tion is warmed to room temperature, the quartet decays and a broad singlet grows in at 1780 ppm from tetramethylstannane. The low-temperature quartet corresponds to SnH_3^+; the singlet is presumably its decomposition product.

The relatively high-field chemical shift observed for SnH_3^+, although not expected from diamagnetic shielding considerations, is nevertheless consistent with the data of Burke and Lauterbur,[7] who generally observed higher field resonances for species expected to have more positively charged tin atoms. We believe that the magnitude of the tin–hydrogen coupling constant is entirely reasonable for a planar SnH_3^+ ion with a fairly high positive charge on the tin atom. Various investigators have shown that coupling constants to tin in neutral species are proportional to the s character of the tin orbital involved in the bond.[8-10] However Grant and Litchman have pointed out that one cannot ignore the fact that the coupling constant is also proportional to the third power of the effective nuclear charge.[11] For stannane (sp^3 hybridization), $J_{119Sn-H}$ is 1933 Hz.[12]

(7) J. J. Burke and P. C. Lauterbur, *J. Amer. Chem. Soc.*, **83**, 326 (1961).
(8) N. Flitcroft and H. D. Kaesz, *ibid.*, **85**, 1377 (1963).
(9) J. R. Holmes and H. D. Kaesz, *ibid.*, **83**, 3904 (1961).
(10) N. A. Matwiyoff and R. S. Drago, *Inorg. Chem.*, **3**, 337 (1964).
(11) D. M. Grant and W. M. Litchman, *J. Amer. Chem. Soc.*, **87**, 3994 (1965).
(12) P. E. Potter, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 524 (1964).

For SnH_3^+ (sp^2 hybridization) we calculate $J_{119Sn-H}$ = 2570 Hz on the assumption that the coupling constant is only influenced by the s character of the tin orbital. The fact that the observed value of $J_{119Sn-H}$ for SnH_3^+ (2960 Hz) is considerably larger is consistent with a relatively high positive charge on the tin atom.

When fluorosulfuric acid is treated with stannane at $-78°$, the resulting solution is more highly conducting than the pure solvent. Barr, Gillespie, and Thompson demonstrated that electrical conductivity in most HSO_3F solutions is almost entirely due to the SO_3F^- ion.[13] Thus the conductivity of a potassium sulfate solution is due to the formation of 2 mol of SO_3F^- per mole of potassium sulfate:[13] $K_2SO_4 + 2HSO_3F \rightarrow 2K^+ + 2SO_3F^- + H_2SO_4.$ We measured the conductances in fluorosulfuric acid at $-78°$ of potassium sulfate and of the stannonium product in the concentration range 0.075–0.250 m. The molal conductances of the potassium sulfate and the stannonium product were in the ratio of 1.94:1, as expected for the formation of 1 mol of SO_3F^- ion per mole of stannane (see reaction 3).

(13) J. Barr, R. J. Gillespie, and R. C. Thompson, *Inorg. Chem.*, **3**, 1149 (1964).

The Synthesis and Characterization of the Halostannanes

BY JOHN R. WEBSTER, MERLE M. MILLARD, AND WILLIAM L. JOLLY*

Stannane, SnH_4, reacts with HCl, HBr, and HI at $-112°$ to give the monohalostannanes and hydrogen. The monohalostannanes are colorless, volatile compounds that decompose as solids above about $-40°$. They have been characterized by the study of their decomposition reactions (which afforded chemical analyses), by mass spectrometry, by infrared spectrometry, and by Raman spectrometry. The Raman spectra of the solids suggest structures involving relatively independent SnH_3^+ cations.

Introduction

There have been many studies of the monohalogen derivatives of silane and germane,[1,2] whereas there has been but a single brief report concerning a monohalostannane, *i.e.*, chlorostannane.[3] Indeed, very little of the inorganic chemistry of stannane has been investigated. This fact is somewhat surprising in view of the importance of the tin–hydrogen bond, *e.g.*, in organic reductions.[4] Although a considerable understanding of the tin–hydrogen bond has come from studies of organostannanes, R_nSnH_{4-n}, we decided to study reactions of unsubstituted stannane, SnH_4, to avoid any possible complications by the organic substituents and

to provide data for comparison with the analogous reactions of unsubstituted silane and germane.

Experimental Section

Stannane was prepared by a published method.[5] The hydrogen halides (Matheson Co.) were purified by distillation at low pressure through a $-112°$ trap. The purity of starting materials was typically checked by mass spectral analysis and/or vapor pressure measurements. Ideal gas behavior was assumed for vapors and gases when making stoichiometric calculations from PVT data.

Halostannane Preparation.—The halostannanes were synthesized in a small (*ca.* 10 cm^3) Pyrex tube equipped with a side arm containing a break-seal through which products could be pumped into the vacuum line. Stannane and hydrogen halide were condensed into the reaction tube at $-196°$. The tube was sealed by glassblowing and was completely submerged in a cold bath for 11.5 hr, during which time the bath slowly warmed from -112 to $-75°$. The reaction mixture was then quenched to $-196°$; the tube was opened, and the hydrogen was Toepler-

(1) A. G. MacDiarmid, *Prep. Inorg. React.*, **1**, 165 (1964).
(2) C. H. Van Dyke, *ibid.*, in press.
(3) E. Amberger, *Angew. Chem.*, **72**, 78 (1960).
(4) For references to the original literature see F. G. A. Stone, "Hydrogen Compounds of the Group IV Elements," Prentice-Hall, Englewood Cliffs, N. J., 1962, pp 85–89.

(5) A. D. Norman, J. R. Webster, and W. L. Jolly, *Inorg. Syn.*, **11**, 171 (1968).

J. R. WEBSTER, M. M. MILLARD, AND W. L. JOLLY

TABLE I

SYNTHETIC AND ANALYTICAL DATA FOR THE HALOSTANNANES

Amt of reactant, mmol		Reaction time, hr	H₂ evolved, mmol	SnH₃X isolated by distilln, mmol	Amt of decompn products, µmol				Empirical formula, Sn:H:X
SnH₄	HX				H₂	SnH₄	SnX₂	HX	
For SnH₃Cl									
0.50	0.50	12	...	0.036	4	23	13[a]	10	1.00:3.05:1.00
1.48	1.64	5	...	0.186	15	118	68[a]	53	1.00:2.98:1.02
0.93	1.98	10	0.97	0.373	32	237	136[a]	104	1.00:2.99:1.01
For SnH₃Br									
1.04	2.05	9	1.05	0.262	147	127	135[b]	None	1.00:3.06:1.03
...	...	2	...	0.098	50	47	50[a]	None	1.00:2.98:1.03
1.02	Excess	9	1.02	0.335	171	165	170[a]	None	1.00:2.99:1.01
For SnH₃I									
...	...		...	0.065	32	33	32[a]	None	1.00:3.01:0.99
0.85	1.07	6	0.70	0.118	59	60	58[b]	None	1.00:3.02:0.99
0.93	1.68	11	0.95	0.106	53	54	52[a]	None	1.00:3.02:0.98

[a] Based on Sn analysis. [b] Based on halide analysis.

pumped out and measured. An empty dewar flask which had been prechilled to −196° was placed around the reaction tube, and, while the system warmed slowly to room temperature (ca. 1.5 hr), the remaining volatile products were pumped out of the reaction tube through −112 and −196° traps. Considerable decomposition of the halostannane occurred during this distillation, as shown by solid residues in the reaction tube and by the evolution of hydrogen. The halostannane collected in the −112° trap.

Halostannane Analysis.—The halostannanes were analyzed by determining the decomposition products that formed when they were warmed to room temperature, i.e., SnH₄, H₂, SnX₂, and, in the case of chlorostannane, HCl. A halostannane to be analyzed was transferred to a U trap equipped with a stopcock on each arm. The stopcocks were closed, and the trap was warmed to and kept at room temperature for 20 min, during which time a solid residue formed on the walls of the trap. The trap was then cooled to −196° and opened, and hydrogen was removed. The stannane was taken off while warming to room temperature.[6] Both compounds were identified by mass spectrometry, and stannane was further characterized by a vapor pressure measurement at −112° (found 17.4 Torr; lit.[7] 17.5 Torr). The solid residue in the U trap was dissolved in slightly acidic air-free water and analyzed for total tin content by standard iodimetric methods.[8] The halide content of the residue was assumed to be twice the tin content except in two runs in which halide was determined by the Volhard method and in which the tin content was assumed to be half the halide content.

Mass Spectrometry.—The mass spectra were obtained using a Granville-Phillips Spectrascan 750 residual gas analyzer with an EAI Quad 250 electronics console. This spectrometer has an m/e range from 1 to 500. Samples of the halostannanes were pumped from the reaction tube directly into the ionization chamber of the mass spectrometer. The best results were obtained when samples were held at ca. −45°; however spectra were recorded of samples at temperatures as high as 0°. Above 0° we were unable to see evidence of halostannanes, presumably because the compounds decomposed too rapidly. Operating pressures were 10⁻⁷–10⁻⁶ Torr, and the energy of the ionizing electrons was 30 eV.

Raman Spectra.—The Raman spectrometer consisted of a Spectra-Physics Model 125 50-mW helium–neon laser operating at 6328 Å, a Spex Industries Model 1400 double monochromator, and an ITT FW-130 photomultiplier tube maintained at −10° by thermoelectric cooling. The electronics of the detector and readout systems has been described previously.[9] Approxi-

mately 0.5-mmol samples of the halostannanes were prepared in 3-mm o.d. glass tubes using essentially the same technique described above. After removal of the evolved hydrogen and the excess hydrogen halide, the capillaries were sealed off by glass-blowing and placed in the spectrometer. The samples were maintained as finely divided solids between −80 and −100° by a stream of cold nitrogen gas, using a device specially designed to avoid frost formation.[10]

Infrared Spectra.—The instability of the halostannanes presented difficulties in obtaining infrared spectra of the compounds. Simple static gas-phase spectra could not be obtained because the samples decomposed during the measurements. The vapor-phase infrared spectrum of SnH₃Cl was obtained while distilling the material at a low pressure through a Beckman 10-m variable path length gas absorption cell. Spectra in the 200–500-cm⁻¹ region were recorded with a Beckman IR-12 spectrometer using polyethylene windows and a 4.6-m path length. Spectra in the 650–2000-cm⁻¹ region were recorded with a Beckman IR-7 spectrometer using NaCl windows and an 8.2-m path length.

Results and Discussion

General Considerations and Physical Properties.—The halostannanes are colorless, volatile, highly unstable compounds. Although they show signs of decomposition at −40°, they can be distilled short distances in a vacuum line with no more than about 10% decomposition. A sample to be distilled is slowly warmed from −196° to room temperature while continuously pumping through a −112° trap. The halostannane condenses in the −112° trap, and a residue of tin(II) halide is left in the original container. When transfer is attempted without efficient pumping, decomposition is generally much greater.

A Stock melting point apparatus[11] was modified so that the halostannanes could be distilled into it as described above. Melting point determinations were attempted, but in each case the halostannane decomposed before or during melting, leaving a ring of tin(II) halide to support the plunger.

Amberger[3] reported an equation for the vapor pressure of chlorostannane for the range −100 to −50° from which one calculates a vapor pressure of 10 Torr at −50°. In several experiments we found chlorostannane to have no appreciable vapor pressure at that temperature, although pressures as low as 1 Torr would have been easily detected. Attempts to measure vapor pressures of each of the halostannanes resulted

(6) In the case of chlorostannane, a mixture of stannane and hydrogen chloride was removed at this point. This mixture was allowed to stand several hours at room temperature so that the stannane could decompose completely to tin and hydrogen. The hydrogen and hydrogen chloride were separated, and the amount of stannane was calculated from the amount of hydrogen. Mass spectrometry was used to verify that all the stannane had decomposed.

(7) S. R. Gunn and L. G. Green, *J. Phys. Chem.*, **65**, 779 (1961).

(8) A. I. Vogel, "Quantitative Inorganic Analysis," 3rd ed, Wiley, New York, N. Y., 1961, p 367. Procedure B was used for our analyses.

(9) H. S. Gabelnick and H. L. Strauss, *J. Chem. Phys.*, **49**, 2334 (1968).

(10) R. D. Burbank and F. N. Bensey, *ibid.*, **21**, 602 (1953).

(11) A. Stock, "Hydrides of Boron and Silicon," Cornell University Press, Ithaca, N. Y., 1933, p 183.

in decomposition (around −40°) before a vapor pressure could be detected with a mercury manometer. Gas pressures were observed, but in each case these could be attributed to decomposition products.

The Preparation and Analysis of the Halostannes.—The halostannanes were synthesized in small vessels so that some of each reactant would be in the liquid phase. We found that a mixture of stannane and hydrogen chloride did *not* react when allowed to stand 24 hr at −78° in the gas phase.

The synthetic and analytical data are summarized in Table I. In the runs for which the hydrogen evolved was measured, it can be seen that the amount of this hydrogen was essentially equal to that of the stannane charged (except for one SnH_3I run, which may have had too short a reaction time). This result indicates that stannane reacts completely with the hydrogen halides to yield only the *mono*halogenated stannanes. The analytical data confirm this conclusion, as shown clearly by the empirical $Sn:H:X$ ratios. In separate experiments with reaction times of 9 hr or more, it was shown that the stannane was completely consumed. Hydrogen halide was found as a decomposition product only in the case of chlorostannane. The tin(IV) halides and tin metal were never found.

Raman Spectra.—The Raman spectra of the solid halostannanes are very simple; the frequencies and intensities of the observed lines are given in Table II.

TABLE II
RAMAN LINES OBSERVED FOR SnH_3Cl, SnH_3Br, AND SnH_3I (CM^{-1})

SnH_3Cl	SnH_3Br	SnH_3I
1880 s	1880 s	1880 s
733 w	733 w	
38 s	54 s	49 s

It is significant that no lines were observed in the regions characteristic of the tin–halogen stretches. (Tin–halogen stretching frequencies generally occur in the regions 300–400 cm⁻¹ for chlorine, 220–250 cm⁻¹ for bromine, and 150–200 cm⁻¹ for iodine.[12]) We interpret the absence of such lines as evidence for structures containing relatively independent SnH_3^+ ions. Probably these cations are planar and are linked into chains by bridging halide ions which make the tin essentially five-coordinate. Many examples of such polymeric structures, involving triorganotin cations, are known.[13] Presumably the strong line at 1880 cm⁻¹ is due to the symmetric Sn–H stretch. The weak line at 733 cm⁻¹ (presumably too weak to be observed in the case of SnH_3I) may be due to the antisymmetric Sn–H stretch or the in-plane bending vibration. The strong line observed below 60 cm⁻¹ is probably due to a lattice vibrational mode.

The infrared spectrum of chlorostannane vapor was obtained for the frequency ranges 200–500 and 650–2000 cm⁻¹. The only features observed (besides those due to stannane impurity) were bands at 383, 370 (sh), 692, and 1927 cm⁻¹. We believe that these bands can be interpreted in terms of SnH_3Cl molecules of C_{3v} symmetry. The pair of bands near 380 cm⁻¹ probably correspond to the P and R branches of the symmetric Sn–Cl vibration band. This frequency lies in the re-

gion characteristic of Sn–Cl vibrations,[12] and the band contour is similar to that observed for the analogous germyl halides.[14] The bands at 692 and 1927 cm⁻¹ probably correspond to tin–hydrogen deformation and stretching, respectively.

Mass Spectra.—Tin has ten isotopes with abundances greater than 0.35%, and both bromine and chlorine have two isotopes with appreciable abundances. Thus the mass spectra of the halostannanes consisted of clusters of closely grouped peaks. In each spectrum the most intense feature was the envelope of peaks with m/e values from 112 to 127, corresponding to SnH_n^+ ($n = 0$–3). The relative intensities of the peaks within this envelope did not differ significantly from those in the same envelope in the spectrum of pure stannane. Indeed, because stannane is known to be a decomposition product of the halostannanes, the envelope may have been largely due to decomposition of the samples *before* entering the ionization chamber. No peak was observed at m/e 128 ($^{124}SnH_4^+$) in the spectra of stannane or the halostannanes.

The second most intense feature in the spectra (usually 10–20% as intense as the SnH_n^+ envelope) was the envelope corresponding to ions SnH_nX^+ ($n = 0$–3; $X = Cl$, Br, I). This envelope appeared at m/e 239–254 for SnH_3I, at m/e 191–208 for SnH_3Br, and at m/e 147–163 for SnH_3Cl. In the latter case, the parent ion $^{124}SnH_3^{37}Cl^+$ at m/e 164 was not observed, although parent ions were seen in the other two cases. We assume that these envelopes are entirely due to the ions SnX^+, $SnHX^+$, SnH_2X^+, and SnH_3X^+. If we also assume that there are no isotope effects on fragmentation, the relative intensities of the peaks in any one of these envelopes can, in principle, be calculated from the relative intensities of any four peaks in the envelope by the solution of four simultaneous equations.[15] By using the data for four intense peaks from each envelope, we calculated the relative intensities of the remaining peaks. The calculated and observed mass spectral envelopes are shown as histograms in Figures 1–3. The
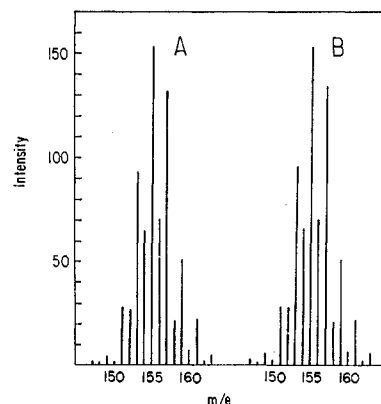

Figure 1.—Mass spectral band for the species SnH_nCl ($n = 0$–3): A, calculated from the intensities of the peaks at m/e 154, 155, 156, and 157; B, observed.

good agreement is evidence for the correctness of the assignments.

As the energy of the ionizing electrons was increased

(12) D. M. Adams, "Metal-Ligand and Related Vibrations," E. Arnold, Ltd., London, 1967.

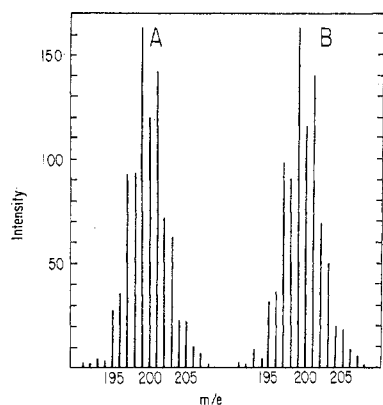(13) B. J. Aylett, *Progr. Stereochem.*, **4**, 213 (1969).

(14) D. E. Freeman, K. H. Rhee, and M. K. Wilson, *J. Chem. Phys.*, **34**, 2908 (1963).

(15) R. W. Kiser, "Introduction to Mass Spectrometry and Its Applications," Prentice-Hall, Englewood Cliffs, N. J., 1965, p 218.

Figure 2.—Mass spectral band for the species SnH_nBr (n = 0-3): A, calculated from the intensities of the peaks at m/e 197, 199, 200, and 201; B, observed.
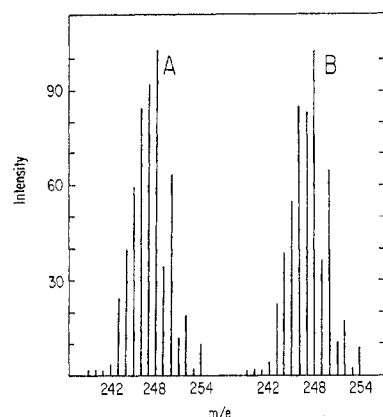

Figure 3.—Mass spectral band for the species SnH_nI (n = 0-3): A, calculated from the intensities of the peaks at m/e 251, 252, 253, and 254; B, observed.
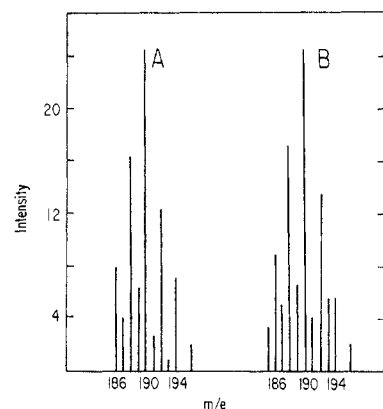

Figure 4.—Mass spectral band for the species SnH_nCl_2 (n = 0-2): A, calculated from the intensities of the peaks at m/e 188, 190, 192; B, observed.

to a maximum of 60 eV, peaks appeared at one-half and one-third the m/e values of the SnH_nX^+ ions. These peaks corresponded to the ions SnH_nX^{2+} and SnH_nX^{3+} and were about 10% as intense as those of the singly charged ions.

It is interesting that a very weak envelope from m/e 186–196 appeared in the spectrum of chlorostannane as the sample was warmed above $-40°$. The envelope became weaker above $-30°$ and disappeared entirely at $0°$. Presumably the species which caused this

envelope decomposed too quickly above $0°$ to be seen in the mass spectrum. The position and size of this envelope and the relative intensities of its peaks indicate that it was due to $SnH_nCl_2^+$ (n = 0-2) from SnH_2Cl_2. In Figure 4 calculated and observed spectra for SnH_2Cl_2 are presented. Envelopes corresponding to ions from SnH_2Br_2 and SnH_2I_2 did not appear when similar experiments were performed with bromo- and iodostannane.

Decomposition of the Halostannanes.—Bromo- and iodostannane (and, to a certain extent, chlorostannane) decompose to stannane, hydrogen, and the corresponding tin(II) halides according to

$$2SnH_3X \longrightarrow SnH_4 + SnX_2 + H_2 \qquad (1)$$
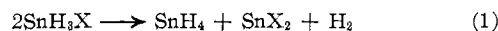
This reaction is complete in 20 min at room temperature and may be explained by the general mechanism

$$2SnH_3X \longrightarrow SnH_4 + SnH_2X_2 \qquad (2)$$

$$SnH_2X_2 \longrightarrow SnX_2 + H_2 \qquad (3)$$
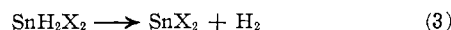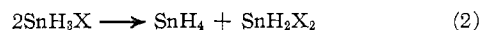
Reaction 2 is an example of a general ligand redistribution reaction which has been observed to proceed (albeit slowly at room temperature) in the case of the monohalosilanes[16,17] and monofluorogermane.[18] The relative rapidity of the SnH_3X redistribution reactions can be explained in terms of the larger size of the tin atom and its greater ability to increase its coordination number beyond 4. The appearance of ions due to dichlorostannane in the mass spectrum of chlorostannane is further support for the occurrence of reaction 2. Dibromo- and diiodostannane probably also form during the decomposition of SnH_3Br and SnH_3I, but probably the dihalo compounds were not seen in the mass spectra because of their lower volatilities at the temperatures where they formed as intermediates.[19–21] Assuming that the volatilities of the dihalogen derivatives of stannane and germane correlate with molecular weights, we would expect SnH_2I_2 to be nonvolatile and SnH_2Br_2 to be at most of marginal volatility, at room temperature.

The driving force of reaction 3 is expected to be appreciable owing to the high bond energy of molecular hydrogen, the high lattice energies of the tin(II) halides, and the low tin–hydrogen bond energy. Lower stability of the divalent halides and higher M–H and M–X (M = Si, Ge) bond energies are the probable reasons that reaction 3 has not been observed for the silicon or germanium analogs.

Decomposition of Chlorostannane.—Decomposition of chlorostannane yields not only stannane, hydrogen, and tin(II) chloride but also hydrogen chloride. We believe that, in this case, reaction 1 is accompanied by the additional reaction

$$3SnH_3Cl \longrightarrow 2SnH_4 + SnCl_2 + HCl \qquad (4)$$
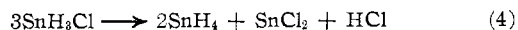
The data for the decomposition products of chlorostannane in Table I are consistent with the following rela-

(16) H. J. Eméleus, A. G. Maddock, and C. Reid, *J. Chem. Soc.*, 353 (1941); H. J. Eméleus and A. G. Maddock, *ibid.*, 293 (1944).

(17) A. Stock and C. Somieski, *Chem. Ber.*, **50**, 1739 (1917); **52**, 695 (1919).

(18) T. N. Srivastava and M. Onyzschuk, *Proc. Chem. Soc., London*, 205 (1963).

(19) Of interest in this regard are the reports that diiodogermane is not volatile at room temperature[20] and that dibromogermane has a vapor pressure of 6.2 Torr at 0°.[21]

(20) S. Cradock and E. A. V. Ebsworth, *J. Chem. Soc. A*, 12 (1967).

(21) T. N. Srivastava, J. E. Griffiths, and M. Onyszchuk, *Can. J. Chem.*, **41**, 2101 (1963).

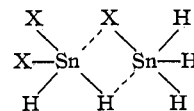tions required by the stoichiometries of reactions 1 and 4

$$n_{HCl} + n_{H_2} = n_{SnCl_2}$$

$$2n_{HCl} + n_{H_2} = n_{SnH_4}$$
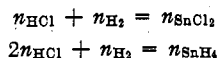
The symbol n represents the number of moles of each product.

The formation of hydrogen chloride suggests the intermediate formation of trichlorostannane (which would be expected to be unstable toward decomposition into tin(II) chloride and hydrogen chloride).[22] Trichlorostannane could reasonably form by a ligand-interchange reaction between chlorostannane and dichlorostannane. Thus we suggest that, in the case of SnH$_3$Cl, the following steps should be added to the general mechanism (reactions 2 and 3) given above

$$SnH_3Cl + SnH_2Cl_2 \longrightarrow SnHCl_3 + SnH_4 \quad (5)$$

$$SnHCl_3 \longrightarrow SnCl_2 + HCl \quad (6)$$
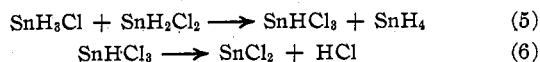
(22) Trichlorogermane is reported to decompose to germanium(II) chloride and hydrogen chloride at temperatures as low as $-30°$: C. W. Moulton and J. G. Miller, *J. Amer. Chem. Soc.*, **78**, 2702 (1956).

A plausible activated complex for reaction 5 is

$$\begin{array}{ccc}
X & X & H \\
\diagdown & \diagup\diagdown & \diagup \\
X{-}Sn & & Sn{-}H \\
\diagup & \diagdown\diagup & \diagdown \\
H & H & H
\end{array}$$

(X = Cl, Br, I). As the halogen atoms, X, become both smaller and more electronegative, the coordination of five ligands around each of the tin atoms should be favored both for steric reasons and because of the development of a more positive charge on the tin atoms. The fact that hydrogen halide was formed only in the case of chlorostannane suggests that only in that case was reaction 5 fast enough to compete effectively with reaction 3.

The Thermal Decomposition of Methyldisilane and 1,2-Dimethyldisilane

By R. B. BAIRD, M. D. SEFCIK, AND M. A. RING*

The gas-phase pyrolyses of CH$_3$Si$_2$H$_5$ and 1,2-(CH$_3$)$_2$Si$_2$H$_4$ have been examined neat and in the presence of excess C$_2$H$_5$SiD$_3$. The results of these experiments demonstrate that 1,2-(CH$_3$)$_2$Si$_2$H$_4$ decomposes solely into CH$_3$SiH and CH$_3$SiH$_3$ while CH$_3$Si$_2$H$_5$ decomposes into CH$_3$SiH, SiH$_2$, CH$_3$SiH$_3$, and SiH$_4$. The results from the observed [SiH$_4$]/[CH$_3$SiH$_3$] are discussed. Both methyldisilanes were found to decompose at a rate which is similar to that of disilane and much greater than that of hexamethyldisilane. This result can be attributed to the different modes of decompositions found between hexamethyldisilane and the other disilanes.

Introduction

Results from the flow pyrolysis of disilane led to the suggestion that disilane decomposed into SiH$_4$ and SiH$_2$ followed by the insertion of SiH$_2$ into Si$_2$H$_6$[1] (eq 1 and 2). This mechanism was verified independently by the

$$Si_2H_6 \longrightarrow SiH_4 + SiH_2 \quad (1)$$

$$SiH_2 + Si_2H_6 \longrightarrow Si_3H_8 \quad (2)$$
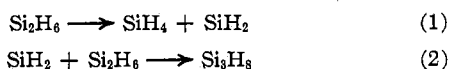
trapping of SiD$_2$ (from Si$_2$D$_6$) into CH$_3$SiH$_3$[2,3] forming CH$_3$SiH$_2$SiD$_2$H. It has been demonstrated that the pyrolysis of (CH$_3$)$_6$Si$_2$ occurs *via* the formation of (CH$_3$)$_3$Si radicals[4] while the results from the pyrolysis of (CH$_3$)$_5$Si$_2$H are best in accord with initial decomposition into (CH$_3$)$_3$SiH and (CH$_3$)$_2$Si.[5] The thermolyses of methoxymethyldisilanes occur *via* the formation of a silane and a silylene *via* transfer of the methoxy group but not the methyl group.[6] It has been proposed that the activated complex leading to silylene formation contains a hydrogen[2] or a methoxy group[6] bridged between the two silicon atoms. All of the above data suggest that methyl groups do not enter the bridged position.

In this paper, we report our results on the pyrolysis of 1,2-(CH$_3$)$_2$Si$_2$H$_4$ and of CH$_3$Si$_2$H$_5$. The goals of this investigation were (1) to demonstrate that methyldisilanes do thermally decompose into a silane and a silylene *via* intramolecular hydrogen atom transfer, (2) to trap the silylene or silylenes formed, (3) to determine the directional effect of the methyl group in the hydrogen-transfer process, and (4) to examine the relative stabilities of the alkyldisilanes and compare these results to those of disilane[1] and the much more stable (CH$_3$)$_6$Si$_2$.[4] A correlation between mechanism and relative stability would be expected.

Results

The following results were obtained from experiments in flow systems with low-temperature trapping.

1. **Pyrolysis of 1,2-(CH$_3$)$_2$Si$_2$H$_4$.**—The thermal decomposition of 1,2-(CH$_3$)$_2$Si$_2$H$_4$ was examined at 400°, the products were methylsilane, a small quantity of hydrogen, and 1,2,3-(CH$_3$)$_3$Si$_3$H$_5$. The mass and nmr spectra of this compound demonstrated that it was a trimethyltrisilane and most likely 1,2,3-(CH$_3$)$_3$Si$_3$H$_5$.

(1) E. M. Tebben and M. A. Ring, *Inorg. Chem.*, **8**, 1787 (1969).

(2) P. Estacio, M. D. Sefcik, E. K. Chan, and M. A. Ring, *ibid.*, **9**, 1068 (1970).

(3) M. Bowrey and J. H. Purnell, *J. Amer. Chem. Soc.*, **92**, 2594 (1970).

(4) I. M. T. Davidson and I. L. Stephenson, *J. Chem. Soc. A*, 282 (1968).

(5) H. Sakurai, A. Hosemi, and M. Kumada, *Chem. Commun.*, 4 (1969).

(6) W. H. Atwell and D. R. Weyenberg, *J. Amer. Chem. Soc.*, **90**, 3438 (1968).