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REACTIONS OF SELECTED METHYL TIN(IV) AND-GERMANIUM(IV) HALIDES IN ANHYDROUS HF, HSO_3F AND HSO_3CF_3*

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SUMMARY

Acidolysis in HSO_3F or HSO_3CF_3 of either tetramethylgermane or trimethylchlorogermane leads, depending on reaction conditions, to $(CH_3)_3GeSO_3X$ or $(CH_3)_2Ge(SO_3X)_2$ with X = F or CF_3. All compounds are obtained as colorless liquids with tetracoordinated germanium and monodentate sulfonate groups. The compounds are characterized by ^{19}F - and ^{1}H - NMR and vibrational spectra. All but $(CH_3)_2Ge(SO_3F)_2$ are obtained in analytically pure form.

Dimethyltin(IV) fluoride is found to act as an ampholyte in anhydrous HF as evidenced by the isolation of $Li_2[(CH_3)_2SnF_4]$, $K[(CH_3)_2SnF_3]$ and a material of the composition $(CH_3)_2SnTaF_7$. Vibrational and ^{119} Sn Mössbauer spectra are reported and discussed. Tin is found to be hexacoordinated in all compounds with linear or nearly linear C - Sn - C groups.

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* Dedicated to Professor Friedo Huber on the occasion of his 60th Birthday.

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INTRODUCTION

Strong protonic acids or superacids may be used in the synthesis of inorganic, organic or organometallic compounds in two general ways: (a) as ionizing or protonating reaction media which may or may not get involved themselves in the overall reaction, and (b) as reactants in acidolysis reactions with direct involvement in the reaction.

Examples are tetraalkyltin and alkyltin(IV)chlorides, where depending on the nature and the mole ratio of the reactants, trialkyl-, dialkyl-or alkyl chlorotin(IV) derivatives of the acids are formed. With acids like anhydrous HF[1], HSO_3X (X=F,Cl,CF_3,CH_3orC_2H_5)[2]-[5] or HPO_2F_2[5] disubstitution normally occurs, with Sn-Cl bonds preferentially cleaved over Sn-C bonds resulting in the evolution of HCl and, or alkane. Of the derivatives obtained, the solid dimethyltin(IV)-derivatives of strong acids are found to have polymeric structures as shown by $(CH_3)_2SnF_2$[6] and $(CH_3)_2Sn(SO_3F)_2$[7] which have linear C - Sn - C groupings, which in turn give rise to rather large quadrupole splittings in their ^{119}Sn Mössbauer spectra.

Our synthetic studies have recently been extended to the superacid media HSO_3F - $M(SO_3F)_4$[8], M = Pt or Sn, and HF - MF_5[9], M = Sb, Nb or Ta, as well as into the 'basic' region of the HSO_3F acid system to generate anionic complexes of the type $M^I_n[(CH_3)_2Sn(SO_3F)_{2+n}]$, M^I = K or Cs, and n=1 or 2, again with linear C - Sn - C groups, as is evident from their ^{119}Sn Mössbauer spectra [10]. The two principal Mössbauer parameters, the isomer shift δ and the quadrupole splitting ΔE_Q have recently been found to decrease linearly with increasing nucleophilicity of the corresponding acid-or superacid counter anion[10] for these dimethyl derivatives of acids and superacids.

Our study described here is concerned with two related aspects:

(i) A more extended use of anhydrous HF (AHF) as a protonic reaction medium in which both the acidic and basic region of the solvent system is invest-

igated. On the acidic side, dimethyltin(IV) salts with fluorometallate anions are obtainable, e.g. $(CH_3)_2Sn[TaF_6]_2$[9]. The ability of tantalum to form fluoroanions like $[TaF_7]^{2-}$[11] suggests the possible existence of $(CH_3)_2Sn[TaF_7]$. On the basic side, anions like $[(CH_3)_2SnF_4]^{2-}$[12] and $[(CH_3)_2SnF_3]^-$[13] have been obtained from aqueous solutions as potassium or ammonium salts, but both are poorly characterized and may be impure as the reported ^{119}Sn Mössbauer spectrum [14] for $K_2[(CH_3)_2SnF_4]$ suggests.
(ii) The use of the sulfonic acids HSO_3F and HSO_3CF_3 in the solvolysis of tetramethylgermanium(IV) or of methylgermanium chlorides will be described. So far only $(CH_3)_3GeSO_3CF_3$ is known [15][16], but in one instance [15] only the IR spectrum is reported, while in the second report a different synthetic route, the acidolysis of bis(trimethylgermyl)carbodiimide is the principal method of preparation [16].

EXPERIMENTAL

Chemicals

Tetramethylgermane and the methylchlorogermanes were obtained from the Ventron Corporation and distilled in vacuo before use. Tantalum(V) fluoride (Ozark Mahoning), fluorosulfuric acid (Allied Chemicals), trifluoromethylsulphuric acid (3M),$AgSO_3CF_3$(Aldrich) and anhydrous HF (Matheson) were also obtained commercially. $(CH_3)_2SnF_2$ was synthesised from $(CH_3)_2SnCl_2$ (Ventron Corp.) and aqueous HF [1]. All remaining starting materials, e.g. KCl, Li_2CO_3 and LiF were obtained commercially in the highest degree of purity available and used without further purification.

Technical grade HSO_3F was doubly distilled at atmospheric pressure [18], while HSO_3CF_3 was distilled at reduced pressure (10 to 20 Torr) from H_2SO_4 before use. AHF was used without further purification.

Instrumentation

Our instrumentation to obtain ^{119}Mössbauer spectra and the calibration of the spectra have been described recently [17]. Raman spectra were obtained with either a Cary 81 or a Spex Ramalog spectrophotometer, equipped with a helium-neon laser (Spectra Physics Model 125) at λ=632.8 nm or an argon ion laser (Spectra Physics Model 164) at λ=514.5 nm, respectively.

Infrared spectra were obtained on Perkin-Elmer 457 or 598 grating spectrophotometers, or on a Pye Unicam SP 1100 instrument. Silver chloride and -bromide were used as window materials. Due to the reactivity of the samples, spectra were studied on thin films. ^{19}F NMR spectra were obtained on a XL-100 spectrometer (Varian Associates) and a Varian T-60 instrument was used for ^{1}H NMR spectra.

Reactions in AHF were performed in vessels made from Kel-F, a fluorochlorocarbon, sufficiently transparent to monitor the reaction visually. The reaction vessels of 25-30 mL volume were equipped with Teflon-coated spin bars and fitted to Monel tops, with Hoke valves. The manifold used for the transfer of volatiles and further details on equipment used in this part of the study have been reported previously [1].

All other reactions were performed in Pyrex reaction vials of about 40-mL capacity, fitted with Kontes Teflon stem valves. Volatile materials were handled using vacuum-line techniques. Solids were handled in a Vacuum Atmospheres Corp. "Dri Lab" Model No. HE-43-2, filled with purified dry nitrogen and equipped with a "Dri-Train" Model No. HE-93-B circulating unit.

Chemical analyses for C and H were performed by Mr. P. Borda of this Department. Additional microanalysis was carried out by Analytische Laboratorien, Gummersbach F.R.G.

Synthetic reactions and Product Isolation

(i) Trimethylgermanium (IV) sulfonates, $(CH_3)_3GeSO_3X$, X=CF_3 or F

A common synthetic procedure is adopted for all acidolysis reactions: To a known amount of the sulfonic acid, kept at liquid N_2 temperature, a slight to moderate excess over the equimolar amount of either $(CH_3)_4Ge$ or $(CH_3)_3GeCl$ is added in vacuo. Details are summarized in Table 1. The reaction mixture is allowed to warm to room temperature and stirred magnetically in an atmosphere of dry nitrogen until all gas evolution ceases. Volatile reaction products (CH_4 or HCl) are collected and identified by their mass and infrared spectra. After reaction overnight, the excess of $(CH_3)_4Ge$ or $(CH_3)_3GeCl$ is removed in vacuo. The course of the reaction is followed by weight. Details of individual reactions: The fluorosulfate $\underline{(CH_3)_3GeSO_3F}$ is prepared in nearly quantitative yield from $(CH_3)_4Ge$ and HSO_3F in 15 hours. After removal of all volatiles a colorless, moisture sensitive, viscous liquid is obtained.

Analysis: Calculated for $C_3H_9FGeO_3S$: C, 16.62 and H,4.19%. Found: C, 16.66 and H 4.24%. NMR: ^1H, single line at 0.80ppm rel to TMS, ^{19}F, single line at 42.5 ppm rel. to $CFCl_3$. An identical product is obtained from HSO_3F and an excess of $(CH_3)_3GeCl$. $\underline{(CH_3)_3GeSO_3CF_3}$ is prepared from $(CH_3)_4Ge$ and freshly distilled HSO_3CF_3 or alternatively from $(CH_3)_3GeCl$ and HSO_3CF_3 within 15 hours. After removal of all volatiles the remaining viscous liquid is purified by distillation at 5 Torr (b.p. 70°C) and isolated as a colorless, moisture sensitive liquid.

Analysis: Calculated for $C_4H_9F_3GeO_3S$: C,18.00 and H,3.40%.
Found: C, 18.20 and H 3.20% NMR: ^1H, single line at 0.80ppm ^{19}F, single line, - 1.2ppm rel. to $CFCl_3$

An identical product is obtained from $(CH_3)_3GeCl$ and $AgSO_3CF_3$ as follows. A solution of 12.34 mmoles of $AgSO_3CF_3$ dissolved in ~50mL freshly distilled acetonitrile is added to 12.34 mmoles of $(CH_3)_3GeCl$, also dissolved in ~50mL acetonitrile. The white precipitate of AgCl which forms immediately is filtered off and the volume of the filtrate is reduced to ~10mL in vacuo. The solution is again filtered and the remaining amounts of acetonitrile removed in vacuo at - 20°C. The final product corresponding to 12.31 mmoles of $(CH_3)_3GeSO_3CF_3$ is identified by its infrared spectrum.

(ii) Dimethylgermanium(IV)trifluoromethylsulfate $(CH_3)_2Ge(SO_3CF_3)_2$

The general procedures outlined above are amended as follows : (a) an excess of HSO_3CF_3 (47.0 mmol) is allowed to react with $(CH_3)_4Ge$ (11.6 mmol), (b) the reaction mixture is heated to 80°C for 2 days, and (c) product separation is by fractional distillation at 5 Torr with HSO_3CF_3 boiling at 42°C and $(CH_3)_2$ Ge $(SO_3CF_3)_2$ at 75°C. The final product is a moisture sensitive, clear, colorless liquid.

Analysis, calculated for $C_4H_6F_6GeO_6S_2$, C,11.99 and H, 1.51%. Found: C, 11.72 and H 1.50%.

(iii) Potassium dimethyltrifluorostannate $K[(CH_3)_2SnF_3]$ and lithium dimethyltetrafluorostannate $Li_2[(CH_3)_2SnF_4]$

To obtain $K[(CH_3)_2SnF_3]$, 760 mg of $(CH_3)_2SnF_2$ or 4.07 mmoles are combined with an equimolar amount of freshly dried KF and loaded into a Kel-F reactor together with a magnetic stirring bar. About 5mL of AHF is distilled onto the reaction mixture which is allowed to react at room temperature for about 20 hours. The solid reactants partly dissolve. The solvent is removed in vacuo and $K[(CH_3)_2SnF_3]$ is isolated as a white solid that does not melt below 250°C.

Analysis: Calculated for $C_2H_6F_3KSn$: K, 15.97; Sn, 48.41; C, 9.81; H, 2.47; and F, 23.28% Found: K, 15.70; Sn, 48.20; C, 9.29; H, 2.46 and F, 23.43% Total 99.08%.

Li_2 $[(CH_3)_2SnF_4]$ is obtained in a similar manner from either a 1:1 molar mixture of Li_2CO_3 and $(CH_3)_2SnF_2$ or a 2:1 molar mixture of LiF and $(CH_3)_2SnF_2$in ~ 7mL of AHF. $Li_2[(CH_3)_2SnF_4]$ is a high melting, white solid (m.p. > 250°C), obtained from a clear solution after removal of all HF in vacuo.

Analysis: Calculated for $C_2H_6F_4Li_2Sn$; Li, 5.81; Sn, ·49.75; C,10.07; H, 2.53 and F, 31.84%. Found: Li, 5.71; Sn, 50.05; C, 10.00; H, 2.56 and F, 31.84%. Total: 100.16%.

(iv) Dimethyltin(IV) heptafluorotantalate(V): $(CH_3)_2Sn[TaF_7]$

The synthetic procedure previously reported [9] for the preparation of $(CH_3)_2Sn[TaF_6]_2$ is adopted here for an equimolar mixture of $(CH_3)_2SnF_2$ and TaF_5, suspended in about 15mL of AHF. The reaction mixture is magnetically stirred for 1 week at room temperature, with solid material persisting throughout this period. The AHF is removed in vacuo and a moisture sensitive, white solid is obtained.

Analysis: Calculated for $C_2H_6F_7SnTa$: Sn, 25.65; Ta, 39.11; C, 5.19; H, 1.39 and F, 28,74% Found: Sn, 26.25; Ta, 39.10; C, 5.13; H 1.30 and F 28.28% Total: 100.06%.

RESULTS AND DISCUSSION

Synthesis: *Acidolysis reactions of methylgermanium chlorides of the type* $(CH_3)_nGeCl_{4-n}$, n=0,1,2,3or4, in HSO_3CF_3 proceed generally along the same lines as those of the corresponding methyltin(IV)chlorides. However there are interesting differences as is evident from the reaction summary in Table 1. While both $GeCl_4$ and $SnCl_4$ will not react with HSO_3CF_3 under the conditions employed, this lack of reactivity is also extended to CH_3GeCl_3 and $(CH_3)_2GeCl_2$. The corresponding methyltin(IV) compounds react readily at roor temperature, resulting in the formation of $(CH_3)_2Sn(SO_3CF_3)_2$ and $CH_3SnCl(SO_3CF_3)_2$[4] Substantially reduced reactivity is also noted for $(CH_3)_4Ge$ and $(CH_3)_3GeCl$. At room temperature, even with HSO_3CF_3 in a moderate excess, only mono-substitution will occur with release of CH_4 or HCl respectively. From a synthetic point of view, reactions with $(CH_3)_4Ge$ or $(CH_3)_3GeCl$ in excess are preferred, because the work-up of the reaction products is facilitated by the higher volatility of the methylgermanium(IV) compounds. Distillation of $(CH_3)_3GeSO_3CF_3$ at reduced pressure allows its

TABLE 1

Reactions of methylgermanium chlorides, $(CH_3)_nGeCl_{4-n}$ (n=0-4), with HSO_3CF_3

Reaction	Substrate	Amount [mmol.]	HSO_3CF_3 [mmol.]	Reaction Temp.[C°]	Time [Hours]	Products
1	$(CH_3)_4Ge$	26.1	10.1	25°	15	$(CH_3)_3GeSO_3CF_3+CH_4$ +unreacted $(CH_3)_4Ge$
2	$(CH_3)_3GeCl$[a]	28.0	7.0	25°	15	$(CH_3)_3GeSO_3CF_3+HCl$ +unreacted$(CH_3)_3GeCl$
3	$(CH_3)_4Ge$[a]	12.0	25.0	25°	15	$(CH_3)_3GeSO_3CF_3+CH_4$ +unreacted HSO_3CF_3
4	$(CH_3)_3GeCl$[a]	11.0	23.0	25°	15	$(CH_3)_3GeSO_3CF_3+HCl$ +unreacted HSO_3CF_3
5	$(CH_3)_4Ge$[b]	11.6	47.0	80°	48	$(CH_3)_2Ge(SO_3CF_3)_2+CH4$ +unreacted HSO_3CF_3
6	$(CH_3)_2GeCl_2$	9.3	19.3	80°	168	No Reaction
7	$CH_3\ GeCl_3$[c]	11.2	34.0	80°	48	No Reaction
8	$GeCl_4$[c]	12.1	48.5	80°	48	No Reaction

[a] Slow warming to 25°, [b] Slow warming to 25°, followed by heating at 80°

[c] 3mL. of benzene was added as solvent

purification. Samples obtained directly are often slightly yellow or light brown due to side-reaction of HSO_3CF_3 with grease.

Because all acidolysis reactions are followed by weight, analysis is confined to the determination of the C and H contents. The reactions described here leading to $(CH_3)_3GeSO_3CF_3$ are simpler and more straightforward than the acidolysis of bis(trimethylgermanium) carbodiimide [6] and even the reaction between $AgSO_3CF_3$ and $(CH_3)_3GeCl$ proceeds far more readily and with a higher yield in acetonitrile than in methylene chloride [16] possibly due to the higher solubility of $AgSO_3CF_3$ in acetonitrile. Acidolysis of $(CH_3)_4Ge$ in an excess of HSO_3CF_3 at 80°C yields after 2 days the previously unreported $(CH_3)_2Ge(SO_3CF_3)_2$ again as viscous liquid. Purification by fractional distillation is possible and advantageous, yielding a colorless reaction product. The product is capable of ligand redistribution with $(CH_3)_4Ge$ under slightly forcing condition according to:

$$(1)\quad (CH_3)_4Ge + (CH_3)_2Ge(SO_3CF_3)_2 \xrightarrow[2d]{80°C} 2\ (CH_3)_3GeSO_3CF_3$$

Similar scrambling reactions proceed for methyltin(IV) sulfonates at room temperature within a few hours [4].

Extension of the acidolysis reactions from HSO_3CF_3 to HSO_3F is possible with a similar reactivity towards HSO_3F noted for both $(CH_3)_4Ge$ and $(CH_3)_3GeCl$. The lower thermal stability of $(CH_3)_3GeSO_3F$ and the previously [18] noted tendency of germanium fluorosulfates to eliminate SO_3, make distillation even at reduced pressure inadvisable. Separation problems appear also to prevent isolation of $(CH_3)_2Ge(SO_3F)_2$. The reaction of $(CH_3)_4Ge$ with a 3-fold excess of HSO_3F at 55°C results in a clear liquid when all CH_4-evolution has stopped after about 24 hours. Removal of all volatiles yields a extremely hygroscopic liquid product with NMR characteristics slightly different from those found for $(CH_3)_3GeSO_3F$: a single ^{19}F resonance at 41.0 vs. 42.5 ppm rel. to $CFCl_3$and a single ^1H resonance at 0.71 vs.0.8ppm. The IR spectrum indicates absence of HSO_3F and shows the expected band pattern for monodentate SO_3F- groups, however, microanalysis is unsatisfactory. A subsequently noted slow darkening of the product points to thermal instability.

The evidence suggests that $(CH_3)_2Ge(SO_3F)_2$ is formed, however problems in isolating and analysing the extremely moisture sensitive liquid prevent its complete characterisation. The observed rather moderate reactivity of $(CH_3)_4Ge$ with HSO_3CF_3 allows comparison with an earlier study [19] of the reactions of $(CH_3)_4Si$ and $(CH_3)_4Sn$ with the same acid. While $(CH_3)_4Si$ fails to react even at 80°C, $(CH_3)_4Sn$ reacts instantanously when added to HSO_3CF_3 cooled with liquid N_2. Tetramethylgermanium appears to fall between these two extremes in its reactivity.

The trifluoromethylsulfates $(CH_3)_3SiSO_3CF_3$ and $(CH_3)_2Si(SO_3CF_3)_2$, obtained from $AgSO_3CF_3$ and the corresponding methyl chloro silanes [19], are, like their germanium analogues, liquids, while the corresponding methyltin-(IV) trifluoromethylsulfates are solids with penta- or hexacoordinated tin according to their ^{119}Sn Mössbauer spectra containing bidentate bridging sulfonate groups. The absence of self-linkage via sulfonate bridges is reflected also in the vibrational spectra to be discussed below.

The second reaction type, involving $(CH_3)_2SnF_2$ as reactant and anhydrous AHF as ionizing solvent, consists of a series of donor-acceptor interactions. Just like $(CH_3)_2Sn(SO_3F)_2$ in HSO_3F [8][12], dimethyltin(IV) fluoride is expected to behave as an ampholyte in HF, capable of acting as a F^- donor towards strong acceptors and as F^- acceptor towards strong donors, according to the general scheme [Me=CH_3 and X=F or SO_3F]

$$[Me_2SnX_4]^{2-} \xleftarrow[HX]{+X^-} [Me_2SnX_3]^{-} \xleftarrow[HX]{+X^-} Me_2SnX_2 \xrightarrow[HX]{-X^-} [Me_2SnX]^{+} \xrightarrow[HX]{-X^-} [Me_2Sn]^{2+}$$

$$\xrightarrow[\text{increasing acidity of solvent}]{\hspace{10cm}}$$

While all four fluorosulfate species have been synthesized from HSO_3F, only $[(CH_3)_2Sn]^{2+}$ salts have been obtained in this manner using SbF_5,TaF_5, NbF_5 or SnF_4 as acceptors[9]. Recently however [20], seemingly weaker F^- acceptors like $CrOF_4$ or CrF_5, have been found to abstract only a single F^- ion, even when present in an excess, giving rise to complexes such as $(CH_3)_2SnF[CrOF_5]$ and $(CH_3)_2SnF[CrF_6]$, which may be considered as containing the cation $(CH_3)_2SnF^+$.

The reaction between $(CH_3)_2SnF_2$ and an equimolar amount of TaF_5 yields a reaction product, which analyses cleanly as $(CH_3)_2SnTaF_7$, but whether the $[TaF_7]^{2-}$ anion is present, there are so far primarily alkali metal salts with this anion known [21], or whether a formulation as $(CH_3)_2SnF[TaF_6]$ is more appropriate, is unclear.

On the basic side of the HF solvent system, reactions proceed rather smoothly and $(CH_3)_2SnF_2$ appears to be appreciably soluble in the presence of F^- ions. Both $K[(CH_3)_2SnF_3]$ and $Li_2[(CH_3)_2SnF_4]$ are readily obtained in analytical purity. A complete analysis is undertaken, to detect any partial hydrolysis when H_2O is produced as side product, e.g. with Li_2CO_3 as reactant. Partial hydrolysis is encountered, as shown by rather low fluorine values, when the previously reported reaction in aqueous medium [12] [14] is employed. In addition, reactions in AHF offer a greater flexibility by allowing stepwise fluoride addition to $(CH_3)_2SnF_2$. We are not aware of any other simple route to salts with the $[R_2SnF_3]^-$ anion.

The noted solubility of the reaction products presents initial evidence for the presence of genuine compounds. While $Li_2[(CH_3)_2SnF_4]$ is appreciably soluble in HF, $K[(CH_3)_2SnF_3]$ will only dissolve in substantially larger quantities of HF, with $(CH_3)_2SnF_2$ seemingly insoluble, probably on account of its polymeric structure [6].

Some efforts were expended to synthesize $K_2[(CH_3)_2SnF_4]$ in addition to the corresponding lithium salt, however all materials obtained gave rather poor analyses with C and H consistently low and the IR spectrum indicating the presence of the HF_2^- ion. It is felt that formation of KHF_2 occurs in competition with formation of $K_2[(CH_3)_2SnF_4]$. On the other hand $Li_2[(n\text{-}C_4H_9)_2SnF_4]$ is readily obtained in a identical procedure from n-butyltin (IV) dichloride.

^{119}Sn Mössbauer Spectra

The relevant ^{119}Sn Mössbauer parameters of the dimethyltin (IV) fluoro-derivatives are summarized in Table 2. Observed spectra for $Li_2[(CH_3)_2SnF_4]$ and $K[(CH_3)_2SnF_3]$ and reported data for $(CH_3)_2SnF_2$[1] are nearly identical, suggesting a strong structural similarity to reported findings for the corresponding SO_3F-derivatives [8][22]. All three fluoro compounds have identical isomer shifts and all three give well resolved Mössbauer spectra at 298K. There are however subtle differences: the quadrupole splitting ΔE_Q is slightly reduced for $K[(CH_3)_2SnF_3]$ and a small line asymmetry, often indicative of polymeric structures, is found for this compound as well as for $(CH_3)_2SnF_2$. The spectral similarities and the known crystal structure of $(CH_3)_2SnF_2$ [6] facilitate structural proposals: tin is octahedrally coordinated with trans methyl groups and four F atoms in the equatorial plane. Fluorine may be either terminal or bridging between two tin atoms, suggesting chain- or sheet-like polymers for $[(CH_3)_2SnF_3]^-$ and $(CH_3)_2SnF_2$[6] respectively. The presence of both terminal and bridging fluorines, for $[(CH_3)_2SnF_3]^-$, particularly with a bridging fluorine in a cis-position, may be sufficient to cause a slight departure from linearity for the C-Sn-C group, thus resulting in a reduced quadrupole splitting. This view is consistent with findings from the vibrational spectra of $K[(CH_3)_2SnF_3]$, discussed subsequently.

The most reasonable alternative structure for the $[(CH_3)_2SnF_3]^-$ anion is a trigonal bipyramid with axial fluorine and the remaining F together with both methyl groups in equatorial position. This however should only have a ΔE_Q of 3.34 mms^{-1}[14] according to point charge calculations. The possible presence of a 1:1 mixture of $(CH_3)_2SnF_2$ and $K_2[(CH_3)_2SnF_4]$ cannot be ruled out from the Mössbauer spectra. However the vibrational spectra and the failure to obtain pure $K_2[(CH_3)_2SnF_4]$ via reactions in AHF provide counter arguements.

The previously reported Mössbauer spectra for $K_2[(CH_3)_2SnF_4]$ [14] do not agree with our finding. In particular ΔE_Q is 4.12 mms^{-1} considerably smaller then found by us. The same discrepancy had been noted and was discussed by us previously for $(CH_3)_2SnF_2$ [1].

The reaction of dimethyltin(IV) fluoride with an equimolar amount of TaF_5 causes a considerable increase in both δ and ΔE_Q by about .4 and .5 mms^{-1} respectively. While the Mössbauer spectrum observed for the resulting products is inconsistent with the presence of a mixture of $(CH_3)_2SnF_2$ and the previously reported $(CH_3)_2Sn[TaF_6]_2$[9], it does not allow us to differentiate between the two other alternative formulations $(CH_3)_2Sn[TaF_7]$ or $(CH_3)_2SnF[TaF_6]$. A slightly smaller ΔE_Q compared to the value reported for $(CH_3)_2Sn[TaF_6]_2$ could be caused either by the more basic counterion or by a departure from linearity for the C-Sn-C group. The failure to obtain a resolvable Mössbauer spectrum at ambient temperature is common to cationic $(CH_3)_2Sn^{2+}$ compound. Nevertheless the observed data are consistent with the presence of a cationic dimethyltin (IV) group and correlate quite well with previous data [10], but they fail to shed light on the nature of the anionic group(s) present.

TABLE 2

Selected ^{119}Mössbauer data of dimethyltin (IV) derivatives

Compound	T[K]	δ[mms^{-1}]	ΔE_Q[mms^{-1}]	Γ_1[mms^{-1}]	Γ_2[mms^{-1}]
$K[(CH_3)_2SnF_3]$	80	1.23	4.44	1.11	1.17
	298	1.17	4.38	0.93	0.99
$Li_2[CH_3)_2SnF_4]$	80	1.26	4.55	1.10	1.10
	298	1.23	4.48	0.85	0.81
$(CH_3)_2SnF_2$ a)	80	1.23	4.52	1.08	1.20
	298	1.20	4.47	0.83	0.87
$(CH_3)_2Sn[TaF_7]$ b)	80	1.65	5.07	0.90	1.12
$(CH_3)_2Sn[TaF_6]_2$ b)c)	80	1.69	5.23	0.93	1.00

δ = isomer shift rel. to SnO_2 at 80K, ΔE_Q = quadrupole splitting

$\Gamma_1\Gamma_2$, = line width of lines 1 and 2 a) ref. [1],

b) no resolvable spectra at 298K c) ref. [9].

Vibrational spectra

The infrared spectrum of $(CH_3)_2SnTaF_7$ offers little information and allows only limited conclusions to be drawn. Of the bands in the low frequency region a broad band at 832 and a strong band at 632 cm^{-1} are attributed to the Sn-CH_3 rock and the asymmetric Sn-C stretch respectively. The remaining bands at: 712, m-s, sharp, 675 msh, 655s, 600s, 555s, 510, 445s and 395 ms have all counterparts in the previously reported IR spectrum of $(CH_3)_2Sn[TaF_6]_2$ except for the two bands at 555 and 395 cm^{-1}. There is little resemblance to reported spectra for $Cs[TaF_6]$ [23] and $K_2[TaF_7]$ [24] [25]

but this is not surprising since fluorine bridging to tin is expected to reduce the symmetry of the anions $[TaF_6]^-$ and $[TaF_7]^{2-}$ [25]. Unfortunately good Raman spectra could not be obtained, but a Raman band at 539 cm^{-1} and the previously discussed Mössbauer parameter suggest linear or nearly linear C-Sn-C groups. The infrared data for $K[(CH_3)_2SnF_3]$ are listed in Table 3 and compared to data for $(CH_3)_2SnF_2$[1] and $K_2[(CH_3)_2SnF_4]$ [26]; the latter spectrum is identical to that of $Li_2[(CH_3)_2SnF_4]$ except for minor details.

Three interesting details emerge in the spectrum of $K[(CH_3)_2SnF_3]$ (i) the CH_3 deformation at ~ 1200 cm^{-1} and the CH_3-Sn rocking mode are split; (ii) a very weak band attributable to νSn-C sym. is found at 539 cm^{-1} and (iii) an additional band at 494 and a shoulder at 420 cm^{-1} respectively are found and a broad band in the Sn-F stretching region is observed at slightly higher frequencies than found for $(CH_3)_2SnF_2$. These differences to the spectra of either $(CH_3)_2SnF_2$ or $K_2[(CH_3)_2SnF_4]$, point to a unique compound rather than a mere mixture, and are consistent with Sn in a 6-coordinate environment with bridging fluorine, possibly in a cis-octahedral configuration, causing a rèduction in symmetry from D_{4h}, as is found in the other two dimethyltin (IV) derivatives. Band splitting of the two CH_3- deformation modes suggests a nonlinear C-Sn-C grouping as does the occurrence of the symmetric Sn-C vibration in the IR spectrum.

The infrared spectra for $(CH_3)_2Ge(SO_3CF_3)_2$ and the trimethylgermanium sulfonates are summarized in Table 4. Agreement with published data for $(CH_3)GeSO_3CF_3$ [16] is good and extends with only minor exceptions also to the band description and the Raman data for this compound. The CH_3-stretching modes are notoriously weak in these compounds and occur at 3000 and 2920cm^{-1} respectively.

The IR spectrum for $(CH_3)_3GeSO_3F$ is rather straightforward with SO_3-stretching vibrations consistently 10 to 20cm^{-1} higher than found for $(CH_3)_3GeSO_3CF_3$. The position of these SO_3 bands is helpful in identifying the CF_3 stretching modes for the SO_3CF_3 - compound, where extensive band mixing often occurs in the stretching region. A partial Raman spectrum with bands at 3000 (vw), 2924(mw), 1220(vw), 1030(w), 675(vw), 636(w), 578(s), 270(w), 196(m,b), cm^{-1} for $(CH_3)_3GeSO_3F$ is observed on the shoulder of an intense fluorescence band and supports the assignments presented here. For $(CH_3)_2Ge(SO_3CF_3)_2$ a pronounced band proliferation is noted affecting primarily the SO_3-stretching modes. In particular the $Ge(...O{-}S)_2$ stretch is split into 2 components at 1001 and 915cm^{-1} on account of vibrational coupling, with similar band separations noted for the remaining νSO_3. As a consequence the asymmetric CH_3 band is now obscured by an intense SO_3 band. Again strong fluorescence prevents the recording of a Raman spectrum, but the picture emerging for all these methylgermanium sulfonates is nevertheless clear. Monodentate - OSO_2X groups, with X=F or CF_3 are present with germanium essentially four-coordinated in contrast to tin where bridging bidentate sulfonate groups produce 5 and 6-coordination respectively.

CONCLUSIONS

Compared to the corresponding stannanes, the methylchlorogermanes of the type $(CH_3)_nGeCl_{4-n}$, n = 0-4, show a markedly reduced reactivity towards the strong acids HSO_3F and HSO_3CF_3, and only $(CH_3)_4Ge$ and $(CH_3)_3GeCl$ are found to undergo acidolysis. The resulting sulfonates $(CH_3)_nGe(SO_3X)_{4-n}$ X=F or CF_3, and n=2 or 3, are liquids with monodentate-OSO_2X groups. The fluorosulfates show limited thermal stability and eliminate SO_3. Unlike tin the central germanium atom shows no tendency towards coordination expansion and prefers tetrahedral coordination in these compounds. This is in striking

TABLE 3

Infrared spectra for $K_2[(CH_3)_2SnF_4]$[a], $K[(CH_3)_2SnF_3]$ and $(CH_3)_2SnF_2$

$K_2[(CH_3)_2SnF_4]$[a]	$K[(CH_3)_2SnF_3]$[a]	$(CH_3)_2SnF_2$[b]	Band Description
$[cm^{-1}]$ Int.	$[cm^{-1}]$ Int,	$[cm^{-1}]$ Int.	
3001 s	3020 w	3020 w	νas. CH_3
2926 sb	2910 w	2930 vw	νsym. CH_3
1410 w	1410 w	1410 w	δas. CH_3
1195 m	1210 m w 1204	1212 w	δsym. CH_3
773s	785 vs 745 s,sh	788s,b	δrock CH_3-Sn
582 s	604 ms	598 m	νas. Sn-C
539*	539 vw	536*	νsym SnC
	494 w		
397 vs	420m sh		νSnF
347	380 vs,b	360 vs,b	νSnF
257 vs			δ SnF_4

* taken from the Raman spectrum. Int. denotes estimates intensities

[a] ref. [26], [b] ref. [1]. Abbreviations used: s=strong, m-medium w=weak, v-very, b=broad, sh=shoulder, as.=asymmetric, sym.=symmetric, ν=stretch, δ=bend, ρ=rock

TABLE 4

Infrared spectra of $(CH_3)_3GeSO_3F$, $(CH_3)_3GeSO_3CF_3$ and $(CH_3)_2Ge(SO_3CF_3)_2$ between 1500 and 300 cm^{-1}

$(CH_3)_3GeSO_3F$ [cm^{-1}] Int.	$(CH_3)_3GeSO_3CF_3$ [cm^{-1}] Int.	$(CH_3)_2Ge(SO_3CF_3)_2$ [cm^{-1}] Int.	Approximate Description
1405 w sh	1422 m	1420 s	δ CH_3
1378 s	1365 s	1345 s	νSO_2 as.
	1247 s	1259 s,sh	νCF_3 as
1246 msh 1214 s	1205 vs,b	1240 s,sh 1205 s	νSO_2syn
	1164 s	1152 ms	νCF_3 sym
1015 s	984 vs,b	1001 s 915 s	νSO Ge
	875 w	875 w	combination band
840 m,sh			ν S F
830 m 790 n	852 sh 832 s	852sh 832 s	Ge-CH_3rock
	771 m	766 m	ν C-S
635	634 m	630 m	ν Ge-C as
582 m	590 m, sh	571 m	δ SO_2
570 m,sh	572 m, sh	571 m	ν Ge-C sym
552 w	532 m-w		OSO_3def.
	513 m	513 mw	
		495 m	
	365 w	360 w	S-CF_3 rock

For abbreviations see Table 3.

contrast to methylfluoro- and methylfluorosulfatostannanes, $(CH_3)_nSnX_{4-n}$, X = F or SO_3F, n=1, 2 or 3 or 4, where Sn is trigonalpyramidally or octahedrally coordinated, and F or SO_3F are bidentate bridging where possible. $(CH_3)_2SnF_2$ is found to act as an ampholyte in anhydrous HF and salts containing the anions $[(CH_3)_2SnF_4]^{2-}$ and $[(CH_3)_2SnF_3]^-$ are obtained. On the acidic side a cationic derivative of the composition $(CH_3)_2SnTaF_7$ with a near linear C-Sn-C groups is isolated but neither ^{119}Sn Mössbauer, nor vibrational spectra allow a clear differentiation between the two structural isomers containing either a true $[TaF_7]^{2-}$ anion or the anions $[TaF_6]^-$ and F^-.

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