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THE CHEMISTRY OF STANNANE

John Robert Webster
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THE CHEMISTRY OF STANNANE

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ABSTRACT

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) and by mass spectrometry of their vapors.

Stannane reacts slowly with strong aqueous acids below -50° to give one mole of hydrogen per mole of stannane. The resulting solutions evolve an additional two moles of hydrogen as they are warmed to room temperature. Stannane undergoes a similar, but relatively rapid, reaction with anhydrous fluorosulfuric acid at -78°; when the resulting solution is warmed to room temperature, the solvent is reduced but no hydrogen is evolved. Conductivity studies of the cold undecomposed fluorosulfuric acid solutions indicate the formation of one mole of fluorosulfate ion per mole of stannane reacted, and ^{119}Sn nmr spectra of such solutions show a 1:3:3:1 quartet. These results are interpreted in terms of the solvated stannonium ion, SnH_3^+.

Stannane and liquid ammonia react at -78° to give a non-volatile red-brown product which decomposes at room temperature. Analysis of the decomposition products indicates that the red-brown material has the empirical composition Sn_2NH_{11}. Low temperature conductivity and nmr studies of solutions of stannane in liquid ammonia lead us to believe that

stannane is deprotonated in ammonia to yield the ammonium and stannyl ions; however there are serious difficulties in reconciling this interpretation with the results of studies of deuterium exchange between ammonia and stannane-$\underline{d}_4$.

Potassium stannyl has been prepared by the reaction of stannane with slurries of finely divided KOH in both dimethylsulfoxide and monoglyme, and by the reaction of stannane with a standard solution of $KGeH_3$ in diglyme. The preparation of CH_3SnH_3 and $C_2H_5SnH_3$ by the reaction of CH_3I and C_2H_5I with these solutions verifies that $KSnH_3$ was actually formed. Reactions of $KSnH_3$ solutions with several lewis acids resulted in apparent decomposition of the stannyl ion.

Part I. THE SYNTHESIS AND CHARACTERIZATION OF THE HALOSTANNANES

Abstract

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) and by mass spectrometry of their vapors.

Introduction

There have been many studies of the halogen derivatives of silane and germane,[1,2] whereas there has been but a single brief report concerning a halostannane, 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

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, or vapor pressure measurements, or both. 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 cc.) 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 hours, during which time the bath slowly warmed from -112° to about -75°. The reaction mixture was then quenched to -196°; the tube was opened, and the hydrogen was Toepler-pumped out and measured. An empty dewar flask which had been pre-chilled 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., SnH_4, H_2, SnX_2, 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 twenty minutes, during which time a solid residue formed on the walls of the trap. The trap was then cooled to -196°, 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; literature[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} to 10^{-6} torr, and the energy of the ionizing electrons was 30 eV.

Infrared Spectrometry. - Solid-film infrared spectra of the halostannanes were recorded in the range 670 - 4000 cm^{-1} using a Perkin Elmer Model 137 Infracord spectrophotometer. The samples were condensed onto a liquid-nitrogen-cooled sodium chloride plate of a standard low-temperature

infrared cell similar to that described by Shriver.[9]

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 ten percent 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[10] 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 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.

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. Although several methods were tried, the only gas-phase spectra observed were those of decomposition products. The low-temperature (-196°) solid-phase spectra showed absorbtions in the region of the tin-hydrogen stretch. Chlorostannane absorbs at 1960 cm^{-1} (s), 1940 cm^{-1} (s), and 1910 cm^{-1} (s); bromostannane at 1930 cm^{-1} (s), and 1905 cm^{-1} (s); and iodostannane at 1910 cm^{-1} (s). The spectrum of iodostannane had a strong absorption at 1880 cm^{-1} which we attribute to stannane from the decomposition of iodostannane during transfer into the cell. The spectra are presented in Fig. 1.

The Preparation and Analysis of the Halostannanes. - 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 hours at -78° in the gas phase.

The synthetic and analytical data are summarized in Table I. In the runs for which the hydrogen evolved at -78° 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 monohalogenated stannanes. The analytical data confirm this conclusion, as shown clearly by the empirical Sn:H:X ratios. Hydrogen halide was found as a decomposition product only in the case of chlorostannane. The tin(IV) halides and tin metal were never found.

Mass Spectra. - Tin has ten isotopes with abundances greater than 0.35 per cent, and both bromine and chlorine have two isotopes with

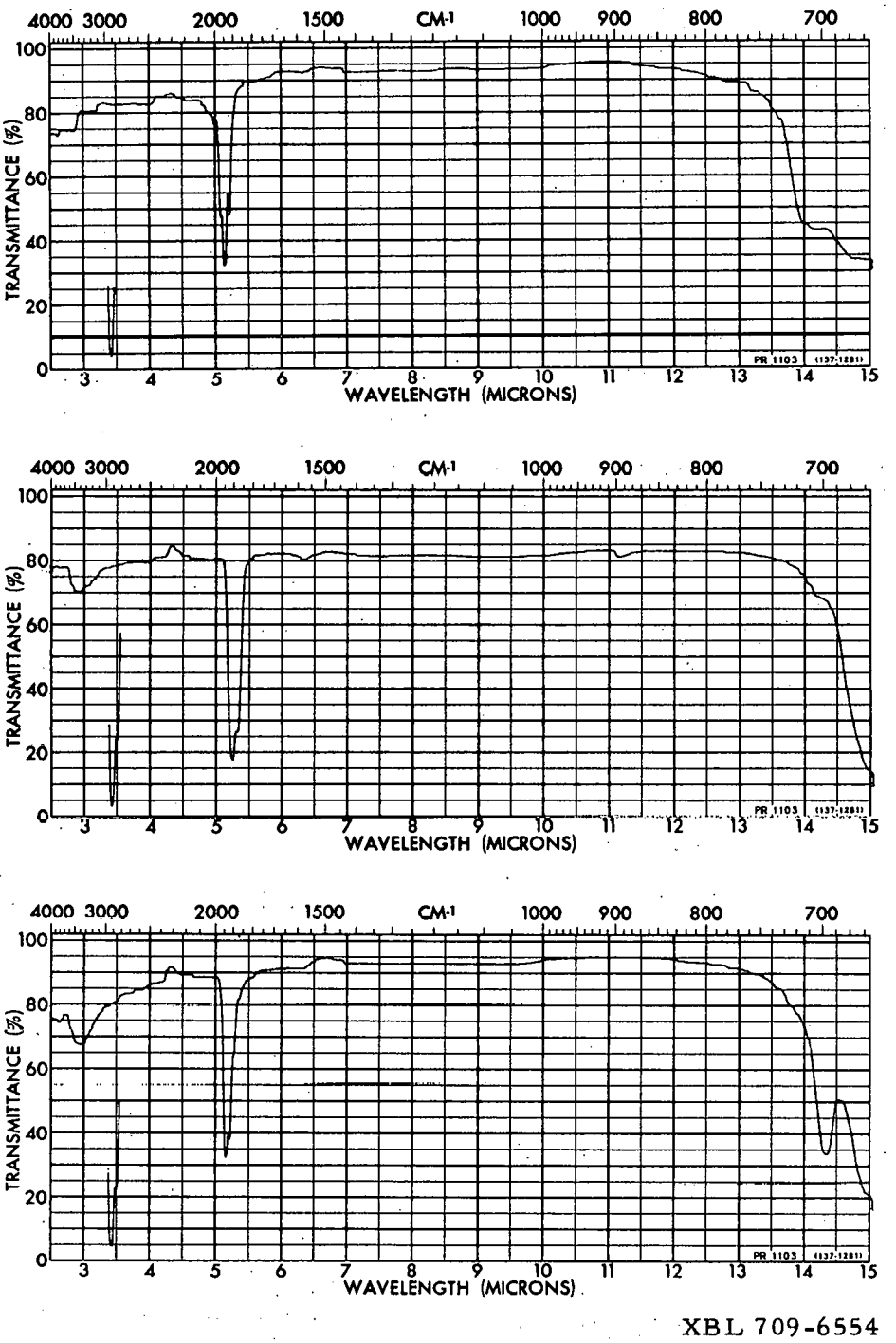


Fig. 1. Solid film infrared spectra of the halostannanes. Upper spectrum SnH_3Cl, middle spectrum SnH_3I, lower spectrum SnH_3Br.

Table I. The analytical data for the decomposition of the halostannes.

Reactants (mmoles) SnH_4	HX	Reaction time (hrs.)	H_2 evolved at low temperature (mmoles)	SnH_3X isolated by distillation (mmoles)	Decomposition products (μmoles) H_2	SnH_4	SnX_2	HX	Empirical formula Sn : H : X
for SnH_3Cl									
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 SnH_3Br									
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	XS	9	1.02	0.335	171	165	170[a]	none	1.00:2.98:1.01
for SnH_3I									
----	----		----	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

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, 1, 2, 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 ten to twenty per cent as intense as the SnH_n^+ envelope) was the envelope corresponding to ions SnH_nX^+ (n = 0, 1, 2, 3, and X = Cl, Br, or I). This envelope appeared at m/e = 239 to 254 for SnH_3I, at m/e = 191 to 208 for SnH_3Br, and at m/e = 147 to 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.[11] 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 Figs. 2-4. The fragmentation patterns, A_0, A_1, A_2, A_3 (where A_0 is the fraction of the total

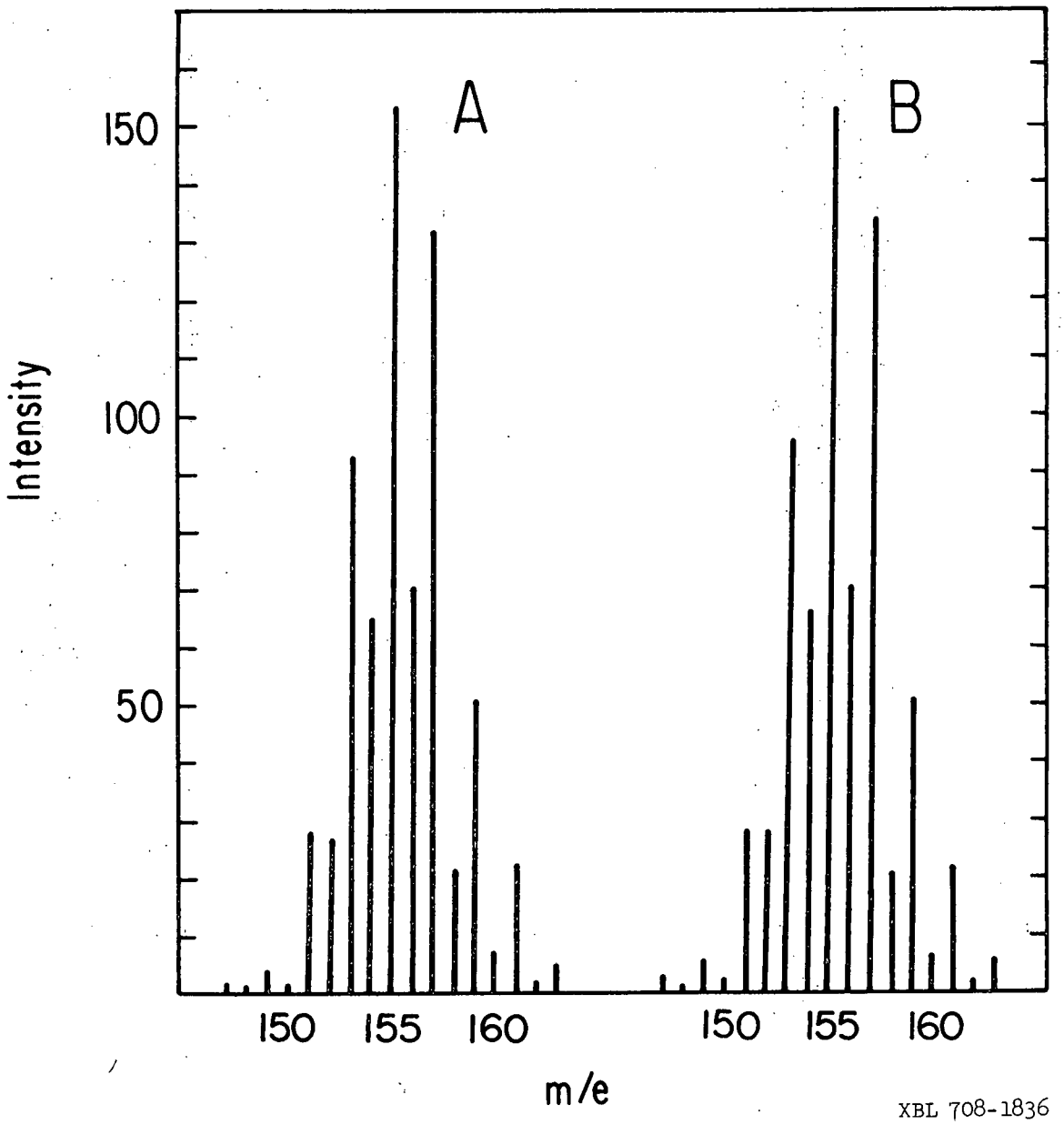
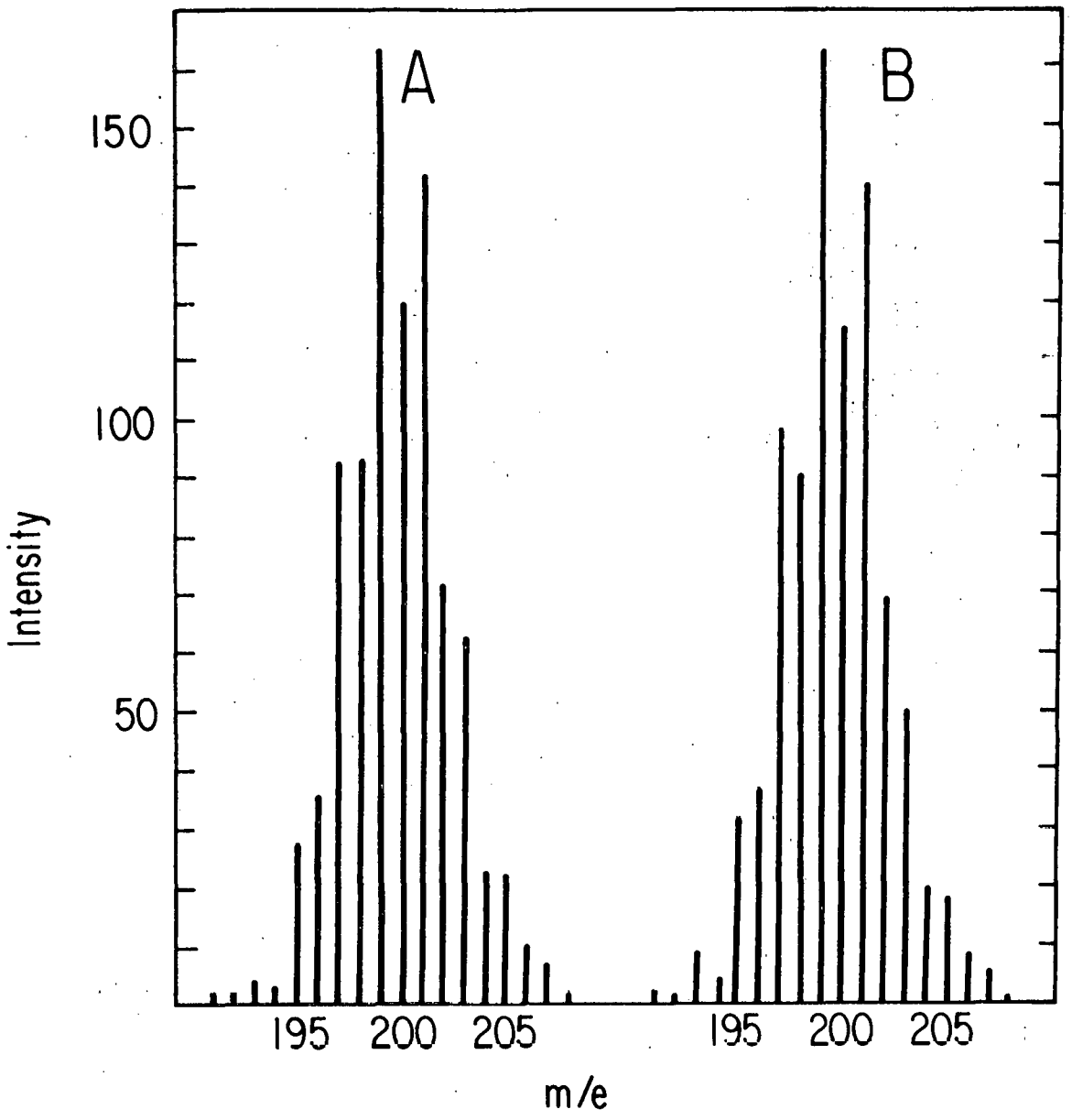


Fig. 2. The calculated (A) and observed (B) mass spectral bands for the species SnH_nCl; n = 0, 1, 2, or 3. The fragmentation pattern is $A_0 = 0.328$, $A_1 = 0.176$, $A_2 = 0.496$, and $A_3 = 0.000$, and was calculated from the intensities of peaks at m/e = 154, 155, 156, and 157.



XBL 708-1833

Fig. 3. The calculated (A) and observed (B) mass spectral bands for the species SnH_nBr; n = 0, 1, 2, or 3. The fragmentation pattern is $A_0 = 0.360$, $A_1 = 0.310$, $A_2 = 0.278$, and $A_3 = 0.051$, and was calculated from the intensities of peaks at m/e = 197, 199, 200, and 201.

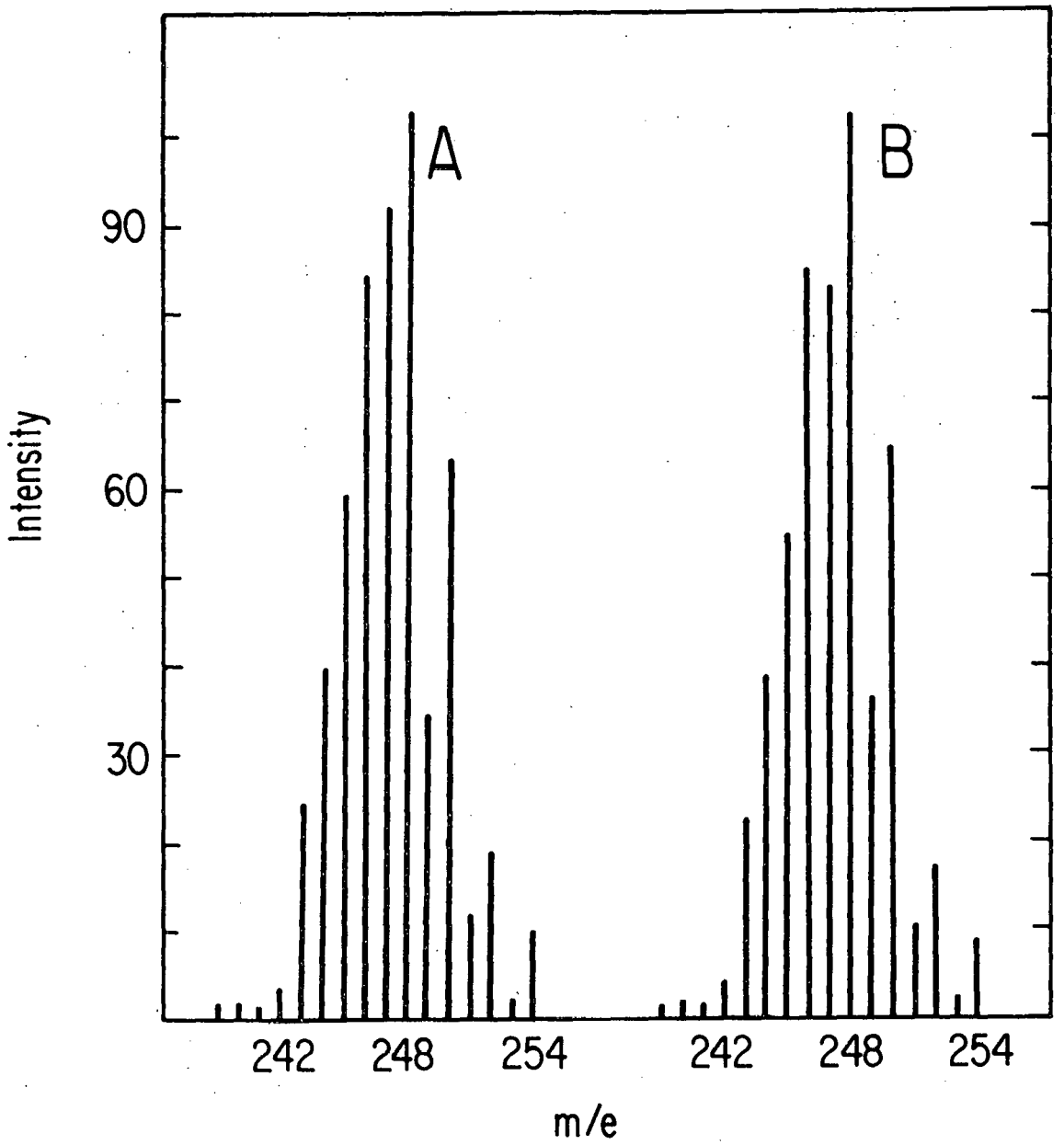


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Fig. 4. The calculated (A) and observed (B) mass spectral bands for the species SnH_nI; n = 0, 1, 2, or 3. The fragmentation pattern is $A_0 = 0.300$, $A_1 = 0.330$, $A_2 = 0.067$, and $A_3 = 0.300$, and was calculated from the intensities of peaks at m/e = 251, 252, 253, and 254.

ions SnH_nX^+ for which n = 0), and the m/e values of the peaks from which they were calculated are given in the figure captions. The good agreement between the calculated and observed spectra is evidence for the correctness of the assignments.

As the energy of the ionizing electrons was increased 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 ten per cent as intense as those of the singly-charged ions.

It is interesting that a very weak envelope from m/e = 186 to 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, 1, 2) from SnH_2Cl_2. In Fig. 5 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 the following equation:

$$2\ SnH_3X \longrightarrow SnH_4 + SnX_2 + H_2 \qquad (1)$$

This reaction is complete in twenty minutes at room temperature, and may be explained by the following general mechanism.

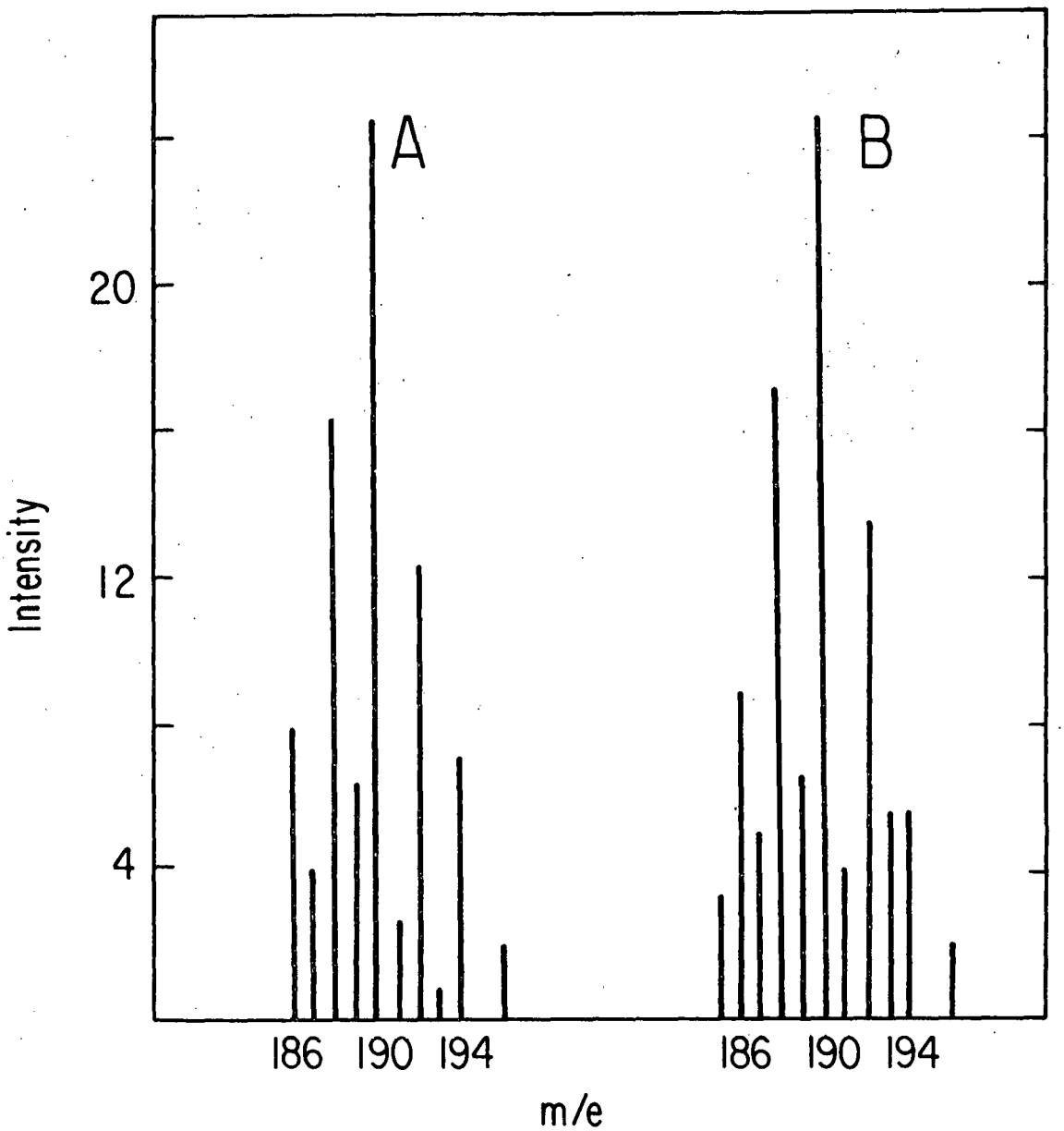

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Fig. 5. The calculated (A) and observed (B) mass spectral bands for the species SnH_nCl_2; n = 0, 1, or 2. The fragmentation pattern is $A_0 = 0.90$, $A_1 = 0.00$, and $A_2 = 0.10$, and was calculated from the intensities of peaks at m/e = 188, 190, and 192.

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

$$SnH_2X_2 \longrightarrow SnX_2 + H_2 \qquad (3)$$

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[12,13] and monofluorogermane.[14] 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 four. 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.[15-17] Assuming that the volatilities of the dihalogen derivatives of stannane and germane correlate with molecular weights, we would expect SnH_2I_2 to be non-volatile, 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 or 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 following additional reaction.

$$3\ SnH_3Cl \longrightarrow 2\ SnH_4 + SnCl_2 + HCl \qquad (4)$$

The data for the decomposition products of chlorostannane in Table I are consistent with the following relations required by the stoichiometries of reactions 1 and 4.

$$\underline{n}_{HCl} + \underline{n}_{H_2} = \underline{n}_{SnCl_2}$$

$$2\ \underline{n}_{HCl} + \underline{n}_{H_2} = \underline{n}_{SnH_4}$$

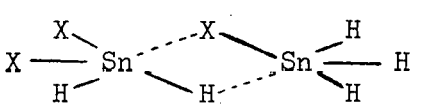
The symbol $\underline{n}$ represents the number of moles of each product.

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).[18] Trichlorostannane could reasonably form by a ligand-interchange reaction between chlorostannane and dichlorostannane. Thus we suggest that, in the case of SnH_3Cl, the following steps should be added to the general mechanism (reactions 2 and 3) given above.

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

$$SnHCl_3 \longrightarrow SnCl_2 + HCl \qquad (6)$$

A plausible activated complex for reaction 5 is the following.



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.

Appendix I

The fragmentation patterns were calculated by solving four simultaneous linear equations of the following form. The solutions were for A_0, A_1, A_2, and A_3.

$$\sum_{\alpha=0}^{3} \sum_{\beta=i_{min}}^{i_{max}} \sum_{\gamma=j_{min}}^{j_{max}} A_\alpha \, B_\beta \, C_\gamma \, \delta_{(\alpha\beta\gamma,ijk)} = I_\omega \qquad (1)$$

A_α = the fraction of total ions SnH_kX^+ for which $k = \alpha$

B_β = the natural abundance of the tin isotope of atomic mass, i, equal to β

C_γ = the natural abundance of the halogen isotope of atomic mass, j, equal to γ

I_ω = the intensity of the peak at m/e = ω, where

$\omega = i_{min} + j_{min}$ to $3 + i_{max} + j_{max}$

$\delta_{(\alpha\beta\gamma,ijk)} = 1$ if $\alpha + \beta + \gamma = i + j + k$

$= 0$ if $\alpha + \beta + \gamma \neq i + j + k$

The calculations were made assuming no isotope effects in the fragmentation. After the fragmentation pattern was determined, the relative intensities of the remaining twelve to fourteen lines of the spectrum were calculated from equation 1.

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Part II. THE SnH_3^+ ION IN ACID SOLUTIONS

Abstract

Stannane reacts slowly with strong aqueous acids below -50° to give one mole of hydrogen per mole of stannane. The resulting solutions evolve an additional two moles of hydrogen as they are warmed to room temperature. Stannane undergoes a similar, but relatively rapid, reaction with anhydrous fluorosulfuric acid at -78°; when the resulting solution is warmed to room temperature, the solvent is reduced but no hydrogen is evolved. Conductivity studies of the cold undecomposed fluorosulfuric acid solutions indicate the formation of one mole of fluorosulfate ion per mole of stannane reacted, and ^{119}Sn nmr spectra of such solutions show a 1:3:3:1 quartet. These results are interpreted in terms of the solvated stannonium ion, SnH_3^+.

Introduction

Evidence for the formation of organo-tin cations was reported as early as 1923.[1] Since then, many investigations of organo-tin systems have been made, and it is now established that ions of the type $R_2Sn(H_2O)_x^{2+}$ and $R_3Sn(H_2O)_x^{+}$ can be prepared in aqueous solution.[2] The existence of such ions, and the observation that diborane reacts with strong aqueous acids at low temperature to give $BH_2(H_2O)_2^{+}$,[3] led us to investigate the possibility of forming the stannonium ion, SnH_3^{+},[4] by treating stannane with strong acids at low temperature.

Experimental

Stannane was prepared by a published method.[5] Fluorosulfuric acid (Research Organic/Inorganic Chem. Co., 99%) was distilled under dry nitrogen (bp 161-162°). Baker and Adamson reagent grade potassium sulfate was used without further purification. Hydroiodic acid (Merck reagent grade) was distilled under dry nitrogen (bp 127°), diluted with distilled water to 49%, stored in the dark, and used within one day of purification. Concentrated aqueous HBr, HCl, and $HClO_4$ (Baker & Adamson reagent grade) were diluted with distilled water to eutectic concentrations[6] and used without further purification. Ideal gas behavior was assumed for stannane and hydrogen when making stoichiometric calculations from PVT data. The purity of stannane was checked by mass spectrometry and vapor pressure measurements. Signal averaging was accomplished with a Varian Associates Model 1024 time-averaging computer. Chemical shifts were measured by sample replacement and are accurate to ± 20 ppm. Shifts to higher field from neat tetramethylstannane are given positive signs; the scale was calibrated using the relation that the separation between the first two side bands is twice the modulation frequency.

Samples were prepared in 11-mm. i.d. Pyrex tubes, and were usually 1 to 4 M in tin. Because natural tin contains about 8% ^{119}Sn, the samples were effectively only 0.08 to 0.32 M. The purified HSO_3F was pipetted into the nmr tube and outgassed at -78° on the vacuum line. Stannane was condensed into the tube and allowed to react several hours at -78°; then the hydrogen was removed, and the nmr tube was sealed by glassblowing. To prevent decomposition, the sample solution was never warmed above -78°.

The Stoichiometry of Reactions of Stannane with Acids. - A diagram of the apparatus is given in Fig. 1. The space between D and C was evacuated, and then twenty ml of the acid was pipetted into the bulb and outgassed by pumping. The acid was kept at the reaction temperature while stannane was condensed at -196° into side arm A, and then the vessel was sealed at B by glassblowing. The apparatus was immersed in a cold bath to a point just below the stopcock, and the reaction mixture was stirred magnetically. After the reaction period, hydrogen and any unreacted stannane were removed through D; constant stirring facilitated removal of the dissolved unreacted stannane - a process which usually required several hours. The hydrogen was identified by mass spectrometry and measured. Stopcock D was then closed, and the solution was warmed to room temperature. During warming, the aqueous solutions effervesced gently for about ten minutes. When effervescence was complete, a second batch of hydrogen was removed, identified, and measured. The anhydrous fluorosulfuric acid solutions did not give more hydrogen when warmed to room temperature, instead sulfur dioxide was evolved.

Nuclear Magnetic Resonance Experiments. - The ^{119}Sn nmr spectrum of the solution formed by the reaction of stannane with fluorosulfuric acid was obtained with a Varian Associates Model V-4311 wide-line spectrometer operated at 8.134 MHz. Resonances were found at about 5100 gauss, and recorded as first side-bands in the absorption mode. The temperature was maintained at -80° ± 3° by blowing cold dry nitrogen around the sample tube, which was placed in a vacuum-jacketed tube to protect the nmr probe from the low temperature. The temperature was measured to ± 0.1° with a copper-constantan thermocouple.

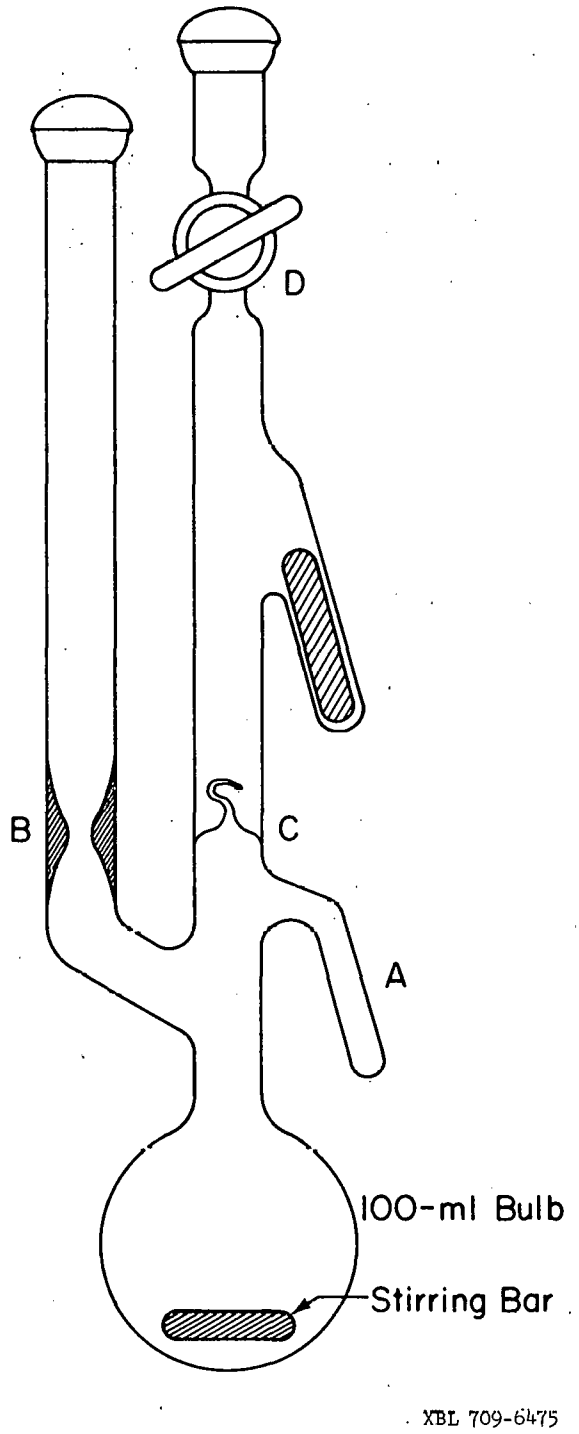

Fig. 1. Apparatus for the reaction of stannane with acids at -78°.

Conductivity Experiments. - The conductivity of both stannane and potassium sulfate in fluorosulfuric acid was determined using an Electro Scientific Industries (ESI) Model 860-A AC generator-detector and an ESI Model 290-A impedance bridge. Cell capacitances were cancelled out with a decade capacitance system. The measurements were made at -78° (dry ice-trichloroethylene slush), and the temperature was checked with a copper-constantan thermocouple. An illustration of the conductivity cell is presented in Fig. 2. The cell constant was determined to be 3.2 cm^{-1} with 0.02 N KCl. Fluorosulfuric acid was pipetted into the cell through A, outgassed on the vacuum line at room temperature, and then the cell was sealed by glassblowing at A. The cell and acid were weighed and the amount of acid was determined by subtracting the previously determined cell tare weight. Stannane was condensed temporarily at -196° in a small tube (B) connected to the conductivity cell by a break-seal (D), and a seal was made by glassblowing at C. The cell was immersed in the cold bath; the resistance of the pure HSO_3F was measured; stannane was introduced through the break-seal, and then the resistance of the solution was followed until it was constant. The resistances of solutions of K_2SO_4 in HSO_3F were measured in a cell similar to that shown in Fig. 2, except the arm containing B, C, and D was replaced by a straight tube (closed at the top by a glass stopper) through which pellets of K_2SO_4 were added. The acid was initially outgassed as above, but the resistances were measured at -78° with an atmosphere of air in the closed cell. The specific conductance of the pure acid was always between $3 - 5 \times 10^{-4}$ mhos cm^{-1}; the lowest value reported is 1.085×10^{-4} mhos cm^{-1}.[7]

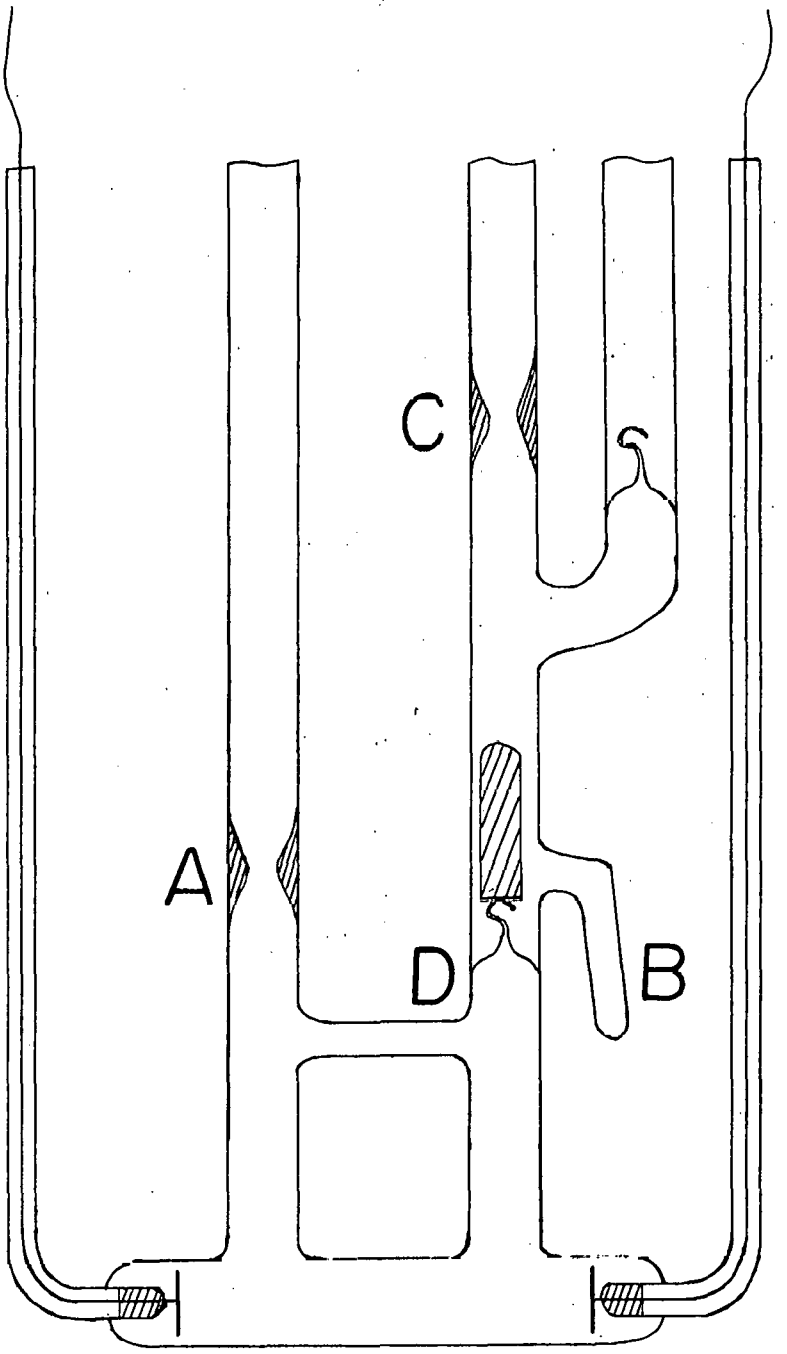

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Fig. 2. The conductivity cell.

Results and Discussion

The results of the reaction of stannane with cold aqueous acids are presented in Table I. The ratio of hydrogen evolved at room temperature to hydrogen evolved at low temperature was always about 2:1. This result is consistent with hydrolysis of stannane to SnH_3^+ at the low temperature, followed by hydrolysis of the SnH_3^+ to tin(II) at room temperature.

$$SnH_4 + H^+ \xrightarrow{-78^\circ} SnH_3^+ + H_2 \qquad (1)$$

$$SnH_3^+ + H^+ \xrightarrow{20^\circ} Sn^{2+} + 2\ H_2 \qquad (2)$$

In one run tin(II) was determined, and the ratio of the hydrogen evolved upon warming to room temperature to tin(II) was found to be 1.95, in close agreement with the value expected from reaction 2. The fact that most of the hydrogen ratios in Table I are slightly smaller than 2 can be explained by the ease with which reaction 2 occurs. Effervescence due to the second reaction began long before the sample solution reached 0°, and it is reasonable to assume that it occurred slowly even at -78°, thus lowering the ratio slightly. Although the reaction times were several hours in every case, only a small amount of the stannane charged reacted. When weaker acids (eutectic aqueous solutions of HBF_4 and H_3PO_4) were treated with stannane at low temperature, no evidence for reaction 1 was observed. Because there seemed to be a correlation between the rate of reaction 1 and the strength of the acid, we hoped to obtain relatively fast reaction (and thus the opportunity to prepare concentrated solutions of SnH_3^+) by treating fluorosulfuric acid (a very strong acid) with stannane at -78°.

Table I. Stoichiometry of the Reaction of SnH_4 with Aqueous Acids.

Acid	Temperature	SnH_4 charged (mmoles)	Reaction time (hrs.)	H_2 evolved at low temp. (mmoles)	$\frac{H_2 \text{ evolved at room temperature}}{H_2 \text{ evolved at low temperature}}$
8 M HCl	-78°	1.22	21.0	0.026	1.96
8 M HCl	-78°	1.49	39.0	0.065	1.99
8 M HCl	-63°	1.44	7.0	0.096	1.92
8 M HCl	-63°	1.31	6.5	0.084	1.94
8 M HCl	-56 ± 3°	1.02	3.0	0.053	1.85
$HClO_4$ (40%)	-53 ± 3°	1.54	9.0	0.023	1.91
$HClO_4$ (40%)	-52 ± 3°	1.63	6.0	0.014	1.86
HI (49%)	-65 ± 3°	1.23	8.5	0.030	1.90
HBr (44%)	-78°	1.14	15.5	0.137	1.87

Indeed, when stannane was treated with fluorosulfuric acid at -78° the stannane was completely consumed and one mole of hydrogen was evolved in a relatively short time. In four experiments with reaction times of from 3 to 18 hours, 0.65, 1.56, 0.29 and 0.49 mmoles of stannane was allowed to react at -78° with HSO_3F. The amounts of hydrogen evolved were 0.64, 1.63, 0.30, and 0.51 mmoles, respectively. These results suggest the following reaction.

$$SnH_4 + HSO_3F \xrightarrow{-78°} SnH_3^+ + SO_3F^- + H_2 \qquad (3)$$

No more hydrogen was evolved on warming the solutions, which were now very light blue, to 20°. However, sulfur dioxide could be pumped out of the solutions. The light blue solutions showed a weak absorption at 5800 Å and a more intense one at about 2800 Å. When a trace of sulfur was dissolved in fluorosulfuric acid, an intense blue color and an absorption band at 5800 Å were observed. Fluorosulfuric acid, through which sulfur dioxide had been bubbled, showed a strong absorption at about 2900 Å. Apparently the SnH_3^+ ion in fluorosulfuric acid does not decompose by a hydrolysis reaction analogous to reaction 2, but rather it reduces the sulfur of the acid to lower oxidation states.

The ^{119}Sn nmr spectrum of the solutions resulting when stannane is treated with fluorosulfuric acid at -78° is a very widely-spaced 1:3:3:1 quartet centered about 186 ppm to higher field from tetramethylstannane. The tin-hydrogen spin-spin coupling constant, $J_{^{119}Sn-H}$, is about 2960 Hz (see Fig. 3). As the solution 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

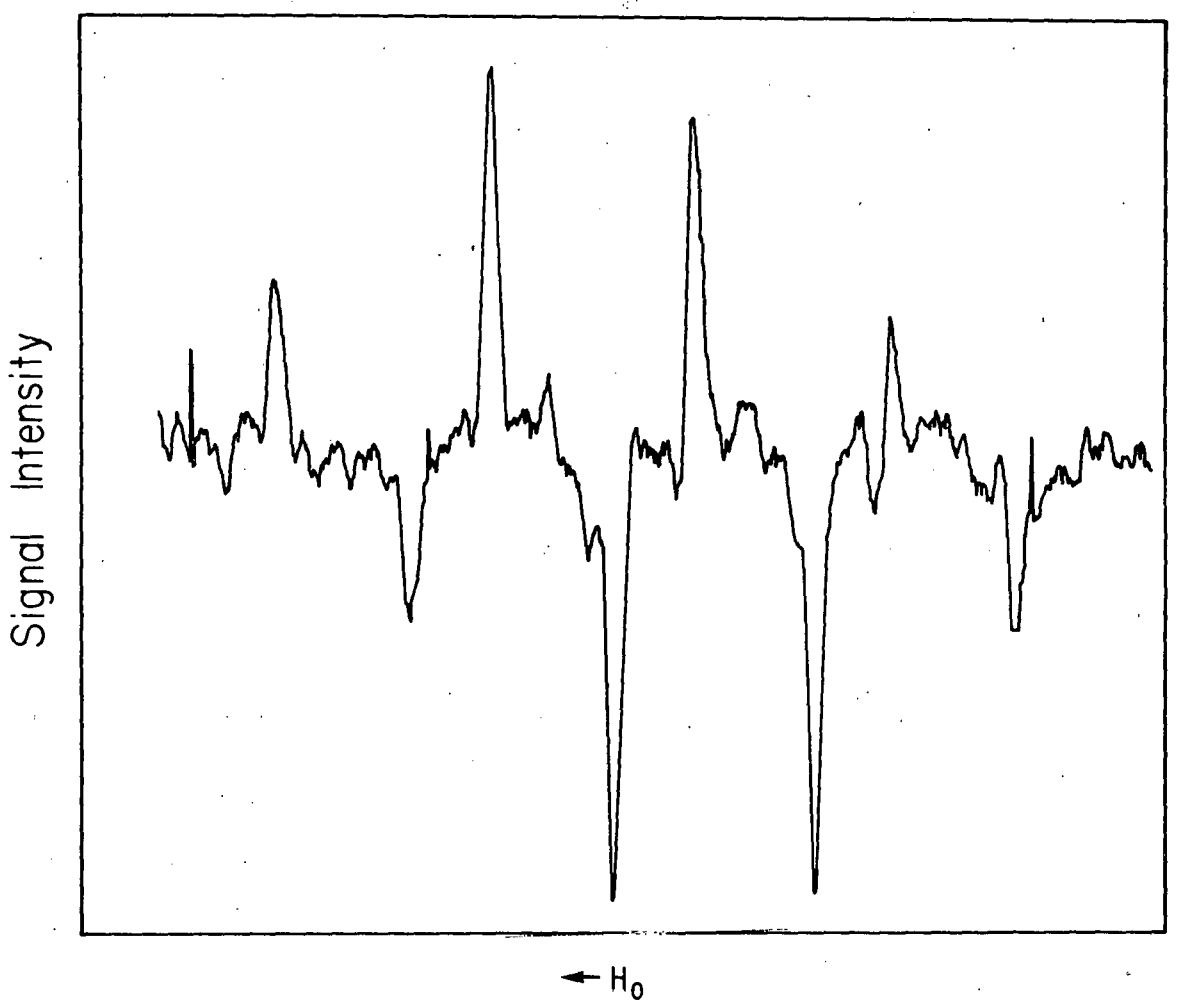

Fig. 3. ^{119}Sn nmr spectrum of stannonium ion in fluorosulfuric acid at -78°.

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 Lauterbur and Burke,[8] 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.[9-11] 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.[12] For stannane (sp^3 hybridization), $J_{^{119}Sn-H}$ is 1933 Hz.[13] For SnH_3^+ (sp^2 hybridization) we calculate $J_{^{119}Sn-H}$ = 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 $J_{^{119}Sn-H}$ 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.[7] Thus the conductivity of a potassium sulfate solution is due to the formation of two moles of SO_3F^- per mole of potassium sulfate.[7]

$$K_2SO_4 + 2\ HSO_3F \longrightarrow 2\ K^+ + 2\ SO_3F^- + H_2SO_4$$

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 molal. The results are presented graphically in Fig. 4. The molal conductances of the potassium sulfate and the stannonium product taken from the graph are in the ratio of 1.94:1, as expected for the formation of one mole of SO_3F ion per mole of stannane (see reaction 3).

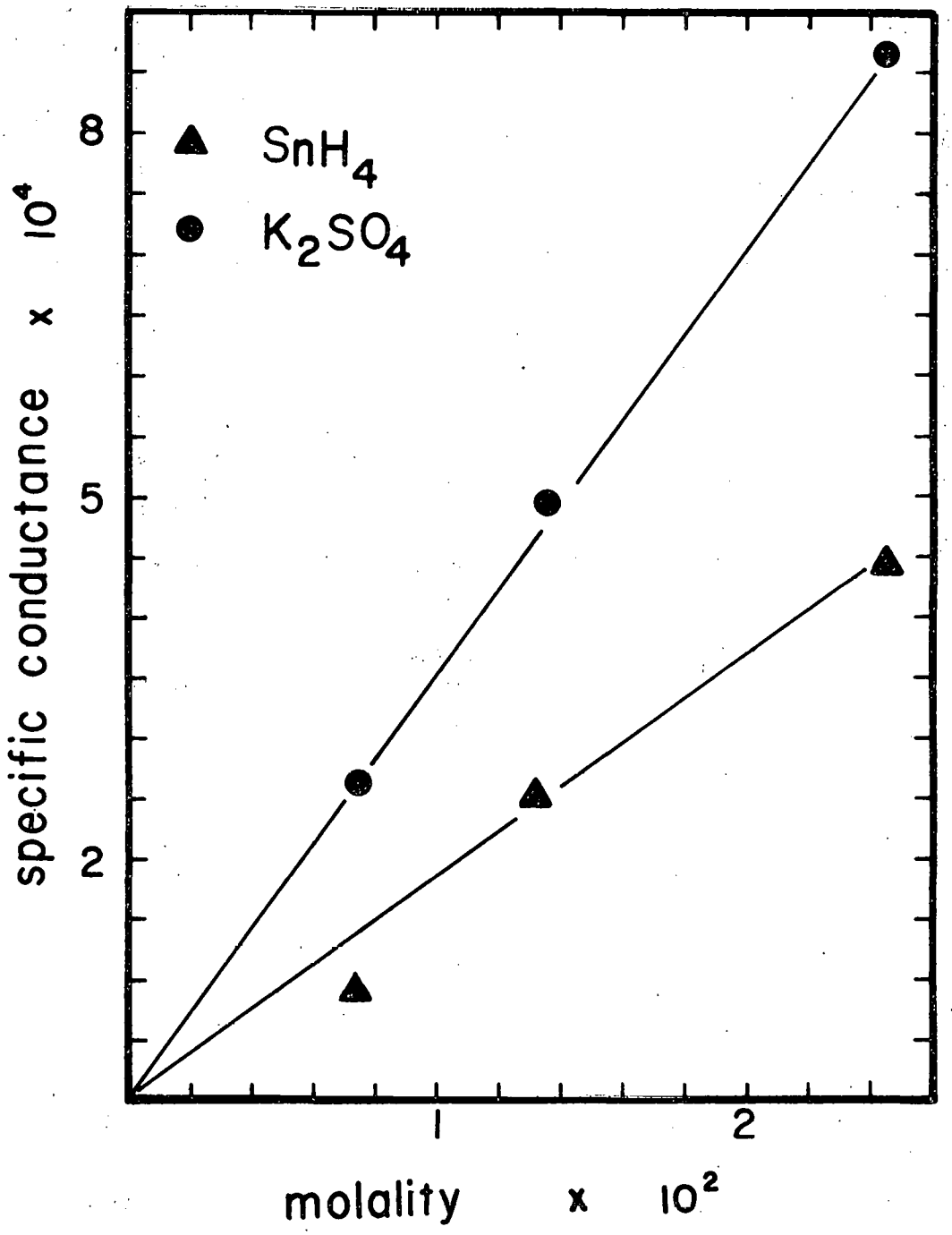

Fig. 4. Results of conductivity studies of stannane and potassium sulfate in fluorosulfuric acid at -78°.

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Part III. REACTIONS OF STANNANE WITH LIQUID AMMONIA

Abstract

Stannane and liquid ammonia react at -78° to give a non-volatile red-brown product which decomposes at room temperature. Analysis of the decomposition products indicates that the red-brown material has the empirical composition Sn_2NH_{11}. Low temperature conductivity and nmr studies of solutions of stannane in liquid ammonia lead us to believe that stannane is deprotonated in ammonia to yield the ammonium and stannyl ions; however there are serious difficulties in reconciling this interpretation with the results of studies of deuterium exchange between ammonia and stannane-$\underline{d}_4$.

Introduction

The observation in this laboratory that stannane decomposes to tin and hydrogen rapidly in the presence of liquid ammonia, and that the liquid phase of that reaction mixture becomes yellow and then darkens to red-brown during the decomposition, led us to investigate the low-temperature reaction of stannane with liquid ammonia in an attempt to determine the composition of the unstable colored intermediate species.

Experimental

Materials. - Stannane and stannane-d_4 were prepared by a published method[1] and purified by fractional condensation at -112°. The purity of both compounds was checked by vapor pressure measurements and by mass spectrometry.[1,2] The isotopic purity of the stannane-d_4 was 98% (found by pyrolysis of the stannane and determination of the deuterium content of the hydrogen evolved). Anhydrous ammonia (Matheson) was purified by distilling from a solution of potassium or potassium amide directly into the reaction vessel. Potassium (Baker and Adamson), potassium hydroxide, and ammonium bromide (Mallinckrodt, analytical reagent) were used without further purification. Monoglyme (Ansul 121) was distilled from calcium hydride. The mass spectrometer used was a Consolidated Electrodynamics Corporation Model 21-620 equipped with a Model 21-063 glass batch inlet system.

Nuclear Magnetic Resonance Experiments. - The ^{119}Sn nmr spectra were recorded under conditions outlined in Part II, except that the sample temperature was kept 5 to 10 degrees warmer. Chemical shifts from tetramethylstannane were measured by the sample replacement method and are accurate to ± 40 ppm. Solutions in pure ammonia were prepared by condensing dry ammonia and stannane into the nmr tube at -196°, then sealing the tube by glassblowing. Spectra were recorded immediately after bringing the sample to about -75°. Solutions of stannane in potassium amide solutions in liquid ammonia were prepared in the same way, except that the amide was previously prepared *in situ* by the reaction of ammonia with potassium using a rusty nail catalyst. The catalyst was removed before spectra were taken. Solutions of potassium stannyl in monoglyme were prepared by the reaction of stannane with a slurry of finely powdered KOH in monoglyme at -20°.[3] This reaction mixture was filtered into the nmr tube *in vacuo*, concentrated by pumping off some of the solvent at about -40°, and stored at -196° after the tube was sealed by glassblowing. Spectra were recorded at -40 ± 1°.

Proton nmr spectra were recorded at -70 ± 5° on a Varian Associates Model A-60 spectrometer equipped with a Varian Associates Model V-6040 variable temperature unit. Samples were prepared as above in 3-mm i.d. tubes less than 2 cm long. The short tubes were used to minimize thermal decomposition resulting from the temperature gradient over the length of the probe cavity, and were held in the probe by placing them in a regular 5-mm i.d. nmr tube.

Conductivity. - The resistance of a solution of stannane in liquid ammonia was measured in a cell similar to that shown in Fig. 2, Part II.

The low-temperature bath consisted of a dewar flask of methanol, stirred mechanically and cooled by a copper rod extending from a liquid-nitrogen reservoir. Temperature was measured to ± 0.5° with an ammonia vapor-pressure thermometer and maintained at -70 ± 1.0° with a bimetallic coil switch and a 10-watt resistance heater. Ammonia was condensed into the cell at -70°; its purity was checked by measuring the resistance; stannane was let in through the break seal, and the resistance of the solution was followed until it was constant. The specific conductance of the pure ammonia was typically 10^{-7} mhos cm^{-1}. The lowest specific conductance recorded for ammonia is 10^{-11} mhos cm^{-1}.[4]

Deuterium Exchange Experiments. - The reaction of stannane-d_4 with ammonia was studied by condensing stannane and ammonia into a flask equipped with a side arm containing a break-seal, sealing the flask by glassblowing, and then allowing the mixture to stand at -78° for reaction. After an appropriate reaction time the break seal was opened, and volatile material was removed at -70° by Toepler-pumping; a red-brown residue remained in the reaction vessel. Hydrogen evolved was collected and measured. Stannane was separated from ammonia by passing the mixture through a trap containing granular magnesium perchlorate (which absorbed the ammonia); the recovered stannane was pyrolyzed, and the hydrogen evolved was collected and measured. The red-brown residue was allowed to decompose at room temperature; the resulting hydrogen was collected and measured. The deuterium content of each of the three portions of hydrogen was found by mass spectrometry.

The Reaction of Stannane with Potassium Amide in Liquid Ammonia. - Potassium amide was prepared in the vessel shown in Fig. 1 by the reaction

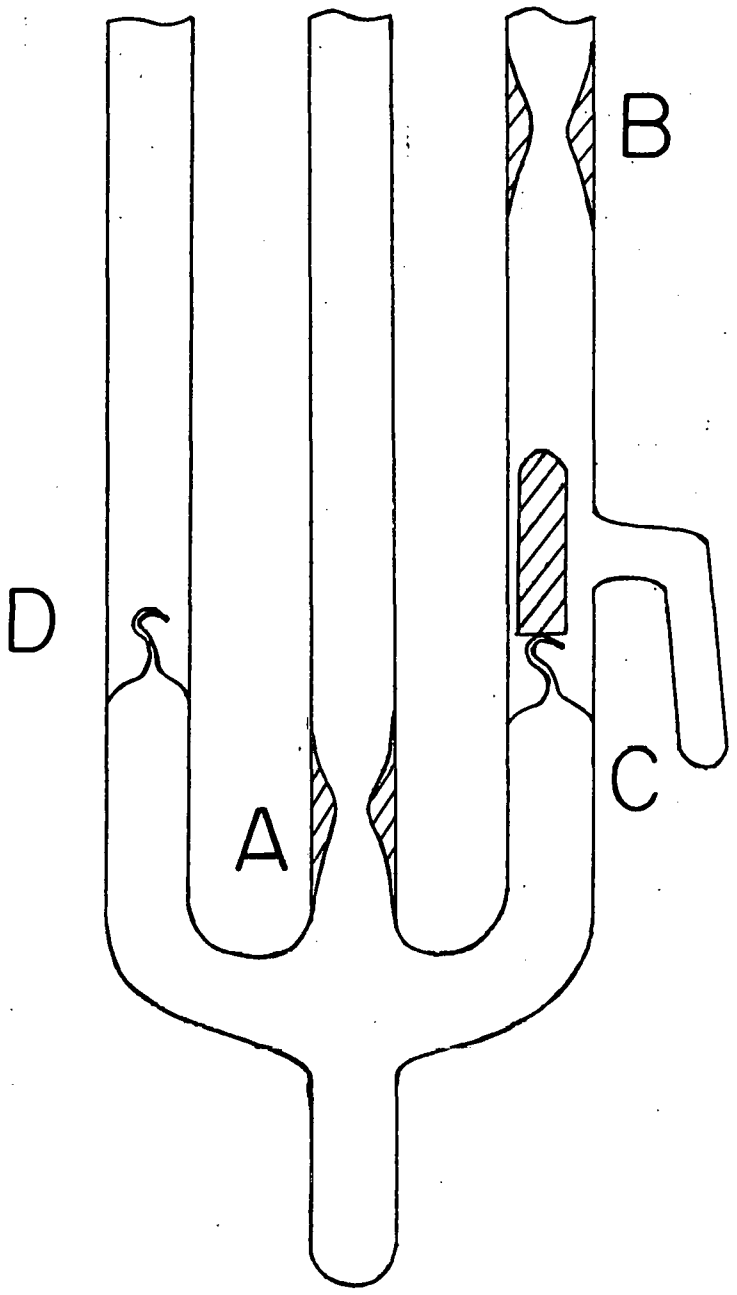

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Fig. 1. Apparatus for the reaction of stannane with potassium amide in liquid ammonia.

of the ammoniated electron with ammonia. Potassium metal and a rusty nail catalyst were introduced through A, then the tube was connected to the vacuum line to remove air. Ammonia was distilled in and allowed to react at about -50°. When the reaction was complete (as judged by the disappearance of the blue color of the ammoniated electron), hydrogen was taken off and measured, the catalyst was removed, and the reaction vessel was sealed by glassblowing at A. The amount of amide formed was assumed to be twice the amount of H_2 evolved, according to $e^- + NH_3 \longrightarrow NH_2^- + 1/2\ H_2$. Stannane was condensed into the side arm, the side arm was sealed at B, the reaction vessel was placed in a -78° bath, and stannane was let in through breakseal C. After reaction, volatile products were removed through D, then water was distilled in and the residue was hydrolyzed.

Analysis of the Residue of the Reaction of Stannane with Liquid Ammonia at -78°. - Stannane and ammonia were allowed to stand for several hours in glass vessels which could be entirely submerged in a cold bath. After reaction, volatile products were removed at about -70°. The red-brown residue which remained in the reaction vessel was warmed to room temperature, allowed to decompose, and the decomposition products (H_2, NH_3, and Sn) were analyzed. Hydrogen and ammonia were separated, identified by mass spectrometry, and measured directly. Tin metal was determined by measuring the hydrogen which evloved when it dissolved in concentrated hydrochloric acid, or by an iodometric titration.[5]

Results

Nuclear Magnetic Resonance Experiments. - The ^{119}Sn nmr spectrum of stannane in liquid ammonia showed initially one strong signal in the range ± 1550 ppm from neat tetramethylstannane. That signal was 750 ppm to higher field from tetramethylstannane and was resolved into a 1:3:3:1 quartet (see Fig. 2). No exact splitting constant of the quartet could be determined, because the splitting was found to increase with time. In two experiments, the splitting was measured as a function of time and was found to increase rapidly at first and then to approach a constant value. At the same time the chemical shift of the quartet moved to lower field. In both experiments the original splitting was around 150 Hz., and the final splitting, after twenty to thirty hours, was 600 to 700 Hz.

The spectra of the samples of stannane and potassium amide in liquid ammonia and the potassium stannyl prepared from KOH in monoglyme, both showed 1:3:3:1 quartets upfield from tetramethylstannane. The chemical shift of the quartet in amide solution is 770 ppm, identical within experimental error to that of stannane in pure ammonia solution. The chemical shift of the quartet in monoglyme was not measured with respect to tetramethylstannane, however a comparison was made to the quartet of the sample of stannane in liquid ammonia. The chemical shifts of those two samples did not differ by more than 50 ppm. Unlike the quartet observed for stannane in liquid ammonia, the quartets in amide solution and in monoglyme were stable with time. The splittings of the quartet lines were 103 ± 7 Hz. in monoglyme and 112 ± 4 Hz. in amide solution. Those splittings did not change appreciably during several hours.

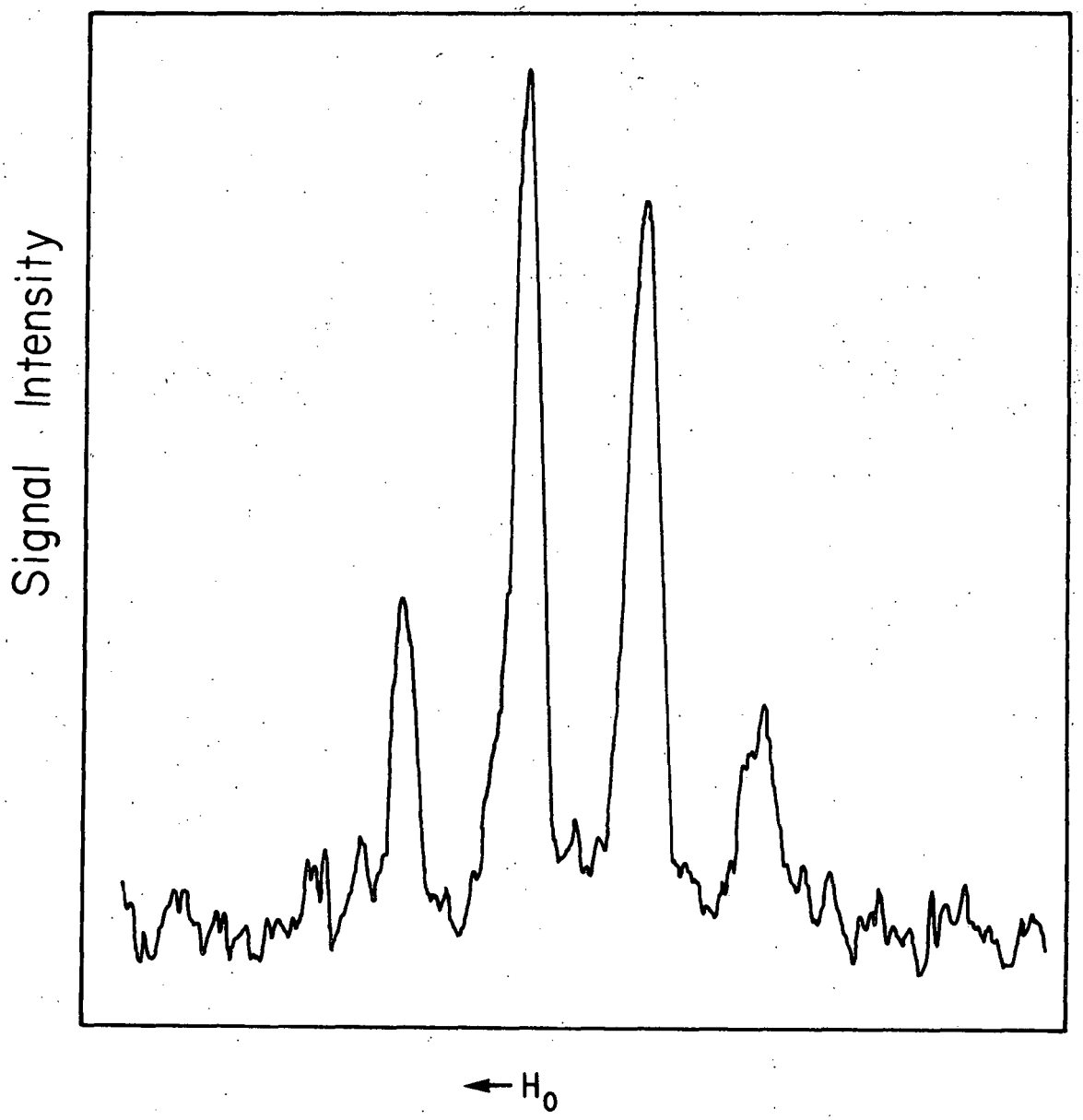

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Fig. 2. ^{119}Sn nmr spectrum of the product of the reaction of stannane with liquid ammonia at -75°.

One other signal was seen in the sample of stannane and potassium amide in liquid ammonia. It appeared 35 ± 10 ppm to lower field from tetramethylstannane and was initially less than 20 per cent as strong as the quartet. The signal was a singlet within the limits of our resolution. When the sample was warmed to -55° for two hours, the low-field signal increased appreciably at the expense of the quartet. After two hours at -55°, the two signals were of comparable intensity. A second signal was also observed in the spectrum of stannane in liquid ammonia. It grew in (also apparently at the expense of the quartet) to higher field from the quartet, and was about 25 per cent of the total signal after 30 hours. This second signal was very broad, but could not be definitely resolved into a multiplet.

The red-brown residue of the reaction of stannane and liquid ammonia at -78° showed no ^{119}Sn nmr spectrum, although it could be redissolved in liquid ammonia (estimated 0.5 M in tin) and was shown to contain tin by analysis of its thermal decomposition products. The same range was swept as for the other samples.

The stability of the nmr samples toward decomposition varied. The sample of stannane and potassium amide in liquid ammonia appeared yellow and did not give any visible sign of decomposition on standing several days at -78°. The solutions of stannane in liquid ammonia were initially clear and colorless or clear and pink. They gradually became light yellow at -78°, and tin mirrors plated out on the walls of the nmr tube above the solution. On standing several days at -78° the initially pink solutions became deep red-brown, and the initially colorless solution again became colorless. Both solutions deposited tin mirrors; the mirrors in the red-brown samples were under the liquid level.

No signals attributable to hydrogen bonded to tin were observed in the proton nmr spectrum of a solution of stannane in liquid ammonia at -70°. The sweep was 2000 Hz. to lower field and 500 Hz. to higher field from tetramethylsilane. The one noticeable feature was the ammonia signal, which changed from a broad singlet in pure ammonia to a sharp singlet shifted slightly to lower field in the solution of stannane in ammonia.

Conductivity Experiments. - When gaseous stannane (0.37 mmole) was admitted to a conductivity cell containing pure ammonia (15.9 ml at -70°) the resistance of the solution changed very rapidly for the first ten minutes, then approached a constant value. After ninety minutes without stirring, the resistance was constant within experimental error, and did not change appreciably when the solution was mixed by shaking the cell. The final resistance was 1300 + 30 ohms, which corresponds to a specific conductance of 0.0024 mhos cm^{-1}. In a separate experiment ammonium bromide (0.37 mmole) was dissolved in ammonia (15.9 ml at -70°), and the resistance of the solution was measured. The latter solution had a specific conductance of 0.0019 mhos cm^{-1}.

The Reaction of Stannane with Potassium Amide in Liquid Ammonia. - A solution (clear and pale yellow) of 0.91 mmole of potassium amide in about 1 ml of liquid ammonia was treated with 0.97 mmole of gaseous stannane at -78°. There was immediate effervescence and formation of a white precipitate. The solution became bright yellow. After one day at -78°, hydrogen was removed from the reaction vessel at -196° (found 1.21 mmoles). A small tin mirror was noticed on the walls of the reaction vessel. All volatile materials were removed by Toepler-pumping while the reaction vessel was brought to room temperature and the residue was flamed.

During that pumping 0.635 mmole of hydrogen was evolved. The condensible volatile materials were passed through a trap containing granular magnesium perchlorate to separate any unreacted stannane from ammonia. No stannane was found. A black residue remained in the reaction vessel, and hydrolysis of that residue yielded 0.212 mmole of hydrogen.

In a second experiment 4.6 mmoles of potassium amide in about 1 ml of liquid ammonia was treated with 0.71 mmole of stannane as described above, except that the reaction time was only two hours. Hydrogen (0.71 mmole) was evolved at -78°. A yellow solid remained when volatile material was removed at -78°; the solid slowly turned black and gave off hydrogen (0.629 mmole) when warmed to room temperature. Hydrolysis of the black residue resulted in 0.113 mmole hydrogen and a trace of nitrogen.

Deuterium Exchange Experiments. Stannane-d_4 (0.167 mmole) was sealed in a glass vessel with ca. 10 ml of ammonia and allowed to stand with occasional shaking at -72 ± 3° for ten hours, then with occasional shaking at -78° for five days. After five days the solution was still clear, colorless, and fluid. While volatile materials were removed at -70° by Toepler-pumping, 0.115 mmole of hydrogen was evolved (mass spectrometry showed 51% D, 89% of the hydrogen was HD). A red-brown residue remained in the reaction vessel. The volatile mixture of stannane and ammonia pumped off at -70° was separated by passing it through a trap containing magnesium perchlorate. A trace of hydrogen (0.015 mmole, 58% D) was evolved during that separation. The separation yielded 0.047 mmole stannane, which when pyrolyzed gave hydrogen that was 70% D. The residue in the original reaction vessel decomposed when it was warmed to room temperature, evolved 0.099 mmole hydrogen (88% D) and 0.026 mmole

ammonia (70% NH_2D), and left a residue presumed to be tin metal.

A second experiment, in which stannane was not reclaimed, resulted in 0.16 mmole hydrogen (57% D, again mostly as HD) evolved during removal of the volatiles, and 0.10 mmole hydrogen (90% D) from the decomposition of the residue. The starting materials had been 0.27 mmole stannane-$\underline{d}_4$ in *ca.* 1.5 ml of ammonia, and the reaction time was 4 hours at -78°.

The product which remains after removing the volatiles at -78° from the reaction of stannane with liquid ammonia, is a red-brown resinous material. This material is very unstable and decomposes instantly at room temperature to tin, hydrogen, and ammonia. In several experiments that residue was decomposed and the decomposition products were analyzed. The results are presented in Table I.

Table I. Analytical data for the residue from the reaction of stannane with liquid ammonia at -78°.

Run	1	2*	3	4	5*	6	7*	8	9
Stannane charged (mmoles)	0.561	0.532	0.380	0.301	1.013	0.677	0.610	0.915	
Hydrogen evolved at -78° (mmoles)	0.376	0.461	0.210	-----	0.638	-----	-----	-----	
Pumping time at -78° (hours)	9	10	7	6	19	11	11	8	
Hydrogen evolved from decomposition of the residue. (mmoles)	0.482	0.504	0.310	0.291	0.016	0.286	0.141	0.026	0.361
Ammonia evolved from decomposition of the residue. (mmoles)	0.125	0.126	0.103	0.105	0.004	0.091	0.034	0.006	0.084
Tin remaining in the reaction vessel after decomposition of the residue. (mmoles)	0.428†	0.493†	-----	-----	0.331‡	-----	-----	-----	
H_2/NH_3 from the residue	3.85	4.00	2.97	2.84	4.00	3.14	4.14	4.34	4.30

* In these runs the condensable volatile materials pumped off at low temperature were plotted vs. time until the curve had a constant small slope. This assured us that all the excess ammonia had been removed, and that any subsequently evolved was from the decomposition of the residue.

† Tin determined by iodometric titration.

‡ Tin determined by measuring the hydrogen evolved when dissolved in concentrated HCl.

Discussion

The ^{119}Sn nmr spectra show that stannane dissolves in liquid ammonia to yield a species containing tin coupled to three magnetically equivalent hydrogens. Because the solvent peak in the proton nmr of stannane in liquid ammonia sharpened and shifted to lower field, we infer the presence of at least a low concentration of ammonium ion.[6] The following reaction is consistent with those results.

$$SnH_4 + NH_3 \longrightarrow SnH_3^- + NH_4^+ \qquad (1)$$

Reaction 1 is also consistent with the conductivity results. The molal conductances of stannane and ammonium bromide in liquid ammonia differ by only about twenty five per cent, thus it seems reasonable to believe that stannane acts as a normal ammonium salt in liquid ammonia.

The quartets in the ^{119}Sn nmr spectra in the monoglyme and amide solutions are certainly due to the stannyl ion, and because the initial chemical shift of the signal observed for stannane in pure ammonia is identical to those quartets in amide and monoglyme, we suppose that a similar species exists in ammonia solution. The fact that the splitting between the lines of the quartet changes with time indicates that the signal is not due to a simple stannyl ion. A changing splitting could arise if stannyl ion were in rapid equilibrium with another tin species which also gave a 1:3:3:1 quartet and if the rate of interconversion from one species to the other were large in comparison to both the difference in chemical shifts of the two species and the magnitude of the larger coupling constant. Under these conditions the chemical shift and the splitting of the observed quartet would be a weighted average of

those of the two species.[7] The other condition necessary to explain the increasing splitting is that the equilibrium between the two tin species be slowly shifting from the species with the smaller coupling constant to that with the larger coupling constant.[8] Reaction 1 accompanied by the following proposed reaction is consistent with the observations.

$$SnH_3^- + NH_4^+ \overset{\text{fast}}{\rightleftharpoons} \underset{(I)}{SnH_3^-NH_4^+} \qquad (2)$$

In reaction 2, I represents an ion pair in which the J_{Sn-H} is larger than, and the chemical shift is different from, that of the free stannyl ion.[9-13] If reaction 2 occurs, the increase in the splitting of the quartet in the ^{119}Sn nmr can be explained by a mechanism that will cause reaction 2 to shift slowly to the right, i.e. one that will cause an increase in the ratio $(SnH_3^-NH_4^+)/(SnH_3^-)$. An increase in concentration would favor ion pairing and drive reaction 2 to the right. Thus if the rate of reaction 1 were limited by slow diffusion of stannane into the ammonia, one might rationalize the observed spectrum as due to a slowly increasing concentration of ions. The nmr samples were not stirred and it is reasonable that mixing might have been slow. However conductivity experiments (on much more dilute solutions) under conditions which required diffusion mixing, showed a constant resistance, indicating that reaction 1 was complete, after 90 minutes. An increase in the ammonium ion concentration could also shift reaction 2 to the right. The following hypothetical reaction provides a mechanism for increasing the ammonium ion concentration.

$$SnH_3^- + NH_3 \longrightarrow SnH_2^{2-} + NH_4^+ \qquad (3)$$

If reaction 3 actually does occur, one would expect to see another tin signal grow into the nmr spectrum, and that is as observed. However if ammonia is a sufficiently strong base to deprotonate the stannyl ion, amide ion should deprotonate it even more readily. Thus one should expect stannane to react with potassium amide in liquid ammonia to give K_2SnH_2 as well as $KSnH_3$. A second ^{119}Sn nmr signal was seen in the amide solutions, but it was at a different chemical shift from that seen in the ammonia solutions. It is possible that K_2SnH_2 would have a lower solubility in ammonia than $(NH_4)_2SnH_2$ and was not observed for that reason.[14]

A study of the reaction of stannane with potassium amide in liquid ammonia gave no evidence for the formation of K_2SnH_2. The only ^{119}Sn nmr signal observed, other than that of SnH_3^-, had a chemical shift different from any signal observed in solutions of stannane in ammonia. Because there is a large amount of hydrogen evolved when stannane is added to amide in ammonia, we conclude that the precipitate formed concurrently with that hydrogen is an ammonolysis product (and is probably responsible for the low field ^{119}Sn nmr signal). If the only side reaction were the formation of K_2SnH_2, one would not expect the evolution of hydrogen. Furthermore we cannot interpret the stoichiometry of the hydrogen evolved when these reaction mixtures are decomposed, in a way consistent with the formation of K_2SnH_2. Because the analogous acid-base reaction does not appear to occur with amide (which is certainly a stronger base than ammonia), we must conclude that neither does the proposed reaction 3 actually occur, and we are left with at best only a partial rationalization of the ^{119}Sn nmr spectrum of stannane in liquid ammonia.

There is another disturbing point to be made concerning the

explanation of the nmr and conductivity results. Reaction 1, which we have proposed to explain both results, would be expected to have a finite reversibility, and through the reverse reaction provide a mechanism for exchange of hydrogen between stannyl ion and the solvent, ammonia. The result of allowing deuterostannane and liquid ammonia to stand together several days is not that expected of a rapid exchange reaction. Instead of losing all the deuterium label to the ammonia, stannane retains a surprising amount of it. Of the stannane-$\underline{d}_4$ charged, 28 per cent is recovered as stannane, a result that indicates reaction 1 is reversible. However the label has not disappeared, but is only lowered by 30 per cent. During removal of volatile materials at -70 ± 3°, hydrogen (greater than 89% HD) corresponding to 34 per cent of the stannane charged is evolved. The last portion of hydrogen (evolved when the red-brown residue is warmed) is even more deuterium rich, being 88% D. If reaction 1 does occur it appears to be a poor mechanism for exchange.

There are three distinct parts to this reaction of stannane-$\underline{d}_4$ with ammonia, two of which involve contradictions. First, if reaction 1 is reversible as indicated by the recovery of stannane, one would expect <u>all</u> the label to be lost rather than only 30 per cent. Second, the evolution of so much HD during Toepler-pumping strongly suggest that both stannane-$\underline{d}_4$ and ammonia are involved in the reaction which produces the hydrogen, i.e. that the reaction is ammonolysis. However ammonolysis is unlikely because only two moles of hydrogen are evolved per stannane charged; ammonolysis requires more hydrogen. Third, the appearance of 88 per cent D in the hydrogen from the residue is strong evidence that the residue is not formed from the SnH_3^- ion, because exchange of the deuteron

off the ammonium ion would assure that the label would be at most only 75 per cent D.

The analytical data (Table I) for the red-brown residue of the reaction of stannane with liquid ammonia at -78°, are also disturbing. The ratio of hydrogen to ammonia evolved when the residue is decomposed at room temperature is 4:1 (within experimental error) for all but three runs. Run 9 gives the hydrogen and ammonia evolved at -78° when the residue was pumped on for several hours after unreacted stannane and ammonia were removed. Apparently the residue decomposes slowly even at -78°, and the ratio of hydrogen to ammonia evolved at that temperature (4:1 within experimental error) is further evidence that a pure compound is formed which contains hydrogen and ammonia in that ratio. We conclude that in runs 3, 4, and 6 for which H_2:NH_3 is less than 4:1, ammonia was not completely removed prior to decomposition of the residue. Tin is also present in the residue, and is apparent as the metal in the decomposition products. The runs for which tin was determined show that there may be as many as three tin atoms per ammonia in the residue. The ratio of hydrogen to ammonia requires at least two stannanes per ammonia; fewer tin atoms cannot provide enough bonding sites to accomodate all the hydrogens. The results of the hydrogen evolved at -78° and the total tin remaining after decomposition are consistent with the empirical formula Sn_2NH_{11}, if one assumes that all H_2 evolved at -78° is from decomposition of the residue. Two possible formulations of Sn_2NH_{11} are the hemi-ammoniate of stannane(II) or the ionic compound(III)

$SnH_4 \cdot NH_3 \cdot SnH_4$ II

$Sn_2H_7^- \; NH_4^+$ III

where $Sn_2H_7^-$ may be thought of as distannane bonded to a hydride ion. Unfortunately neither of these species is particularly satisfying as regards other evidence from nmr or conductivity experiments of stannane in liquid ammonia.

In summary, the results of the exchange experiments lead us to believe that there are three different species in solution. The fact that two ^{119}Sn nmr signals were observed and that the red-brown residue was shown to have no apparent signal, makes the nmr consistent with three species. We suggest that one species is SnH_3^-, either free or ion paired, another is the material which eventually becomes the residue when the solvent is removed, and the third is an unknown species which presumably could explain the ^{119}Sn nmr results if identified. We have shown that the latter is a product which forms from SnH_3^- (nmr signal grows in as the quartet decays), it appears to higher field than SnH_3^- in the nmr, and the hydrogen evolved when it decomposes in ammonia is almost all HD. These observations as well as the changing quartet in the ^{119}Sn nmr, might all be explained by assuming the unknown species to be SnH_2^{2-}, however the lack of evidence for such an ion in the reaction of stannane with potassium amide in liquid ammonia rules it out.

In view of the interesting results of these several experiments on stannane in liquid ammonia and the present lack of any unifying explanation of those results, it is appropriate to indicate some experiments which might lead to a resolution of the problem. A few of those are as follows -

Tin nmr with stannane enriched ten-fold in ^{119}Sn would require 1/100 the number of scans to

achieve the signal to noise ratio we observe in our spectra. The spectra could be recorded faster, thus minimizing resolution problems due to magnetic field drift and perhaps complications due to signal-averaging. Perhaps a clue to the composition of the high-field species or a signal due to the red-brown residue would result.

The proton nmr should be investigated over a larger chemical shift range. The proton nmr of the germyl ion is in the range that we studied, but because tin is more electropositive than germanium it is possible that diamagnetic shielding would cause the protons on stannyl ion to be at higher fields. Of course proton nmr for potassium stannyl should be done as a reference for comparison to any signal observed for solutions of stannane in ammonia.

Determination of the resistance of a solution of the red-brown residue redisolved in liquid ammonia, might suggest whether that material ionizes or not.

The precipitate formed in the reaction of stannane with potassium amide in liquid ammonia might be isolated and analyzed. If it is an ammonolysis product it would be interesting in itself, if not its

identification might help to explain the nmr results.

There are of course many other experiments which might prove fruitful. Some are obvious, some not so obvious. Those above are only a few, offered as a possible starting point to anyone who finds the problem interesting enough to pursue.

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9. According to concepts discussed by Bent,[10] one should expect the s character of the valence shell orbitals in SnH_3^- to be less than sp^3 in the orbitals directed to hydrogens and greater than sp^3 in the lone pair orbital. Thus if a partial bond were to form from tin to a fourth hydrogen, one would expect a change in hybridization of tin to increase s character in the orbitals directed to the three original hydrogens. It has been shown that coupling constants to tin are proportional to the per cent s character of the tin orbital involved in the bond to the coupling nucleus.[11-13] Thus the result of a hydrogen-bonded ion pair between SnH_3^- and NH_4^+ would be an increase in J_{Sn-H}. If a hydrogen-bonded ion pair is actually responsible for the observed change in J_{Sn-H}, it is reasonable that the change would

not be observed for solutions of potassium stannyl in liquid ammonia, because potassium ion cannot hydrogen-bond. Indeed, no such change is observed.

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Part IV. PREPARATION OF POTASSIUM STANNYL IN NONAQUEOUS SOLVENTS

Abstract

Potassium stannyl has been prepared by the reaction of stannane with slurries of finely divided KOH in both dimethylsulfoxide and monoglyme, and by the reaction of stannane with a standard solution of $KGeH_3$ in diglyme. The preparation of CH_3SnH_3 and $C_2H_5SnH_3$ by the reaction of CH_3I and C_2H_5I with these solutions verifies that $KSnH_3$ was actually formed. Reactions of $KSnH_3$ solutions with several lewis acids resulted in apparent decomposition of the stannyl ion.

Introduction

The discovery that weak acids can be deprotonated by slurries of KOH in non-hydrogen-bonding solvents,[1] and that solutions of the germyl ion, GeH_3^-, react with lewis acids to give complex ions,[2,3] prompted interest in similar reactions with stannane. The stannyl ion, SnH_3^-, had been previously prepared only in liquid ammonia,[4] and we hoped to demonstrate that solutions of $KSnH_3$ could be prepared in more conveniently handled solvents.[5] It was also thought that such solutions might be used as a means to interesting tin compounds. Only the first objective was achieved.

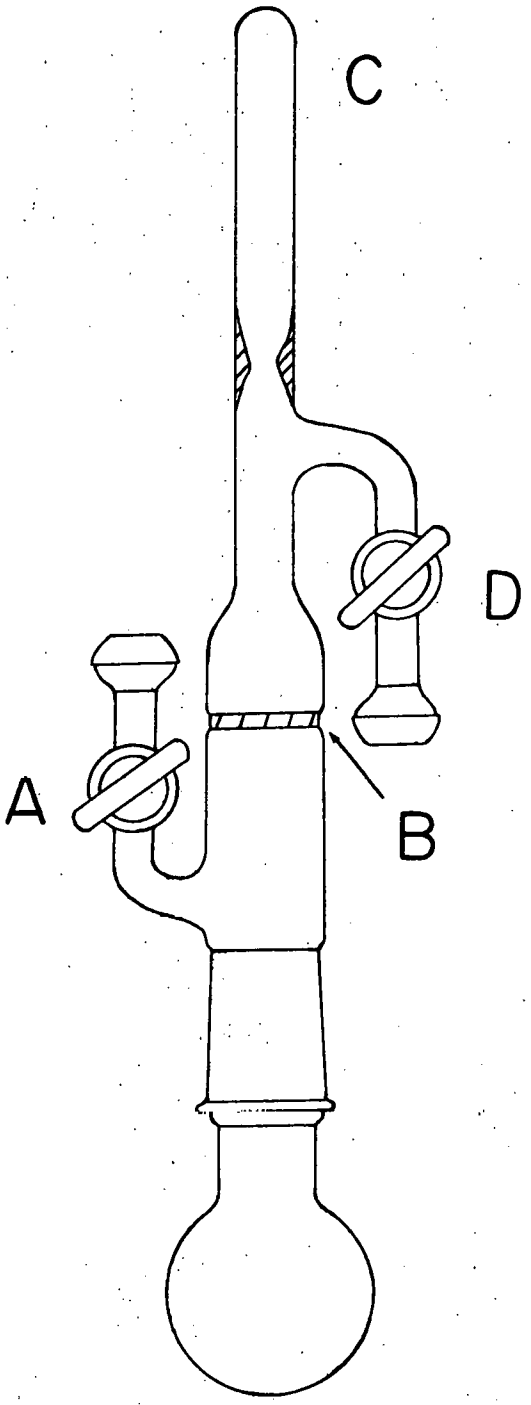
Experimental and Results

Materials and General Procedures. - Stannane was prepared as in part I, and monoglyme as in part II. Diglyme was distilled at atmospheric pressure from KOH (bp. 159-161°), then at reduced pressure from $LiAlH_4$. Dimethylsulfoxide (Matheson, reagent grade) was used without further purification. Standard solutions of $KGeH_3$ in diglyme were graciously provided by Mr. Robert Dreyfuss.[6]

Potassium Stannyl in Dimethylsulfoxide. - Demethylsulfoxide (DMSO, 10 ml) and powdered KOH (5.3 gram) were placed in a round-bottomed flask equipped with a stopcock, and outgassed on the vacuum line for five minutes at room temperature. While the slurry was stirred magnetically, stannane 0.46 mmole) was expanded into the reaction vessel and allowed to react; a tin mirror formed on the walls of the flask almost immediately. After 20 minutes, volatile products were Toepler-pumped out of the flask (found 0.28 mmole H_2, no unreacted stannane), the stopcock was closed, and the reaction vessel was removed from the vacuum line and placed in a dry-nitrogen glove bag. The product solution was filtered into a second round-bottomed flask, then the filtrate (now free of KOH) was returned to the vacuum line and outgassed. A solution of excess CH_3I in DMSO was added dropwise while stirring, and volatile products were pumped off after each addition. After addition was complete, CH_3SnH_3 (0.17 mmole, 37% yield based on stannane) was separated from unreacted CH_3I and identified by mass and infra-red spectra. A similar experiment in which C_2H_5I was added to the $KSnH_3$ solution in DMSO gave $C_2H_5SnH_3$ in 29% yield. All handling of the solutions was done quickly to avoid loss due to decomposition, signs of which were apparent at room temperature.

Potassium Stannyl in Monoglyme. - A method similar to that outlined above was used to prepare potassium stannyl in monoglyme except that the reaction temperature was -20° and the reaction vessel (Fig. 1) was designed so that filtration of the slurry could be done quickly and without exposure to the nitrogen atmosphere. This was necessary because the $KSnH_3$ decomposed more readily in monoglyme than in DMSO. Powdered KOH (0.2 gram) and monoglyme (ca. 3 ml) were put into the round bottomed flask and the system was outgassed at -78° through A. Stannane (2.30 mmoles) was condensed into the flask at -196°, then the slurry was brought to -20° and stirred 15 minutes. A tin mirror formed on the walls of the flask and the slurry turned yellow. The apparatus was inverted, and the slurry was filtered through a medium porosity glass disc (B) into C which was held at -196°. Hydrogen was Toepler-pumped out through D (found 2.25 mmoles), then the filtrate was warmed to -40° and concentrated by pumping off some of the solvent (estimated final concentration, 1 M). The result was a light amber solution that showed the expected 1:3:3:1 quartet in the ^{119}Sn nmr spectrum.

Potassium Stannyl in Diglyme. - Stannane (0.266 mmole) was condensed onto 7.07 ml of a 0.035 ± 0.0004 M solution of $KGeH_3$ in diglyme (0.247 ± 0.004 mmole, the titer of this solution was determined by adding water to an aliquot, measuring the GeH_4 evolved, and titrating the KOH formed with aqueous HCl), the solution was brought to -40° and allowed to warm to -20° over a period of four hours. The reaction was mixed by occasional shaking. Volatile products were removed at -60° (found 0.244 mmole GeH_4 and a trace of H_2). A small tin mirror had formed on the wall of the flask. The clear colorless solution of $KSnH_3$ could be stored



XBL 709-6557

Fig. 1. Apparatus for the synthesis of potassium stannyl by the reaction of stannane with potassium hydroxide in monoglyme.

one hour without apparent decomposition. Addition of CH_3I (0.386 mmole) at 0° gave SnH_3CH_3 (0.205 mmole after 20 minutes).

Reaction of Solutions of $KSnH_3$ with Lewis Acids. - The solutions of $KSnH_3$ in DMSO were treated with the lewis acids CO_2, BCl_3, BF_3 and B_2H_6. In each case addition of the acid at room temperature seemed only to hasten the decomposition of the potassium stannyl. In general the solution darkened to gray or black, and hydrogen was evolved. Carbon dioxide was absorbed at -75° by a dilute solution (0.035 M) of $KSnH_3$ in diglyme with no apparent change in the solution. As this solution was warmed to room temperature, it became red-brown and cast down a flocculent precipitate of the same color. At room temperature the solution steadily darkened, but did not effervesce. After six hours at 0° the solution was clear and colorless, the precipitate had turned gray, and decomposition had occurred, evidence of which was the large amount of hydrogen which had evolved.

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