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The Stannonium Ion in Acid Solutions

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Stannane reacts slowly with strong aqueous acids below −50° to give 1 mol of hydrogen per mole of stannane. The resulting solutions evolve an additional 2 mol 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 1 mol 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 organotin cations was reported as early as 1923.[1] Since then, many investigations of organotin 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 Section

Stannane was prepared by a published method.[5] Fluorosulfuric acid (Research Organic/Inorganic Chemistry Co., 99%) was distilled under dry nitrogen (bp 161–162°). Baker and Adamson reagent grade potassium sulfate was used without further purification. Hydriodic acid (Merck reagent grade) was distilled under dry nitrogen (bp 127°), diluted with distilled water to 49%, stored in the dark, and used within 1 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.

Tin(II) was determined by treatment with standard triiodide solution, followed by titration with standard thiosulfate solution.

The Stoichiometry of Reactions of Stannane with Acids.—A diagram of the apparatus is given in Figure 1. The space between D and C was evacuated, and then 20 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, break-seal C was opened and 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 and measured. Stopcock D was then closed, and the solution was warmed to room temperature. During warming, the aqueous solutions effervesced gently for about 10 min. 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 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 G 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. 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 1–4 *M* in tin. Because natural tin contains about 8% ^{119}Sn, the samples were effectively only 0.08–0.32 *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°.

Conductivity Experiments.—The conductivity of stannane 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 canceled out with a decade capacitance system. The measurements

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[1] C. A. Kraus and C. C. Callis, *J. Amer. Chem. Soc.*, **45**, 2624 (1923).

[2] For references to the original literature see R. S. Tobias, *Organometal. Chem. Rev.*, **1**, 93 (1966).

[3] W. L. Jolly and T. Schmitt, *Inorg. Chem.*, **6**, 344 (1967).

[4] The SnH_3^+ ion could equally well be called the stannyl cation. For a discussion of the nomenclature of such species see G. A. Olah, *Science*, **168**, 1298 (1970).

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

[6] S. U. Pickering, *Phil. Mag.*, [5] **36**, 111 (1893); S. U. Pickering, *Chem. Ber.*, **26**, 277, 2307 (1893); L. H. Brickwedde, *J. Res.*, **42**, 309 (1949).

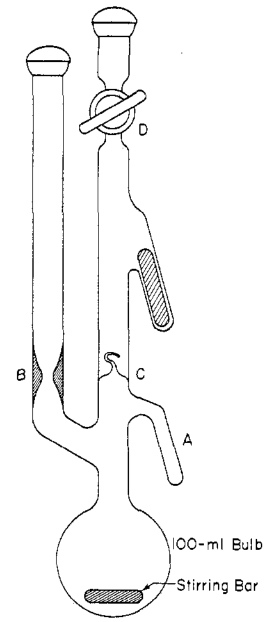

Figure 1.—Apparatus for the reaction of stannane with acids at −78°.

were made at −78.5° (Dry Ice–trichloroethylene slush), and the temperature was checked with a copper–constantan thermocouple. Stannane was condensed temporarily at −196° in a small tube connected to the conductivity cell by a break-seal. 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.

Results and Discussion

The results of the reactions 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 (eq 1 and 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	Temp, °C	SnH_4 charged, mmol	Reaction time, hr	H_2 evolved at low temp, mmol	H_2 evolved at room temp/H_2 evolved at low temp
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

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

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

Indeed, when stannane was treated with fluorosulfuric acid at −78°, the stannane was completely consumed and 1 mol of hydrogen per mole of stannane was evolved in a relatively short time. In four experiments with reaction times of from 3 to 18 hr, 0.65, 1.56, 0.29, and 0.49 mmol of stannane were allowed to react at −78° with HSO_3F. The amounts of hydrogen evolved were 0.64, 1.63, 0.30, and 0.51 mmol, respectively. These results suggest the 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 Figure 2). As the solu-

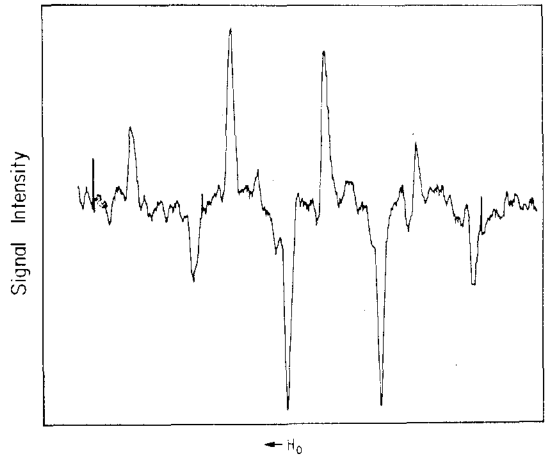

Figure 2.—The ^{119}Sn nmr spectrum of stannonium ion in fluorosulfuric acid at −78°.

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), $J_{^{119}Sn-H}$ is 1933 Hz.[12] 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.[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).

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The Synthesis and Characterization of the Halostannanes

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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-

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