Concerning the Structure of Trimethyltin Fluoride

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Recently there has been much interest in the structure of organotin compounds. Among the trimethyltin halides, trimethyltin fluoride is markedly different in physical and chemical properties from the remaining halides; the fluoride has a high melting point (>360°C) and does not sublime, while the other halides melt and sublime at lower temperatures. The former is soluble in hot alcohol, slightly soluble in water, and almost insoluble in non-polar organic solvents, while the latter are soluble in common organic solvents.

The structures of trimethyltin chloride, bromide, and iodide have been determined[1] by electron diffraction to be nearly tetrahedral in the vapor state, but no structural determination had been made on the fluoride until recently. In 1960, one of the present authors reported[2] on the basis of infrared spectral evidence that the fluoride contains a planar trimethyltin group. However, the X-ray analysis by Clark et al.[3] showed that the electron-density distribution could be equally well interpreted either in terms of a planar or pyramidal trimethyltin group. To clear up this ambiguity concerning the structure of the trimethyltin group and the nature of the bond represented by Clark et al.[3] as Sn–F···Sn (the bond distance; Sn–F 2.1 Å, Sn···F 2.2—2.6 Å) in this compound, it is necessary to consider the most probable structure of this compound with reference to some findings from the infrared and Raman spectra, as well as a few additional X-ray data obtained from this compound and from related trimethyltin compounds which have been studied in our laboratory.

In the infrared spectrum of this compound only one band* is observed at 556 cm^{-1}, which is assigned to the Sn–C stretching vibration, and we can assume the following two possible structures for the trimethyltin group. One is the planar equilateral triangular structure with the tin atom at the center and three carbon atoms at the corners, which gives infrared active degenerate and inactive symmetric stretching vibrations associated with the Sn–C bonds. Another possible structure is a pyramidal one. If we assume a point group of C_{3v} for this molecule, this structure would give two Sn–C stretching vibrations of A_1 and E species in the infrared spectrum according to the selection rule. Our infrared studies seem to rule out this structure, but it is also possible** that the frequency associated with the Sn–F stretching vibration might be close enough to that of the Sn–C symmetric stretching vibration to cause coupling. We may then expect that one would be higher and the other lower than either of the original ones by this coupling; one of these two bands could fall near 550 cm^{-1}, overlapping with the Sn–C stretching vibration of E species. However, the Raman spectrum of solid trimethyltin fluoride showed that the assumed coupling does not take place, and hence the second structure is not probable, since two bands which are associated with the Sn–C stretching vibrations.

1) H. A. Skinner, L. E. Sutton, *Trans. Faraday Soc.*, **40**, 164 (1944).
2) R. Okawara, D. E. Webster and E. G. Rochow, *J. Am. Chem. Soc.*, **82**, 3287 (1960).
3) H. C. Clark, R. J. O'Brien and J. Trotter, *Proc. Chem. Soc.*, **1964**, 85,; *J. Chem. Soc.*, **1964**, 2332.

* Although it is reported in Ref. 3. that another band was observed at 515 cm^{-1} in the infrared spectrum of very concentrated Nujol mulls of trimethyltin fluoride, no band was observed in this region in our repeated experiments.

** This was tentatively suggested by Dr. Ichiro Nakagawa of the The Universiuy of Tokyo.

at 517 cm^{-1} (s) and 556 cm^{-1} (w) were observed in the Raman spectrum.

Clark et al.[3] reported that the structure of this compound has trimethyltin groups and fluorine atoms arranged alternately in a chain-like manner along the a axis, and they offered two interpretations of the three dimensional electron-density distribution. One is that the non-planar trimethyltin group is ordered in any chain. The bond angles calculated by us from the electron-density distribution map given by them are about 111° and 117° for C_2-Sn-C_3 and C_1-Sn-C_2, respectively. This distortion of the trimethyltin group from the normally trigonal coplanar structure should give a fairly intense infrared absorption band due to the Sn-C symmetric stretching vibration. Their second structure, in which the planar trimethyltin groups are tilted alternately with respect to the a axis, should give a repeat distance of twice the cell length. Though we repeated their X-ray diffraction measurements with a larger crystal, we could not observe any reflection which corresponds to twice their reported cell length along the needle axis even with long exposures, and this suggests that their second structure also is not suitable.

If we assume that the space group given by Clark et al. is reasonable, the peculiarities in the electron-density distribution can be interpreted in terms of disorder in the crystal structure. Clark et al. proposed that the chains could be disordered with respect to each other. This kind of disorder was observed in trimethyltin hydroxide[4] and formate[5], which are now being studied in our laboratory. Besides, in the hydroxide, we found that the trimethyltin groups are disordered also in a chain, forming a helix-like structure. A structure having random chains has been found also in polyvinyl alcohol.[6] In the structure of trimethyltin fluoride, the disorder in one chain should also be taken into account.

Determination of the precise structure of any compound containing a heavy metal atom, such as tin, by X-ray diffraction is usually difficult, for there is often some ambiguity in the position of the light atoms. In the analysis of the fluoride, Clark et al. were not able to use the (h00) reflections, and the determination of the positions of carbon and fluorine atoms seems to be difficult, especially in the x-coordinates. We would like to propose a reasonable structure which is consistent with

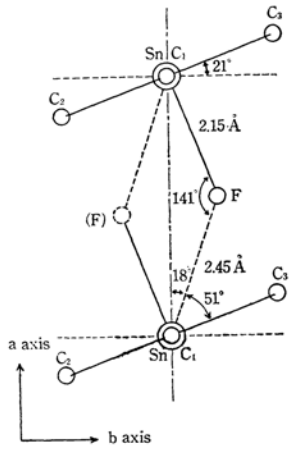

Fig. 1. A projection of the probable crystal structure of trimethyltin fluoride down to the (001) plane.
F and (F) indicates the two possible positions of fluorine atom of the same potential energy.

the results of the X-ray diffraction study by Clark et al., and takes into account the results from infrared and Raman spectra. We assume that the trimethyltin group forms a planar equilateral triangular structure and is inclined to the plane perpendicular to the a axis, and that one of the Sn-C bonds, Sn-C_1, lies along the c axis, and further that the trimethyltin groups and the fluorine atoms are arranged alternately along the a axis as shown in Fig. 1. Concerning the Sn-F bond, we observed a broad strong band at 350 cm^{-1} in the infrared spectrum and assign this to the Sn-F stretching vibration. We could not observe any Raman line due to the Sn-F symmetric stretching in the region down to about 150 cm^{-1}, where the Raman lines due to the SnC_3 deformations are usually observed. It can be concluded, therefore, that one of the two Sn-F bonds is fairly strong and the other is weak, and this is consistent with the results of the X-ray study by Clark et al. The angle formed by the covalent Sn-F bond and the Sn-C_1 bond is shown to be almost 90° by the electron-density distribution map of Clark et al., but the angle between the covalent Sn-F bond and the plane of trimethyltin group can not be determined from their work. Taking for this angle a value of 90° and an Sn-F bond distance of 2.15 Å, the calculated distance between the fluorine atom and the carbon atoms in other chains is larger than the sum of the van der Waals radii of the atoms; this is consistent with the compound's crystal habit, i. e., bundles of very fine needles. As the repeat distance along the a axis has been determined[3] to be

4) N. Kasai, K. Yasuda and R. Okawara, *J. Organometal.*, 3, 172 (1965).
5) N. Kasai, H. Matsumoto, N. Tanaka and R. Okawara, presented at the 17th Annual Meeting of the Chemical Society of Japan, Tokyo, 1964.
6) J. Kakinoki, *The Annual Reports of the Textile Research Institute of Osaka Univ.*, 5, 19 (1950) (in Japanese).

4.32 Å, the planes of the trimethyltin groups should be parallel to each other in the chain. The weak Sn···F bond is in the opposite direction to the strong Sn-F bond with respect to the plane, and the angle between the weak Sn···F bond and the plane of trimethyltin is calculated to be about 51°, so that the F-Sn···F bond is not linear and should have a bond angle of about 141°. This is consistent with the results of Clark et al. that the integrated electron-density of the Sn peak in the a axis projection was 50.08 electrons, indicating that the fluorine atom is not situated on the axis connecting the tin atoms, which is parallel to the a axis. This value for the Sn-F···Sn angle is reasonable if we take into account the fact that in solid hydrogen fluoride the angle H···F-H is about 134° [7] and that this bond angle is explained[8] in terms of participation of the lone pair orbital of the fluorine atom. This distorted bipyramidal configuration around the tin atom could be explained by assuming that the d-orbitals are involved in the hybridization of the orbitals in the tin atom; this is also expected to be the case in trimethyltin hydroxide. In the structure of trimethyltin fluoride proposed above, we can expect two positions of minimum potential energy for the fluorine atom, F and (F) given in Fig. 1. The potential barrier between them is considered to be small, and this can explain the anomaly in the electron-density distribution of the fluorine atom.

7) R. Gunther, K. Holm and H. Strunz, *Z. phys. Chem.*, B33, 229 (1939).
8) W. G. Schneider, *J. Chem. Phys.*, 23, 26 (1955).

Experimental

The infrared spectrum of trimethyltin fluoride as a Nujol mull was recorded in the 4000—270 cm^{-1} region on a Perkin-Elmer double beam spectrometer model 221 equipped with NaCl or KBr optics, and on a Koken double beam spectrometer model DS-401 G equipped with a grating and CsBr optics. The Raman spectrum for the solid state was recorded on a Nippon Yuki-gosei Raman Spectrograph.

The needle crystal with average width 0.3 mm., used for the CuK_α oscillation photograph, was obtained by recrystallization of trimethyltin fluoride from ethyl alcohol.

Summary

The structure and the nature of the bonds in trimethyltin fluoride are discussed on the basis of the infrared and the Raman spectra with reference to the results of the X-ray diffraction study by Clark et al. and a few additional X-ray data obtained on the fluoride and related trimethyltin compounds. The most reasonable structure is one in which the planar trimethyltin group is bridged by the fluorine atom forming a non-linear unsymmetrical Sn-F···Sn bond. The distorted bipyramidal configuration around the tin atom can be explained in terms of involvement of the d-orbitals of the tin atom in the bonding.

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