Fluoro Salts of the Trimethyltin Group[1a]

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The new compounds trimethyltin hexafluoroarsenate and trimethyltin hexafluoroantimonate are reported. Attempts to prepare the corresponding hexafluorophosphate in sulfur dioxide solution gave phosphorus(V) oxytrifluoride and an impure solid product containing trimethyltin fluoride. The infrared spectra of trimethyltin tetrafluoroborate, hexafluoroarsenate, and hexafluoroantimonate are interpreted in terms of structures involving planar $(CH_3)_3Sn$ groups bridged by BF_4 or MF_6 groups (M = As or Sb), the tin atoms being essentially five-coordinate. Spectroscopic evidence shows AsF_6^- to form *trans* fluorine bridges to trimethyltin, while SbF_6^- forms *cis* bridges. The nonexistence of the free $(CH_3)_3Sn^+$ ion is briefly discussed.

Evidence has accumulated rapidly to show that trimethyltin derivatives rarely contain a free $(CH_3)_3Sn^+$ ion. Trimethyltin fluoride[1b] contains essentially five-coordinate tin atoms and nonlinear Sn–F---Sn bridging groups, and is clearly not a purely ionic solid. Trimethyltin perchlorate[2,3] has been shown, on the basis of its infrared spectrum, to consist of planar $(CH_3)_3Sn$ groups joined in a chain structure through bridging ClO_4 units, the tin atom again being five-coordinate. A preliminary report[4] indicates that trimethyltin tetrafluoroborate has a similar structure with bridging BF_4 groups. Both trimethyltin perchlorate and nitrate react with anhydrous ammonia to form the derivatives $[(CH_3)_3Sn(NH_3)_2]^+X^-$ (X^- = ClO_4^- or NO_3^-), in which the cation again contains five-coordinate tin.[2] The remarkable ability of the trimethyltin group to interact with tetrahedral anions such as ClO_4^- suggested that a study should be made of trimethyltin salts containing octahedral anions. For this reason, we now report the results of our studies of the compounds $(CH_3)_3SnMF_6$, where M = P, As, or Sb. The infrared spectrum of trimethyltin tetrafluoroborate is also discussed in much greater detail and several features not mentioned by Hathaway and Webster[4] are described.

Experimental

Compounds were prepared either in anhydrous methanol or in liquid sulfur dioxide, and the products were manipulated in a nitrogen atmosphere in a drybox. Samples for infrared examination were prepared in the drybox as either Nujol or hexachlorobutadiene mulls.

Trimethyltin Tetrafluoroborate.—Trimethyltin bromide (5.349 g., 22.0 mmoles) and silver tetrafluoroborate (4.275 g., 21.9 mmoles) were allowed to react in liquid sulfur dioxide solution, and the precipitated silver bromide was removed by filtration. Evaporation *in vacuo* of the sulfur dioxide solution gave trimethyltin tetrafluoroborate as a white, crystalline solid, which is extremely hygroscopic and very soluble in liquid sulfur dioxide. *Anal.* Calcd. for $C_3H_9SnBF_4$: C, 14.41; H, 3.60; F, 30.4. Found: C, 14.24, H, 3.39; F, 29.8.

Trimethyltin Hexafluorophosphate.—An attempt was made to prepare this compound from trimethyltin bromide and silver hexafluorophosphate in sulfur dioxide solution. The precipitated silver bromide was shown by an X-ray diffraction powder photograph to contain trimethyltin fluoride, and fractionation of the volatile material from the sulfur dioxide solution gave a fraction rich in phosphorus(V) oxytrifluoride, POF_3, which was identified by its infrared spectrum. The solid remaining on removal of the sulfur dioxide was clearly a mixture and pure trimethyltin hexafluorophosphate could not be obtained.

Trimethyltin Hexafluoroarsenate.—Trimethyltin bromide (2.981 g., 12.3 mmoles) and silver hexafluoroarsenate (3.453 g., 11.7 mmoles) gave, following the removal of precipitated silver bromide (11.0 mmoles) and evaporation of the sulfur dioxide solvent, a white solid, identified as the sulfur dioxide adduct, $(CH_3)_3SnAsF_6 \cdot SO_2$. *Anal.* Calcd. for $C_3H_9SnAsF_6SO_2$: C, 8.66; H, 2.16. Found: C, 8.67; H, 2.18. Prolonged pumping removed the sulfur dioxide to give the white, crystalline trimethyltin hexafluoroarsenate. *Anal.* Calcd. for $C_3H_9SnAsF_6$: C, 10.3; H, 2.56. Found: C, 10.3; H, 2.68.

Trimethyltin Hexafluoroantimonate.—This was prepared from trimethyltin bromide (1.718 g., 7.05 mmoles) and silver hexafluorantimonate (2.413 g., 7.00 mmoles) in liquid sulfur dioxide. Other preparations using methanol as solvent gave identical products. Removal of the precipitated silver bromide (7.14 mmoles) and the solvent gave white, crystalline trimethyltin hexafluoroantimonate. *Anal.* Calcd. for $C_3H_9SnSbF_6$: C, 9.1; H, 2.2; F, 28.5. Found: C, 9.2; H, 2.2; F, 27.5.

Discussion

The infrared spectra of trimethyltin tetrafluoroborate and of silver tetrafluoroborate are shown in Fig. 1. The ν_3 vibration (asymmetric B–F stretch, triply degenerate) is clearly resolved into three strong bands at 930, 1070, and 1170 cm.$^{-1}$ in the trimethyltin compound, in contrast to a single, broad band at 1000–1150 cm.$^{-1}$ in the silver salt which contains the free BF_4^- ion. Furthermore, ν_1 (symmetric B–F stretch), which is infrared inactive in the symmetrical BF_4^- ion but appears as a weak, "forbidden" transition at 771 cm.$^{-1}$ in the spectra of ionic tetrafluoroborates,[5] is now an intense band at 746 cm.$^{-1}$. The rocking of CH_3 about the tin atom gives the usual intense band at 800 cm.$^{-1}$. The complete removal of the degeneracy of ν_3 is consistent with C_{2v} symmetry for the BF_4 group,[6] and is identical with the similar lowering of symmetry observed in the spectrum of trimethyltin perchlorate.[2,3]

(1) (a) For a preliminary communication, see H. C. Clark and R. J. O'Brien, *Proc. Chem. Soc.*, 113 (1963); (b) H. C. Clark, R. J. O'Brien, and J. Trotter, *ibid.*, 85 (1963).

(2) H. C. Clark and R. J. O'Brien, *Inorg. Chem.*, **2**, 740 (1963).

(3) R. Okawara, B. J. Hathaway, and D. E. Webster, *Proc. Chem. Soc.*, 13 (1963).

(4) B. J. Hathaway and D. E. Webster, *ibid.*, 14 (1963).

(5) N. N. Greenwood, *J. Chem. Soc.*, 3811 (1959).

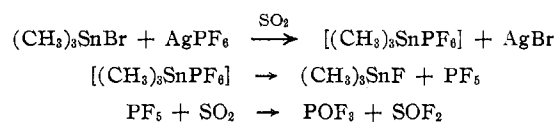(6) B. J. Hathaway and A. E. Underhill, *ibid.*, 3091 (1961).

For the tetrafluoroborate, at least five minor components appear as shoulders to the three strong bands in the 900–1300 cm.$^{-1}$ region. One of those at approximately 1200 cm.$^{-1}$ will be the CH_3 symmetrical deformation, while the shoulders at 960, 1115, and the second shoulder at 1200 cm.$^{-1}$ are probably due to the B^{10}, i.e., to the B^{10}–F stretching modes.

The moderately intense band at 558 cm.$^{-1}$ is the Sn–C asymmetric stretch, but it is difficult to determine whether the Sn–C symmetric stretch is also present. Silver tetrafluoroborate gives a sharp doublet at 525 and 536 cm.$^{-1}$, these being assigned as ν_4 (asymmetric bend), the splitting again being due to the two isotopes of boron.[5] Trimethyltin tetrafluoroborate gives an unresolved band, involving possibly two maxima at approximately 525 and 512 cm.$^{-1}$; these may again arise from the ν_4 mode of the ion, or alternatively one at least may be the Sn–C symmetric stretch. In view of the similar effects observed in the spectra of trimethyltin perchlorate[2] and tetrafluoroborate, we consider the Sn–C symmetric stretch probably is absent.

A noticeable feature of the spectrum of $(CH_3)_3$-$SnBF_4$ is the appearance of a broad band at 446 cm.$^{-1}$. In agreement with Hathaway,[4] this is assigned as arising from the splitting of the ν_4 mode of the tetrahedral ion, and may be either a rocking mode or a symmetrical bending mode of the BF_4 group with C_{2v} symmetry.

The infrared spectrum of trimethyltin tetrafluoroborate therefore is interpreted in terms of bridging BF_4 groups of C_{2v} symmetry and planar $(CH_3)_3Sn$ groups, these interacting to give a polymeric chain structure in which the tin atom is essentially five-coordinate. This, as might be anticipated, is identical with the structure proposed for trimethyltin perchlorate.[2,3]

Although pure trimethyltin hexafluorophosphate, $(CH_3)_3SnPF_6$, could not be obtained, the reaction products from the attempted preparation are interesting in that they suggest very strong interaction between $(CH_3)_3Sn^+$ and the PF_6^- anion. The results can only be interpreted according to the scheme

$$(CH_3)_3SnBr + AgPF_6 \xrightarrow{SO_2} [(CH_3)_3SnPF_6] + AgBr$$

$$[(CH_3)_3SnPF_6] \rightarrow (CH_3)_3SnF + PF_5$$

$$PF_5 + SO_2 \rightarrow POF_3 + SOF_2$$

This is supported by the fact that silver hexafluorophosphate can best be prepared from liquid sulfur dioxide,[7] so that POF_3 cannot arise from direct reaction of PF_6^- with SO_2. The stability of the PF_6^- ion and the considerable Lewis acidity of PF_5 also emphasize the strong interaction between $(CH_3)_3Sn^+$ and PF_6^-.

The sulfur dioxide adduct, $(CH_3)_3SnAsF_6 \cdot SO_2$, is a white, crystalline solid, from which the nonsolvated hexafluoroarsenate can be obtained by the slow removal of the sulfur dioxide *in vacuo*. The infrared spectrum of $(CH_3)_3SnAsF_6$ showed the expected absorptions at 2900–3000 (C–H stretch), 1405 (CH_3 asymmetric de-

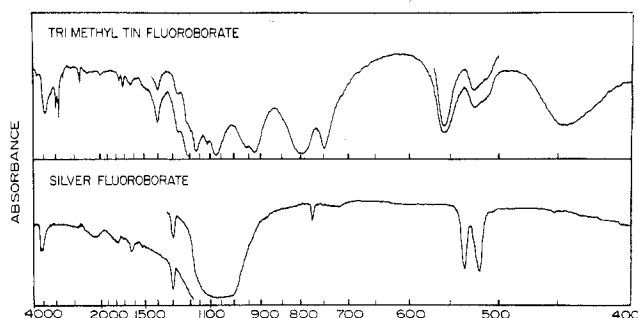Fig. 1.—Infrared spectra of $(CH_3)_3SnBF_4$ and $AgBF_4$.

formation), and 1215 cm.$^{-1}$ (CH_3 symmetric deformation). The CH_3 rocking mode is at 792 cm.$^{-1}$ and is seen as an unsymmetrical band, apparently with an unresolved component to slightly higher frequencies. The spectrum in the 400–800 cm.$^{-1}$ region is shown in Fig. 2. The octahedral AsF_6^- ion gives a strong absorption, seen[8] as a rather broad, but symmetrical band at approximately 700 cm.$^{-1}$, with subsidiary peaks at 1300, 1065, 970, and 825 cm.$^{-1}$. The band at 700 cm.$^{-1}$ is assigned as ν_3, and the ν_4 vibration is reported[9] as occurring at 400 cm.$^{-1}$. In the spectrum of $(CH_3)_3SnAsF_6$, no bands could be resolved at frequencies below approximately 550 cm.$^{-1}$; a new band is seen at 603 cm.$^{-1}$, and ν_3 is clearly split into two components at 675 and 710 cm.$^{-1}$, the latter being about twice as intense as the former. The Sn–C vibrations (symmetric and asymmetric) are not observed in the usual 500–560 cm.$^{-1}$ region.

We consider the 603 cm.$^{-1}$ band to be a Sn–C vibration, presumably the asymmetric mode shifted 50 cm.$^{-1}$ to higher frequencies as a result of very strong interaction with the AsF_6^- group. Since no bands are observed below 580 cm.$^{-1}$, the Sn–C symmetric vibration must be infrared inactive, or at least of such low intensity that it cannot be observed above the background absorption, indicating that the $(CH_3)_3Sn$ group is essentially planar. The splitting of ν_3 into *two* components is significant, since this vibrational mode, which is triply degenerate in regular octahedral symmetry, should be split in this manner when the symmetry is lowered to D_{4h}. The AsF_6 group can acquire D_{4h} symmetry by interaction through *trans* F atoms with planar $(CH_3)_3Sn$ groups to form a chain structure in which the Sn atom is five-coordinate.

Trimethyltin hexafluoroantimonate, $(CH_3)_3SnSbF_6$, shows related features in its infrared spectrum. The C–H vibrations and the CH_3 deformations are observed at 2900–3000, 1405, and 1210 cm.$^{-1}$, respectively. New bands, of comparable intensity to the CH_3 rocking mode at 810 cm.$^{-1}$, are observed at 870 and 990 cm.$^{-1}$. The spectra of "normal" hexafluoroantimonates [e.g., $AgSbF_6$] do not show bands in the 800–1000 cm.$^{-1}$ region, and these must therefore be vibrational modes, infrared inactive for the octahedral SbF_6^- ion, which have become infrared active as a result of distortion of the SbF_6^- group by $(CH_3)_3Sn$. It is interesting that

(7) D. R. Russell and D. W. A. Sharp, *J. Chem. Soc.*, 4689 (1961).

(8) D. W. A. Sharp and A. G. Sharpe, *ibid.*, 1855 (1956).

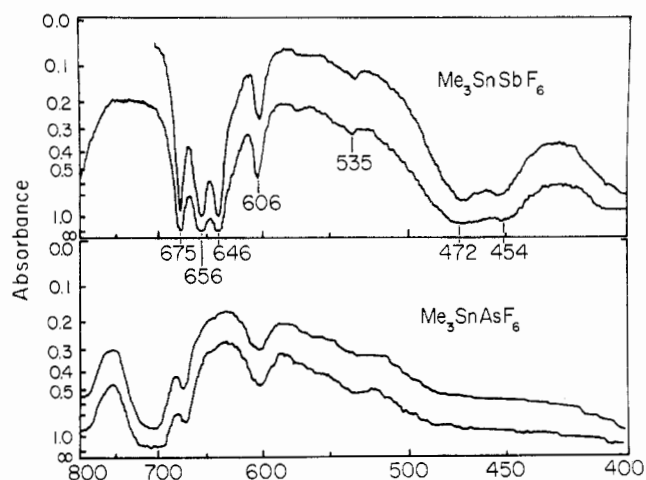(9) R. D. Peacock and D. W. A. Sharp, *ibid.*, 2762 (1959).

Fig. 2.—Infrared spectra of $(CH_3)_3SnAsF_6$ and $(CH_3)_3SnSbF_6$.

these bands at 870 and 990 cm.$^{-1}$ seem similar to the subsidiary peaks found[8] at 825 and 970 cm.$^{-1}$ for AsF$_6$$^-$.

The ν_3 vibration of SbF$_6$$^-$ is observed[9] at 660 cm.$^{-1}$, but, as can be seen from Fig. 2, this band for $(CH_3)_3$-SnSbF$_6$ is well resolved into *three* components at 675, 656, and 640 cm.$^{-1}$. Such complete removal of the degeneracy of the ν_3 mode of a symmetrical, octahedral ion is consistent with a lowering of the symmetry to C$_{2v}$, the symmetry expected if two *cis* F atoms are interacting with $(CH_3)_3$Sn groups. Moreover, a new intense band, not reported for the SbF$_6$$^-$ ion, is now found in the 440–480 cm.$^{-1}$ region, consisting of two components at 454 and 472 cm.$^{-1}$. The triply degenerate ν_4 mode has not been reported for the free SbF$_6$$^-$ ion, and these bands may well be two of the three possible components. Extension of the spectroscopic studies to lower frequencies is necessary to confirm this. In the 500–620 cm.$^{-1}$ region, two bands are observed, one being very poorly resolved at 535 cm.$^{-1}$ and of uncertain origin. The other is a sharp, well-defined band at 606 cm.$^{-1}$ which is clearly similar to the 603 cm.$^{-1}$ band in the $(CH_3)_3SnAsF_6$ spectrum, and which is therefore tentatively assigned as the Sn–C asymmetric stretch. The spectroscopic evidence, in particular the splitting of ν_3 and the appearance of new, low-frequency absorptions, is consistent with a structure in which essentially planar $(CH_3)_3$Sn groups are bridged by *cis* fluorine atoms of distorted SbF$_6$ groups, so that the Sn atom is again five-coordinate. It is of some interest that this is also consistent with the structure of antimony pentafluoride,[10] in which *cis* F atoms act as bridges between SbF$_6$ octahedra.

An attempt was also made to examine the F^{19} nuclear magnetic resonance spectra of concentrated solutions (approximately 2 g./ml. of solution) of $(CH_3)_3SnBF_4$ and $(CH_3)_3SnSbF_6$ in liquid sulfur dioxide. In both cases, only a single sharp absorption was observed, and even for samples slowly warming from −196° to

room temperature, no fine structure could be detected. However, it is significant that the chemical shift for $(CH_3)_3SnBF_4$ was +57.5 p.p.m. to high field from trifluoroacetic acid. The BF$_4$$^-$ ion in aqueous solution shows[11] a chemical shift of +72.3 p.p.m. and a quartet is observed owing to the B^{11}–F^{19} coupling. Even allowing for the effects of different media, the difference in chemical shift is appreciable, and it appears likely that the single absorption for $(CH_3)_3SnBF_4$ is a consequence of a dynamic equilibrium between BF$_4$$^-$ ions and some other BF$_4$ species.

There thus appears to be an interesting sequence in the compounds $(CH_3)_3SnMF_6$, where M = P, As, or Sb. The hexafluorophosphate is unstable, the PF$_6$$^-$ group loosing fluoride to the $(CH_3)_3Sn^+$ group. Trimethyltin hexafluoroarsenate and -antimonate, which are derived from the progressively stronger Lewis acids AsF$_5$ and SbF$_5$, are stable, the anion in the former acting as a *trans* and in the latter as a *cis* bridging group. It should be emphasized that we consider the difference in the splittings of ν_3 for the AsF$_6$$^-$ and SbF$_6$$^-$ compounds to be genuine and not due just to a lack of resolution of ν_3 for $(CH_3)_3SnAsF_6$. The two compounds were prepared from reactants of similar purity, their spectra were recorded under the same conditions, and several preparations of each compound gave the same spectrum.

No compound $(CH_3)_3SnX$ has yet been prepared in which the $(CH_3)_3$Sn group does not interact strongly with X. Either an essentially covalent compound with tetrahedral orientation about the tin atom is obtained as in $(CH_3)_3SnCl$ or $(CH_3)_3SnONO_2$,[2] or else a chain structure is formed giving five-coordination to the tin atom, as in $(CH_3)_3SnF$,[1] $(CH_3)_3SnBF_4$, or $(CH_3)_3$-SnSbF$_6$. It is not possible to account for the infrared spectra of these latter compounds in terms of ion-pairs, since such a model cannot reconcile the planarity of $(CH_3)_3$Sn with the bidenate nature, of, for example, ClO$_4$ in $(CH_3)_3SnClO_4$. It seems reasonable to suggest that the tin atom in the planar $(CH_3)_3$Sn group has sp^{3}d rather than sp^2 hybridization and that the two apical orbitals are involved in interaction with any group X. However, there seems no obvious explanation for the apparent instability of the free $(CH_3)_3Sn^+$ ion and for its very strong acceptor properties. Further studies are necessary to determine if this behavior is peculiar to $(CH_3)_3Sn^+$, or whether it is general for all R$_3$Sn$^+$ ions, and it will also be of interest to examine the behavior of R$_2$SnX$_2$ compounds such as $(CH_3)_2Sn(ClO_4)_2$ in terms of the existence or nonexistence of the free R$_2$Sn^{2+} ion. Such work is now in progress.

(10) C. J. Hoffman, B. E. Holder, and W. L. Jolly, *J. Phys. Chem.*, **62**, 364 (1958).

(11) R. D. Chambers, H. C. Clark, L. W. Reeves, and C. J. Willis, *Can. J. Chem.*, **39**, 258 (1961).