and Discussion

Hexamethylcyclotrisilazane (I) (Figure 1) and Octamethylcyclotetrasilazane (II) (Figure 2). The intensity of the parent-ion peak in both spectra is minor, the base peak being in each case due to M – 15. We ascribe this to the loss of a methyl group, by analogy with the spectrum of hexamethyldisilazane.[5] There is good agreement between the computed and observed relative intensities of isotopic peaks in both spectra, *i.e.*, the relative intensities of *m/e* 204, 205, and 206 in I and of *m/e* 277, 278, and 279 (in II) given in Table I. This is further proof that the ion contains three silicon atoms in compound I and four in compound II. Similar calculations were not carried out for lower mass ions since a number of alternative fragmentation routes can lead to the same ion, thus making any calculation of isotopic abundances rather ambiguous. For example, the ion at *m/e* 189 in compound I can be due to isotopic silicon contributions from *m/e* 187 as well as 188, and also to a methyl elimination from *m/e* 204.

Table I. Computed and Observed Relative Abundances of Isotopic Ions of the Composition M – CH_3

	Relative abundance			Relative abundance	
m/e	Computed	Obsd	*m/e*	Computed	Obsd
	Compound I			Compound II	
204	1	1	277	1	1
205	0.220	0.237	278	0.297	0.33
206	0.117	0.128	279	0.171	0.187
	Compound III			Compound IV	
166	1	1	186	1	1
167	0.150	0.173	187	0.139	0.135
168	0.400	0.404	188	0.725	0.700
			189		0.01
			190	0.155	0.165

Table II. Metastable Transitions Observed in Silazanes

Compound	Transition	Computed apparent mass $m^* = m_2^2/m_1$	Approx obsd mass[a]	Approx rel intensity[b]
Hexamethyldisilazane	$146^+ \rightarrow 130^+ + 16$	115.8	116	...
I	$204^+ \rightarrow 187^+ + 17$	171.4	171.5	0.5
	$188^+ \rightarrow 171^+ + 17$	155.5	155.5	0.2
II	$277^+ \rightarrow 260^+ + 17$	244.0	244	0.5
	$261^+ \rightarrow 244^+ + 17$	228.1	228	0.1
III	$166^+ \rightarrow 130^+ + 36$	101.8	102	0.5
IV	$186^+ \rightarrow 150^+ + 36$	121.0	121	0.5
	$166^+ \rightarrow 130^+ + 36$	101.8	102	0.2
V	$178^+ \rightarrow 162^+ + 16$	147.4	147.5	0.2
	$178^+ \rightarrow 148^+ + 30$	123.1	123	1.0
	$148^+ \rightarrow 118^+ + 30$	94.1	94	0.5
	$162^+ \rightarrow 132^+ + 30$	107.6	107.5	0.1
	$132^+ \rightarrow 102^+ + 30$	78.8	79	0.05

[a] Maximum intensity. [b] Per cent of total ionization.

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(6) S. D. Brewer and C. P. Haber, *J. Am. Chem. Soc.*, **70**, 3888 (1948).

(7) J. Silbiger and J. Fuchs, *Inorg. Chem.*, **4**, 1371 (1965).

(8) J. Silbiger, J. Fuchs, and N. Gesundheit, *ibid.*, **6**, 399 (1967).

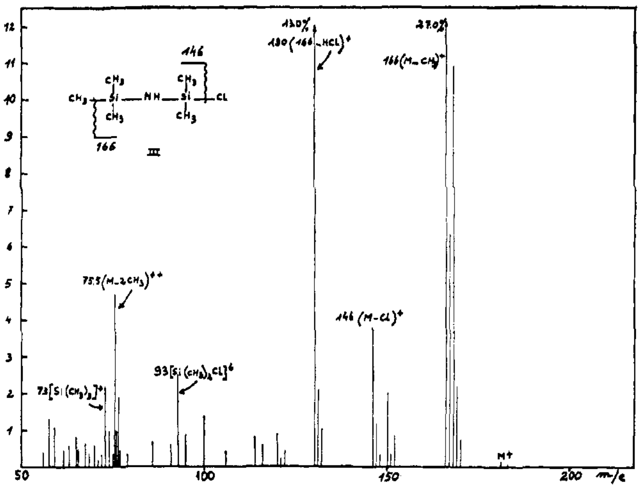


Figure 3. Mass spectrum of pentamethylchlorodisilazane (III).

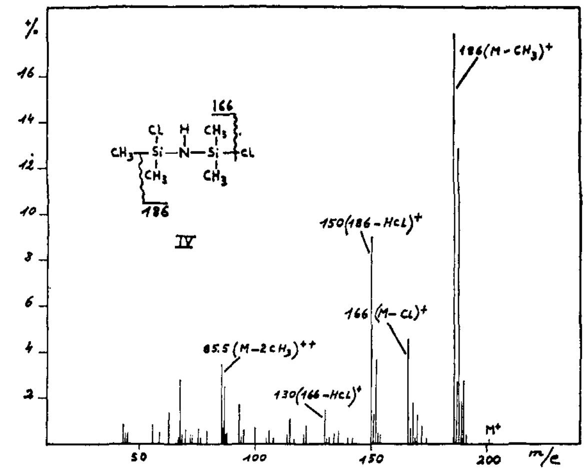
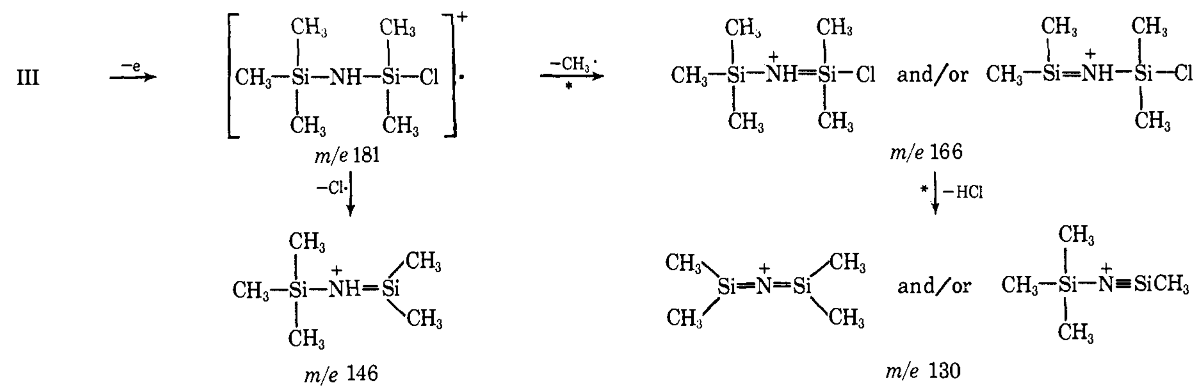


Figure 4. Mass spectrum of 1,3-dichlorotetramethyldisilazane (IV).

Intense peaks have been observed in both spectra for ions corresponding to the loss of 16 and 17 mass units from the M − 15 ion. A similar loss of 16 mass units from the M − 15 ion occurs in hexamethyldisilazane.[5] Metastable peaks for these fragmentations have been detected (Table II). They are very broad, due to the presence of isotopic species, and for this reason could not be well resolved. However, the maximum of the observed metastable peaks multiplet corresponded in both I and II to the computed *m/e* value corresponding to the loss of 17 mass units.

Scheme I



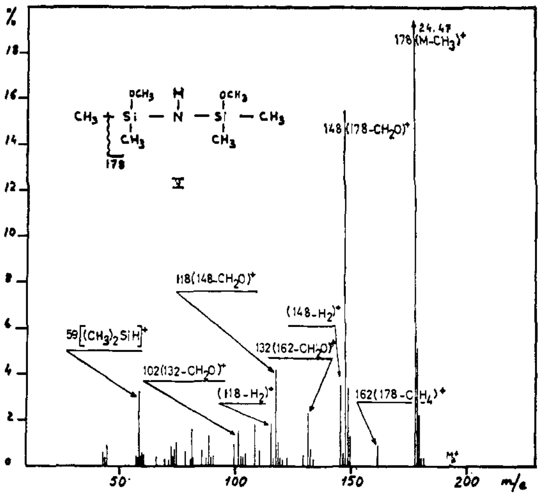


Figure 5. Mass spectrum of 1,3-dimethoxytetramethyldisilazane (V).

The loss of 16 mass units could be due to the loss of either methane or NH_2 and is most probably due to the loss of methane by analogy with hexamethyldisilazane.[5] The loss of 17 mass units can, however, be unambiguously assigned to the loss of ammonia, since no other combination of atoms giving 17 mass units is conceivable. This in both I and II would require a very elaborate rearrangement prior to decomposition. Similar expulsion reactions have recently been observed in other molecules.[9]

An alternative explanation for the ions at *m/e* 188 and 261 (in compounds I and II, respectively) can be given in terms of the SiH_3 loss from the parent ion. This, however, seems unlikely, since the parent ions, which are of very low intensity in both spectra, are probably too short-lived to allow such elaborate rearrangements to take place.

The loss of 16 mass units from M − 15 is followed in both I and II by a loss of 17 mass units (NH_3) (from *m/e* 188 to 171 in I and from *m/e* 261 to 244 in II), and the corresponding metastable transitions have been observed (see Table II).

The most intense doubly charged ion in both spectra is due to the loss of two methyl radicals from the molecular ion, in analogy to the behavior of other silicon compounds containing more than one silicon

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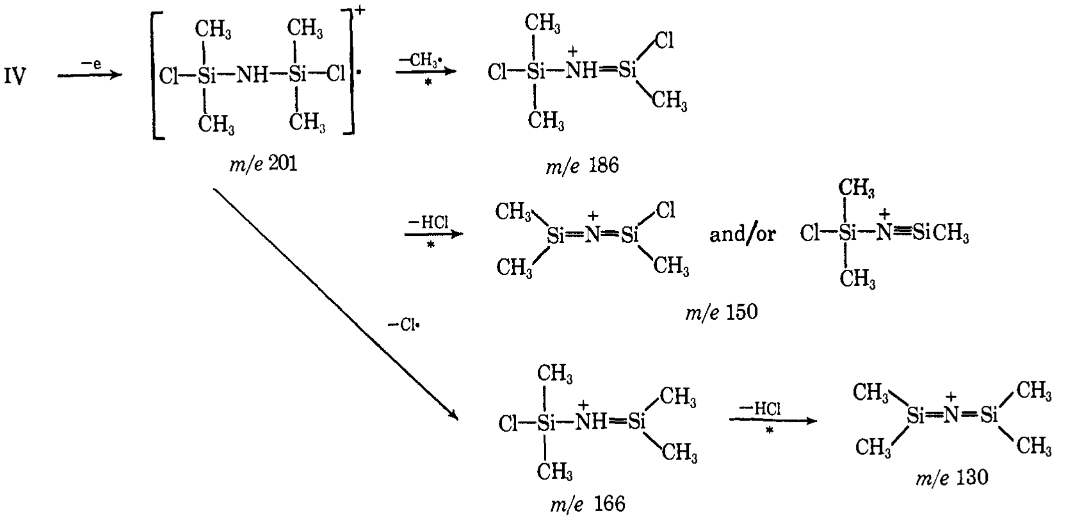
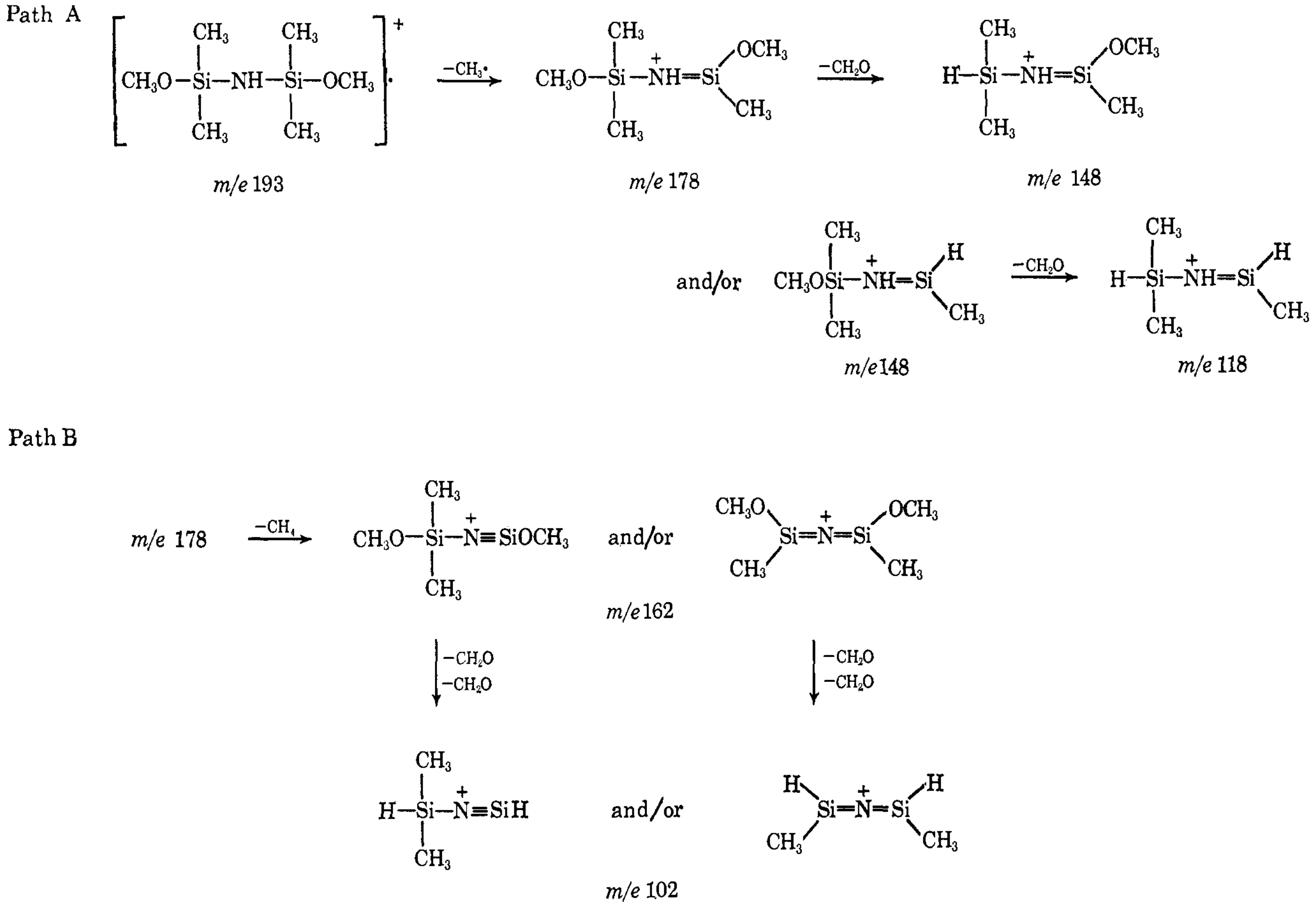
[9] R. G. Gillis and J. L. Occolowitz, *Tetrahedron Letters*, 1997 (1966).

Scheme II



Scheme III



atom.[5,10] In I this peak appears at *m/e* 94.5, $[(CH_3)_4Si_3(NH)_3]^{2+}$, and in II at *m/e* 131, $[(CH_3)_6Si_4(NH)_4]^{2+}$ (based on ^{28}Si).

The spectra of these compounds are somewhat similar to those of the cyclic silicon–methylene compounds studied previously.[11]

Pentamethylmonochlorodisilazane (III) (Figure 3) and 1,3-Dichlorotetramethyldisilazane (IV) (Figure 4). The intensity of the parent ion in both spectra is again very low. The two major primary reactions of the parent ion are loss of a methyl group and loss of a chlorine atom. The loss of methyl radical from the parent ion is followed in both compounds by the loss of HCl. The corresponding metastable peaks have been observed (Table II). The fragmentation pattern in Scheme I is suggested for III.

In compound IV the chlorine atom loss is followed by the loss of HCl, since this compound contains two chlorine atoms. This fragmentation is also accompanied by a metastable transition (Table II). The fragmentation pattern in Scheme II is suggested for IV.

The most intense doubly charged ions in both spectra

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(10) V. H. Diebeler, F. L. Mohler, and R. M. Reese, *J. Chem. Phys.*, 21, 180 (1953).

(11) G. Fritz, H. Buhl, J. Grobe, F. Aulinger, and W. Reering, *Z. Anorg. Allgem. Chem.*, 312, 201 (1961).

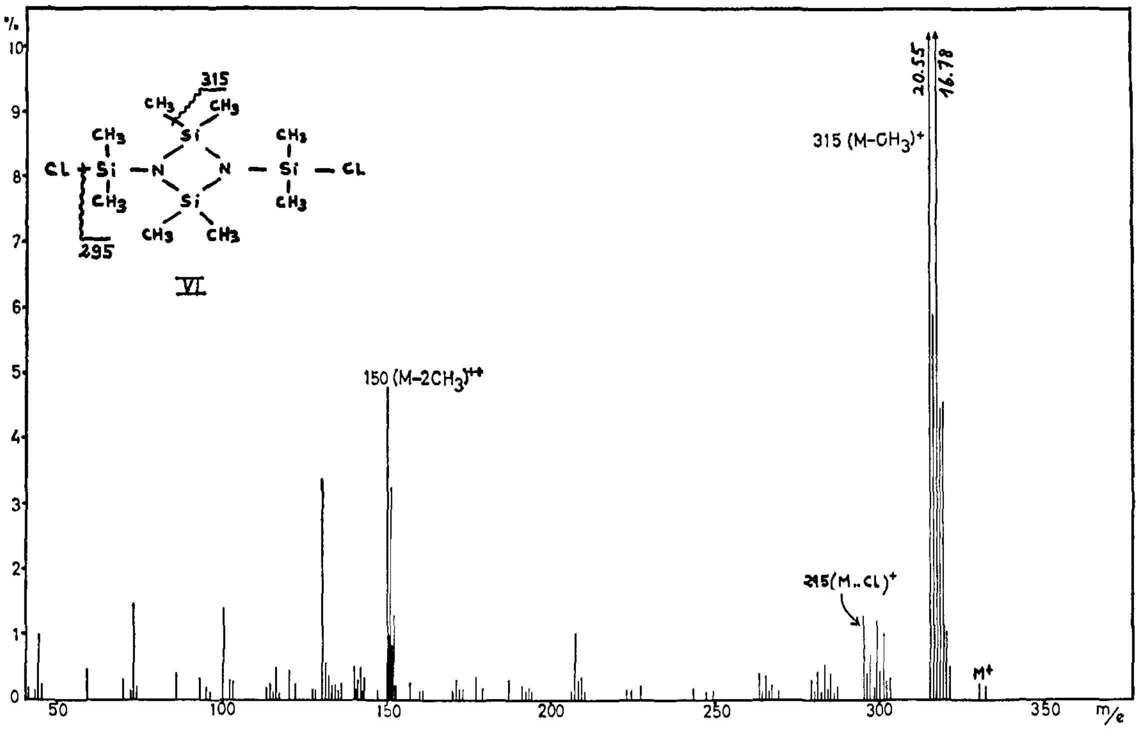

Figure 6. Mass spectrum of 1,3-bis(dimethylchlorosilyl)tetramethylcyclodisilazane (VI).

are again due to the loss of two methyl groups. This accounts for the peaks at *m/e* 75.5 in III and at *m/e* 85.5 in IV (with their isotopes). The impurity $Si(CH_3)_3Cl$ (see Experimental Section) contributes to the spectrum of compound III mainly at *m/e* 93.

1,3-Dimethoxytetramethyldisilazane (V) (Figure 5). The parent ion (*m/e* 193) is again of very low abundance. An intense *m/e* 178 peak is due to the loss of CH_3 from the parent ion. This is followed by the loss of two formaldehyde molecules, giving rise to *m/e* 148 and 118 ions. An alternative, less important decomposition path for M − CH_3 is the loss of 16 mass units (probably methane by analogy to hexamethyldisilazane). The ion thus formed (*m/e* 162) loses consecutively two formaldehyde molecules, giving rise to *m/e* 132 and 102 ions. All the fragmentations are supported by the corresponding metastable peaks (Table II). The ion at *m/e* 162 could be partly due to a direct transition from the parent due to a loss of OCH_3. However, this forms a minor contribution only. The two major reaction paths are therefore A and B in Scheme III.

The loss of formaldehyde to give a rearranged ion in which the hydrogen atom is probably bound to the silicon atom was also found in the case of $(CH_3)_3SiOCH_3$.[5] The rearrangement ion $(CH_3)_2SiH^+$ (at *m/e* 59) formed in that case is also abundant in the spectrum of compound V (see Figure 5).

Other major peaks present in the spectrum of compound V are at *m/e* 146 and 116. These two might be formed from *m/e* 148 and 118 (see sequence A), respectively, by the loss of H_2. Apparently, since the rearrangement ions *m/e* 148 and 118 have hydrogen atoms bound to the silicon atom as well as to the nitrogen atom, loss of H_2 becomes a likely reaction path.

The most intense doubly charged *m/e* 81.5 ion is due to the loss of two CH_3 groups from the parent ion. Another doubly charged ion is at *m/e* 73.5 and may be due to the loss of CH_3 and OCH_3 from the parent ion. A third doubly charged *m/e* 65.5 ion is most probably $(M - 2OCH_3)^{2+}$.

1,3-Bis(dimethylchlorosilyl)tetramethyldisilazane (VI) (Figure 6). The most intense peak is again due to M − 15, *i.e.*, to loss of a methyl group from the parent ion. The next intense peak is due to the doubly charged ion $(M - 2CH_3)^{2+}$ at *m/e* 150. The *m/e* 295 ion is formed by the loss of chlorine atom from the parent ion. No significant CH_4 or HCl eliminations were detected in this case. This can be explained by the absence of hydrogen atoms from the silicon and nitrogen atoms, thus making β eliminations impossible.