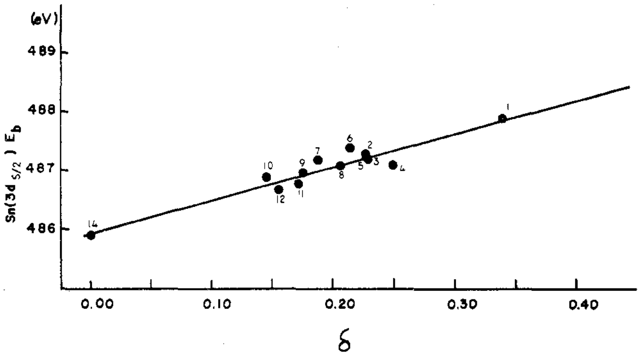

Figure 1.—Sn($3d_{5/2}$) binding energies *vs.* estimated atomic charge on the tin atom.

thus result in the deviation observed, especially in view of the known dependence of the isomer shifts upon hybridization (s character).

Figure 1 is a plot of the estimated atomic charge (δ) on the central tin atom in this series of compounds *vs.* the measured Sn($3d_{5/2}$) electron binding energy. The charges were obtained by a relatively simple method of electronegativity equalization.[24] While there is no way to obtain absolute charges experimentally to validate these estimates, their success in numerous applications[24-27] indicates that their relative magnitude is accurate. The least-squares fit of the binding energy data yields

$$E_b = 486.4 + 0.57\delta$$

with $r = 0.93$.

It is interesting to note that the values of the correlation coefficient do not vary greatly in the three correlations. It should be noted, however, that we have chosen Pauling-type empirical electronegativities[23,28] for the correlation given above and that other systems of electronegativities based on *a priori* assumptions such as the Allred-Rochow system of electrostatic electronegativities[29] yield somewhat poorer fits ($r = 0.92$). This is because purely empirical schemes such as that of Pauling tend to have "built-in" adjustments for such factors as orbital hybridization and charge capacity, shown to be extremely important in the determination of charge distribution.[24-27] Thus, although a simple, one-parameter system (summation of electronegativities) may often provide excellent correlation of experimental data, we feel that the increased power of a two-parameter, orbital electronegativity system provides significant advantages at a minimum increase in computational work.

We are currently studying additional compounds of this type to elucidate further the relationship among electron binding energy, Mössbauer isomer shifts, and molecular parameters.

Acknowledgments.—This work was supported in part by a grant from the Advanced Research Projects Agency, Department of Defense. We should like to thank the University of Maryland Computer Science Center for computer time for statistical analysis of the work.

---

[24] J. E. Huheey and J. C. Watts, *Inorg. Chem.*, **10**, 1553 (1971).

[25] J. C. Watts and J. E. Huheey, *Chem. Phys. Lett.*, **14**, 89 (1972).

[26] J. C. Watts, Doctoral Dissertation, University of Maryland, 1971.

[27] J. E. Huheey, *J. Phys. Chem.*, **69**, 3284 (1965); **70**, 2086 (1966); *J. Org. Chem.*, **31**, 2365 (1966); *J. Chem. Phys.*, **45**, 405 (1966).

[28] L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1960.

[29] A. L. Allred and E. G. Rochow, *J. Inorg. Nucl. Chem.*, **5**, 264 (1958).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
THE UNIVERSITY OF BRITISH COLUMBIA, VANCOUVER 8, BRITISH COLUMBIA, CANADA

Synthetic and Structural Studies of Some Methyltin(IV) Chlorosulfonato Compounds

BY P. A. YEATS, J. R. SAMS, AND F. AUBKE*

Received August 26, 1971

The synthesis of some new methyltin(IV) chlorofluorosulfates and trifluoromethanesulfonates of the general type $(CH_3)_nSnCl_m(SO_3X)_{4-(n+m)}$, where n and m can be 0, 1, or 2 and X = F and CF_3, is described. Two general synthetic routes are employed: (a) the acid solvolysis of methyltin(IV) chlorides in the corresponding sulfonic acids and (b) ligand redistribution reactions of methyltin(IV) chlorides and sulfonates. Structural proposals are based on infrared, Raman, and ^{119}Sn Mössbauer studies.

A. Introduction

The solvolysis of methyltin(IV)–chloro compounds in some monobasic sulfonic acids of the type HSO_3X with X = F, Cl, CF_3, CH_3, or C_2H_5 has resulted in the preparation of the series $(CH_3)_2Sn(SO_3X)_2$[1] using $(CH_3)_3SnCl$ and $(CH_3)_2SnCl_2$ as solutes and the series $(CH_3)_3SnSO_3X$ with X = F,[2] CF_3,[3] and CH_3,[2] when an excess of $(CH_3)_4Sn$ has been used as solute. Structural proposals were based on infrared and Raman spectra as well as on ^{119}Sn Mössbauer spectra.[1,2] In addition the detailed X-ray diffraction study of $(CH_3)_2Sn(SO_3F)_2$ has been carried out.[4] In all cases the SO_3X group was found to act as a bidentate bridging group with coordination to tin occurring through oxygen bridges, thus resulting in pentacoordination for the series $(CH_3)_3SnSO_3X$ and in hexacoordination for compounds of the type $(CH_3)_2Sn(SO_3X)_2$. The latter series was found to be closely related to compounds of the

---

[1] P. A. Yeats, B. F. E. Ford, J. R. Sams, and F. Aubke, *Chem. Commun.*, 151 (1969).

[2] P. A. Yeats, J. R. Sams, and F. Aubke, *Inorg. Chem.*, **10**, 1877 (1971).

[3] M. Schmeisser, P. Sartori, and B. Lippsmeier, *Chem. Ber.*, **103**, 868 (1970).

[4] F. A. Allen, J. Lerbscher, and J. Trotter, *J. Chem. Soc. A*, 2507 (1971).

type $Y_2Sn(SO_3F)_2$ with Y = SO_3F,[5] Cl,[5] and F,[6] which have been obtained by us using different synthetic routes.

It became interesting to conduct a more systematic solvolysis study of the solutes $(CH_3)_nSnCl_{4-n}$, with n = 1, 2, 3, and 4, under various conditions in search of compounds of type $(CH_3)_nSnCl_m(SO_3X)_{4-(n+m)}$ with n and m being 1 or 2. Similar methyltin(IV) chloride fluorides have been synthesized recently[6] with anhydrous hydrogen fluoride. It was found advantageous to restrict this part of the study to the more reactive acids HSO_3F and HSO_3CF_3.

An alternative synthetic route for the preparation of such compounds was seen in ligand redistribution reactions between methyltin(IV) chlorides and methyltin(IV) sulfonates. The rapid formation of $Cl_2Sn(SO_3F)_2$ from $Sn(SO_3F)_4$ and an excess of $SnCl_4$ at room temperature[5] were taken as an indication that fluorosulfates are particularly reactive in this respect. Some redistribution reactions of alkyltin(IV) chlorides and alkyltin(IV) carboxylates have been reported very recently.[7] This reaction type is apparently commonly used in the synthesis of dialkyltin(IV) chlorocarboxylates of the type $R_2SnCl(O_2CR')$.

Even though vibrational assignments for bidentate bridging SO_3X groups with C_s symmetry had been obtained previously for some of the derivatives,[2,5] it became interesting to see whether the other substituents on tin may cause a different conformation of the SO_3X group recognizable in particular in the stretching frequency region. The fluorosulfate derivatives are ideally suited for this purpose because by far the larger number of examples is known here. In addition vibrational coupling and the coincidence of absorption bands as found, *e.g.*, for CF_3 and SO_3 modes in ionic SO_3CF_3 compounds,[8] resulting in considerable uncertainty in the assignment, should be absent for the fluorosulfates.

The tin-119 Mössbauer spectra on such a closely related group of compounds should allow us to observe trends in both isomer shift and quadrupole splitting. The previously[1,2] reported ^{119}Sn parameters were found to be quite exceptional. The quadrupole splitting for $(CH_3)_2Sn(SO_3F)_2$ and $(CH_3)_2Sn(SO_3CF_3)_2$ are, at ~5.50 mm/sec,[1] wider than any previously reported values and also the corresponding trimethyltin(IV) derivatives show wider splittings[2] than are commonly observed for pentacoordinated organotin compounds. To explain these observations a discussion of bonding in all the compounds will be presented.

B. Experimental Section

I. Chemicals.—Tetramethyltin(IV) was obtained from Penninsular ChemResearch and purified by distillation. The methyltin(IV) chlorides were obtained from Alfa Inorganic Chemicals and purified where necessary by vacuum sublimation. Fluorosulfuric acid (Allied Chemical Corp.), technical grade, was purified by double distillation at atmospheric pressure as described previously.[9] Trifluoromethanesulfonic acid was prepared from the barium salt by treating it with concentrated sulfuric acid. We are grateful to 3M Co. for a gift of $Ba(SO_3CF_3)_2$. All solvents (CCl_4 and $CHCl_3$) were of reagent grade and dried before use over Linde's molecular sieves.

II. Instrumentation.—Infrared spectra were recorded on a Perkin-Elmer 457 grating spectrophotometer. Silver chloride, cesium iodide and KRS-5 windows (all from Harshaw Chemicals) were used either with Nujol or without any mulling agent.

Raman spectra on the solid samples were obtained with a Cary 81 spectrometer, equipped with a Model 125 He–Ne gas laser (Spectra Physics Corp.). The 6328-Å wavelength line was used as exciting light. The samples were contained in 5 mm o.d. Pyrex tubes with flat bottoms.

The Mössbauer spectrometer has been described before in detail.[5] Measurements were made with the absorber either at 80 or at 298°K and the Ba $^{119m}SnO_3$ source at 298°K. All isomer shifts are reported relative to SnO_2 absorber at 80°K. The accuracy for both isomer shifts and quadrupole splittings is judged to be ±0.03 mm/sec.

All manipulations of solid materials were carried out in a Vacuum Atmosphere Corp. "Dri-Lab," Model No. HE-43-2, filled with purified dry nitrogen and equipped with "Dri-Train," Model No. HE-93B.

III. Synthetic Reactions.—All solvolysis reactions at ambient temperature were performed in 100-ml two-part reaction flasks equipped with magnetic stirring bars. The solutes were added in the dry atmosphere box and the acid was added by vacuum (HSO_3CF_3) or atmospheric pressure distillation. After gas evolution had stopped, the reaction mixture was stirred at room temperature. The excess acid was removed *via* vacuum distillation and the products were isolated after prolonged pumping under gentle heating of the reaction flask to about +70°. Low-temperature filtration of the crystallized products and subsequent pumping to remove the remaining traces of acid was used as an alternative isolation method. For reactions at elevated temperature one-part glass reactors fitted with Teflon stem needle valves were used.

Ligand redistribution reactions were carried out in two-part reactors. The reactors were charged in the dry atmosphere box and the mixture was stirred magnetically. Further details on the synthesis are contained in Tables II and III. All compounds were used without further purification. The synthesis of dimethyltin(IV) bis(*p*-tolylsulfonate) dihydrate was adapted from the reported synthesis of the *n*-butyl compound,[10] but in contrast to the report a dihydrate crystallized out of the solution in the form of rather large colorless crystals. Conversion into the anhydrous compound was accomplished by drying at +105°.

IV. Analytical Details.—Microanalysis of carbon and hydrogen contents was carried out by Mr. P. Borda of this department. Elemental analysis of Sn, S, and the halogens was performed by Alfred Bernhardt Laboratories, Mülheim, West Germany. Reliable microanalysis for C and H could be performed on the moderately hygroscopic substances only. Details are listed below on the SO_3F and SO_3CF_3 derivatives together with the vibrational spectra from 2000 to 250 cm^{-1}.

A number of dimethyltin(IV) salts listed in the Mössbauer section of this study have apparently not been reported previously. The carbon and hydrogen analysis results are listed in Table I.

TABLE I

ANALYTICAL DETAILS ON SOME DIMETHYLTIN(IV) SALTS

Compound	% C		% H	
	Calcd	Found	Calcd	Found
$(CH_3)_2Sn(SO_3CH_3)_2$	18.54	18.37	4.67	4.59
$(CH_3)_2Sn(SO_3C_2H_5)_2$	19.62	19.78	4.39	4.19
$(CH_3)_2Sn(SO_3C_6H_4CH_3)_2\cdot 2H_2O$	36.45	36.18	4.58	4.31
$(CH_3)_2Sn(SO_3C_6H_4CH_3)_2$	39.10	39.25	4.11	4.0

(1) **Dimethyltin(IV) Bis(fluorosulfate), $(CH_3)_2Sn(SO_3F)_2$.**—White, platelike crystals, moderately hygroscopic, dec pt 253°. *Anal.* Calcd for $(CH_3)_2Sn(SO_3F)_2$: C, 6.92; H, 1.72; Sn, 34.22; S, 18.49; F, 10.96. Found: C, 7.01; H, 1.80; Sn, 34.54; S, 18.67; F, 11.09. Infrared spectrum (cm^{-1}): 3048 m, 2952 mw, 2860 vw, 2425 w, 1455 mw, 1350 vs, b, 1222 m, 1180 vs, b, 1088 m, sh, 1072 s, b, 827 m, sh, 798 vs, b, 650 vw, 620 m, sh, 590 ms, 576 s, 554 ms, 417 s, 360 w, 304 m.

---

[5] P. A. Yeats, B. L. Poh, B. F. E. Ford, J. R. Sams, and F. Aubke, *J. Chem. Soc. A*, 2188 (1970).

[6] L. E. Levchuk, J. R. Sams, and F. Aubke, *Inorg. Chem.*, **11**, 43 (1972).

[7] A. D. Cohen and C. R. Dillard, *J. Organometal. Chem.*, **25**, 421 (1970), and references therein.

[8] M. G. Miles, G. Doyle, R. P. Cooney, and R. S. Tobias, *Spectrochim. Acta., Part A*, **25**, 1515 (1969).

[9] J. Barr, R. J. Gillespie, and R. C. Thompson, *Inorg. Chem.*, **3**, 1149 (1964).

[10] D. Seyferth and F. G. A. Stone, *J. Amer. Chem. Soc.*, **79**, 516 (1957).

Raman spectrum (cm^{-1}): 2944 m, 2906 s, 2871 m, 1354 s, 1230 m, 1088 s, 826 m, 610 m, 584 m, 551 mw, sh, 531 vs, 420 w, 367 mw, 320 mw.

(2) **Dimethyltin(IV) Bis(trifluoromethanesulfonate), $(CH_3)_2Sn(SO_3CF_3)_2$.**—Synthesized from $(CH_3)_3SnCl$ and HSO_3CF_3. White, slightly hygroscopic solid, mp 336–337°. *Anal.* Calcd for $(CH_3)_2Sn(SO_4CF_3)_2$: C, 10.74; F, 25.51; H, 1.35. Found: C, 10.70; F, 26.52; H, 1.50. Infrared spectrum (cm^{-1}): 1322 s, 1229 sh, 1212 w, sh, 1196 s, 1150 s, 1035 m, 822 ms, 773 w, 643 m, 632 m, 584 m, 520 w, sh, 513 s, 370 m. Raman spectrum (cm^{-1}): 1033 m, 776 m, 530 vs, 348 m.

(3) **Methyltin(IV) Chlorobis(fluorosulfate), $CH_3SnCl(SO_3F)_2$.**—White, very hygroscopic crystals, mp 161–162°. *Anal.* Calcd for $CH_3SnCl(SO_3F_2)$: Cl, 9.68; S, 17.46; F, 10.35. Found: Cl, 9.84; S, 17.70; F, 10.33. Infrared spectrum (cm^{-1}): 1440 m, 1361 s, 1230 sh, w, 1165 vs, b, 1072 s, 830 s, sh, 812 vs, b, 640 vw, 620 m, sh, 590 s, sh, 578 s, 555 s, 420 m, 385 ms, 305 mw. Raman spectrum (cm^{-1}): 623 m, 603 w, 585 m, 562 m, 423 m, 390 s, 308 mw, 255 m; no reliable absorption could be detected above 700 cm^{-1}.

(4) **Methyltin(IV) Chlorobis(trifluoromethanesulfonate), $CH_3SnCl(SO_3CF_3)_2$.**—Synthesized from CH_3SnCl_3 and HSO_3CF_3. White, very hygroscopic crystals, mp 178–180°. *Anal.* Calcd for $CH_3SnCl(SO_3CF_3)_2$: S, 14.04; F, 24.50. Found: S, 13.85; F, 24.62. Infrared spectrum (cm^{-1}): 1368 w, sh, 1321 s, b, 1228 s, 1195 s, 1155 s, 1021 s, 816 ms, b, 774 w, sh, 628 vs, 585 ms, 575 m, sh, 518 m, sh, 510 s, 395 w, sh, 384 ms, 372 ms, 368 m, 355 w, 312 w.

(5) **Dimethyltin(IV) Chlorofluorosulfate, $(CH_3)_2SnCl(SO_3F)$.**—Synthesized from $(CH_3)_2Sn(SO_3F)_2$ and $(CH_3)_2SnCl_2$. White, very hygroscopic crystals, mp 108°. *Anal.* Calcd for $(CH_3)_2SnCl(SO_3F)$: Sn, 41.90; S, 11.32; F, 6.71. Found: Sn, 42.25; S, 11.49; F, 6.31. Infrared spectrum (cm^{-1}): 1403 w, 1343 s, 1190 vs, b, 1072 s, 820 ms, sh, 795 vs, b, 607 s, 590 m, 578 m, 555 s, 527 m, 409 m, 345 ms. Raman spectrum (cm^{-1}): 1320 w, b, 1213 w, 1074 w, 825 mw, 603 w, 594 m, 582 m, 562 m, 535 s, 416 w, 345 m, 306 m.

(6) **Methyltin(IV) Dichlorofluorosulfate, $CH_3SnCl_2(SO_3F)$.**—Synthesized from $CH_3SnCl(SO_3F)_2$ and CH_3SnCl_3. White, hygroscopic solid, mp 112–115°. *Anal.* Calcd for $CH_3SnCl_2(SO_3F)$: Sn, 39.1; S, 10.56; Cl, 23.35; F, 6.26. Found: Sn, 38.7; S, 10.78; Cl, 23.09; F, 5.96. Infrared spectrum (cm^{-1}): 1405 vw, 1350 s, 1250 vs, b, 1095 s, 1065 m, 825 ms, 806 vs, b, 605 ms, 588 s, 576 vs, 555 ms, 405 mw, 384 s, 366 s, 300 w. Raman spectrum (cm^{-1}): 1360 w, 1250 m, 1080 m, 610 w, 560 m, 405 w, 387 m, sh, 368 s, 305 w, 247 w.

C. Results and Discussion

I. Synthesis.—Previous preparative routes to alkyltin(IV) sulfonates[11] had involved the neutralization of bis(alkyl)tin(IV) oxides, the transesterification of alkyltin(IV) trifluoroacetates, and the interaction of dialkyltin(IV) halides with silver salts of the corresponding sulfonic acids. These rather elaborate methods had been applied only to the synthesis of methane- and ethanesulfonates.

Acid solvolysis of alkyltin(IV) compounds in contrast should be a simple synthetic route provided the cleavage reaction proceeds cleanly. The method has found some previous application in organotin(IV) chemistry,[12-16] using carboxylic acids as solvents and tetraalkyl or -vinyl compounds as substrates resulting generally in the cleavage of one or two tin–carbon bonds. In exceptional cases[16] all four Sn–C bonds are cleaved. The mechanism of such substitution reactions has been discussed recently.[17] In addition to the listed preparative application of acid solvolysis, the method has been used to form the solvated cation Me_3Sn^+ in H_2SO_4 solution.[18] The use of methyltin(IV) chlorides as solutes can result in more complex reactions since here both the Sn–C and the Sn–Cl bond can be cleaved. Previous reports[1,3,19] provide examples for both the preferential cleavage of the Sn–Cl bond[1,3] and the Sn–C bond[19] under mono-[19] or disubstitution.[1,3]

In order to gain a clearer understanding of the course of such reactions, a systematic study was undertaken with compounds of the series $(CH_3)_nSnCl_{4-n}$ with n = 1, 2, 3, or 4 and two acids HSO_3F and HSO_3CF_3. Details of the solvolysis in HSO_3F are listed in Table II. The corresponding study with HSO_3CF_3 gave mostly similar results, and the other sulfonic acids were found to be less reactive. As can be seen, the Sn–Cl bond is cleaved preferentially when the reaction mixture is kept at room temperature or lower. Disubstitution occurs when the acid is present in excess. This results in the formation of the ternary compounds $CH_3SnCl(SO_3X)_2$ with X = F and CF_3, when CH_3SnCl_3 is used as the solute. That same pattern is apparently also followed when $SnCl_4$ is reacted with HSO_3F; however, this reaction reportedly proceeds very slowly even at ~100° with the formation of rather impure $SnCl_2(SO_3F)_2$.[20] A departure from the observed pattern is found when CH_3SnCl_3 is reacted with an excess of HSO_3F in order to achieve complete substitution of Cl by SO_3F. The obtained product is identified as $SnCl_2(SO_3F)_2$, identical in every regard (decomposition point, vibrational, and Mössbauer spectrum) to the previously reported compound.[5] It appears that under high-temperature conditions both one Sn–Cl bond and the Sn–C bond are cleaved. In the absence of other synthetic routes, the corresponding solvolysis of CH_3SnCl_3 in HSO_3CF_3 appeared to be a convenient method in the synthesis of dichlorotin(IV) bis(trifluoromethanesulfonate); however, under identical conditions $Sn^{II}(SO_3CF_3)_2$ is formed instead. The characterization of this compound and a discussion of its formation will be reported elsewhere.[21]

Even though the solvolysis of $(CH_3)_3SnCl$ proceeds in two clearly distinct steps,[1] immediate HCl evolution followed by slow CH_4 formation, we were unable to isolate pure $(CH_3)_3SnSO_3F$ from the mixture. As indicated by reaction 7, this compound is easily converted into dimentyltin(IV) bis(fluorosulfate) by an excess of acid.

All attempts to obtain further ternary methyltin(IV) chlorofluorosulfates by partial solvolysis resulted only in complex mixtures or incomplete reaction.

A more convenient route to the remaining two methyltin(IV) chlorofluorosulfates $(CH_3)_2SnCl(SO_3F)$ and $(CH_3)SnCl_2(SO_3F)$ could be found in some ligand redistribution reactions listed in Table III. The reported reaction of $SnCl_4$ with $Sn(SO_3F)_4$[5] to form $SnCl_2(SO_3F)_2$ at room temperature without a solvent had shown that ligand scrambling occurs for tin(IV) fluorosulfates with remarkable ease. This is confirmed for the methyltin(IV) sulfonates. Whereas reaction 2

---

(11) H. A. Anderson, *Inorg. Chem.*, **3**, 108 (1964).

(12) R. Sasin and G. S. Sasin, *J. Org. Chem.*, **20**, 770 (1955).

(13) G. S. Sasin, A. L. Borror, and R. Sasin, *ibid.*, **23**, 1366 (1958).

(14) D. Seyferth, *J. Amer. Chem. Soc.*, **79**, 2133 (1957).

(15) A. Saitow, E. G. Rochow, and D. Seyferth, *J. Org. Chem.*, **23**, 116 (1958).

(16) A. Henderson and A. K. Holliday, *J. Organometal. Chem.*, **4**, 337 (1965).

(17) V. Bade and F. Huber, *J. Organometal. Chem.*, **24**, 387 (1970), and references herein.

(18) R. J. Gillespie, R. Kapoor, and E. A. Robinson, *Can. J. Chem.*, **44**, 1197 (1966).

(19) C. S. Wang and J. M. Shreeve, *Chem. Commun.*, 151 (1970).

(20) E. Hayek, J. Puschmann, and A. Czaloun, *Monatsh. Chem.*, **85**, 359 (1954).

(21) P. A. Yeats, J. R. Sams, and F. Aubke, submitted for publication.

TABLE II

SOLVOLYSIS REACTIONS IN FLUOROSULFURIC ACID

No.	Solute	mmol of solute	mmol[a] of HSO_3F	Reaction temp, °C	Reaction time, hr	Reaction products
1	$(CH_3)_4Sn$	74.2	26.2	−80	0.25	$(CH_3)_3SnSO_3F$, CH_4
2	$(CH_3)_4Sn$	2.5	125	25	1.0	$(CH_3)_2Sn(SO_3F)_2$, CH_4
3	$(CH_3)_3SnCl$	9.2	75	25	0.5	$(CH_3)_2Sn(SO_3F)$, CH_4, HCl
4	$(CH_3)_2SnCl_2$	2.3	75	25	0.5	$(CH_3)_2Sn(SO_3F)_2$, HCl
5	CH_3SnCl_3	2.1	250	25	2.0	$CH_3SnCl(SO_3F)_2$, HCl
6	CH_3SnCl_3	4.2	500	140	120	$SnCl_2(SO_3F)_2$, HCl, CH_4
7	$(CH_3)_3SnSO_3F$	0.5	75	25	1.0	$(CH_3)_2Sn(SO_3F)_2$, CH_4

[a] The values listed are approximate except for the first.

TABLE III

LIGAND REDISTRIBUTION REACTIONS OF SOME TIN(IV) FLUOROSULFATES

No.	Substrate I	mmol	Substrate II	mmol	Reaction temp, °C	Reaction time, hr	Reaction product	Ref
1	$Sn(SO_3F)_4$	12.0	$SnCl_4$	80	25	0.5	$SnCl_2(SO_3F)_2$	5
2	$(CH_3)_2Sn(SO_3F)_2$	1.4	$(CH_3)_4Sn$	5.0	25	2.0	$(CH_3)_3SnSO_3F$	This work
3	$(CH_3)_2Sn(SO_3F)_2$	1.4	$(CH_3)_2SnCl_2$[a]	3.0	25	5.0	$(CH_3)_2SnClSO_3F$	This work
4	$CH_3SnCl(SO_3F)_2$	1.5	CH_3SnCl_3[a]	3.0	25	8.0	$CH_3SnCl_2SO_3F$	This work

[a] About 20 ml of $CHCl_3$ was added to the reaction mixture.

represents an alternative route to $(CH_3)_3SnSO_3F$, the two following reactions lead to new compounds. Exchange of Cl against SO_3F seems to take place. In order to ensure complete reaction, $(CH_3)_2SnCl_2$ and CH_3SnCl_3 were added in solution of $CHCl_3$, with both methyltin(IV) chlorides in slight excess over the required amount. The reaction mixture was purified by filtration in a closed system, followed by repeated washing with dry $CHCl_3$ in order to remove the excess methyltin(IV) chloride.

Whereas methyltin(IV) chlorocarboxylates of the type $(CH_3)_2SnClOOCR$ are known,[19,22] no precedents for $CH_3SnCl(SO_3X)_2$, with X = F and CF_3, and $CH_3SnCl_3SO_3F$ could be found in the literature. The corresponding fluorides CH_3SnCl_2F and $(CH_3)_2SnClF$ have been obtained only very recently.[6]

Attempts to extend this reaction type to trifluoromethanesulfonates resulted in incomplete reaction under the reaction conditions described above. It can be argued that the bulkier CF_3 group gives rise to greater steric hindrance and could conceivably make the uncoordinated oxygen atom in the SO_3X group less accessible. The fact that ligand scrambling can take place for methyltin(IV) compounds with bridging SO_3F groups but not for the structurally related fluorides may serve as evidence that the formation of intermediates under the conditions described may proceed initially *via* noncoordinated oxygen or even fluorine.

In general, both reaction types were found to lead quantitatively to the desired products. Vibrational spectroscopy and in particular ^{119}Sn Mössbauer spectroscopy are well suited to decide whether the obtained compounds of the type $(CH_3)_nSnCl_m(SO_3F)_{4-(n+m)}$ are true compounds or merely addition compounds with the tin atom in different environments.

II. Vibrational Spectra.—The vibrational frequencies for the new fluorosulfate and trifluoromethanesulfonates are listed in the Experimental Section. Good and well-resolved Raman spectra could not be recorded in all cases and in some instances only a limited number of the expected vibrational modes are found. The interpretation will be primarily restricted to the infrared spectra.

Since detailed assignments for the series $(CH_3)_3SnSO_3X$ with X = F, CF_3, and CH_3 are known,[2] it seemed indicated to restrict the discussion of the vibrational data to two points: the vibrational assignment for the SO_3F group for all compounds reported here and elsewhere,[2,5,6] in order to decide whether all these compounds are structurally related, and the assignment of tin–carbon and tin–chlorine stretching modes, based where possible on both infrared and Raman data, in order to decide whether linear or bent SnC_2 and $SnCl_2$ groups are present. The symmetric stretch for such a triatomic group of the type SnX_2 with X = C or Cl is only Raman active, and the asymmetric stretch only infrared active when the group is linear or nearly linear. This mutual exclusion rule breaks down for bent SnX_2 groups which have both stretching modes infrared and Raman active.

All vibrational modes due to the CH_3 groups are usually not very intense and are found not to vary much in their position for different compounds. We find the CH_3 stretches at 2870–3000 cm^{-1}, the CH_3 bending modes at 1420–1400 cm^{-1} and at about 1220 cm^{-1}, and the Sn–CH_3 rock at about 800 cm^{-1}, the last being very intense in the infrared but barely detectable in the Raman spectrum.

The modes due to the SO_3F groups are clearly distinguishable for the most part. Ambiguity exists in the 800-cm^{-1} region where the SF stretch is expected, but often obscured by the Sn–CH_3 rocking mode in the infrared spectrum. Assignment is aided in this region by the Raman spectra. In addition some SO_3F deformation modes are found in the Sn–C stretching range (530–620 cm^{-1}). Again a combination of infrared and Raman data is necessary. In addition the SO_3F bending modes are found in approximately the same place for some tin fluorosulfates without methyl groups, such as $SnCl_2(SO_3F)_2$[5] and $SnF_2(SO_3F)_2$.[6]

As pointed out previously[1,2,5,6] the symmetry of the free SO_3F ion is reduced to C_s when the group acts as either a monodentate or a bidentate covalent group. The bidentate group has been confirmed for $(CH_3)_2Sn(SO_3F)_2$ by an X-ray diffraction study.[4] As a consequence of the symmetry reduction, the number of fundamentals for the SO_3F group will increase from six

---

[22] R. Okawara and E. G. Rochow, *J. Amer. Chem. Soc.*, **82**, 3285 (1960).

TABLE IV

VIBRATIONAL MODES OF THE SO_3F GROUP IN VARIOUS TIN AND METHYLTIN(IV) FLUOROSULFATES

Compound	$\nu(SO_3)$ (A″)	$\nu(SO_3)$ (A′)	$\nu(SO_3)$ (A′)	$\nu(SF)$	$\delta(SO_3F)$ (A′)	$\delta(SO_3F)$ (A″)	$\delta(SO_3F)$ (A′)	SO_2 rock	SO_3F torsion
$(CH_3)_2Sn(SO_3F)_2$	1350	1180	1076[a]	827	620	590	554	417	304
$(CH_3)_3Sn(SO_3F)$	1355	1207[a]	1068	820	630	596	555	410	298
$(CH_3)_2SnCl(SO_3F)$	1343	1190	1072	820	607	590	555	409	306[b]
$CH_3SnCl(SO_3F)_2$	1361	1165	1072	830	620	590	555	420	305
$CH_3SnCl_2(SO_3F)$	1350	1250	1080[a]	825	605	588	555	405	300
$SnCl_2(SO_3F)_2$	1385	1130	1087	864	628	586	555	446	312
$SnF_2(SO_3F)_2$	1420[a]	1101[a]	1068	855	630	590	548	430	280

[a] Denotes average value. [b] Denotes value taken from Raman spectrum.

(3A and 3E modes) to nine (3A″ and 6A′ modes). The modes can be approximately described as SO_3 stretching (3), SF stretching (1), SO_3F bending (3), SO_2 rocking (1), and torsional SO_2F mode (1). In addition small splittings due to solid-state effects are found, affecting in particular the SO_3 stretching modes.

As can be seen from Table IV, the observed vibrational modes due to the SO_3F group fall in a rather narrow range for all seven compounds with only one SO_3 stretching mode noticeably displaced. It is on this basis safe to say that all compounds do contain only bidentate SO_3F groups possibly acting as bridging groups as in $(CH_3)_2Sn(SO_3F)_2$,[4] thus resulting in polymeric chain or sheet-like structures. The frequency separation between the two highest SO_3 stretching modes seems to increase when the other substituents on tin become more electronegative as is best apparent for the two dihalotin(IV) bis(fluorosulfates). The following rationale may be applied here. The observed three SO_3 stretching modes (at 1340–1400, 1100–1210, and at ~1070–1080 cm^{-1}) are produced from two modes for ionic SO_3F^- groups (at 1285 (E) and 1079 (A_1) for KSO_3F[23]) by splitting of the E mode at 1280 cm^{-1} into two components, one of higher and one of lower wavelength with the A_1 mode remaining in the same place. A larger splitting might then be interpreted as a greater departure from ionic toward covalent character.

The ionic character of the SO_3F group becomes apparent from the reported interatomic distances compared with those of KSO_3F[24] as listed in Table V. The reported sulfur–oxygen distances are at 1.42 and 1.43 Å, identical within the conventional error limits. It is in particular interesting that no drastic difference is found for the two coordinating SO groups and the noncoordinating one in the bidentate SO_3F group. Only the SF distance is noticeably shorter than for KSO_3F.[24] This is reflected in the shift to higher frequencies for $\nu(SF)$ by about 70–100 cm^{-1} from the value of 745 cm^{-1} for KSO_3F,[23] with the highest values found for the two dihalotin(IV) fluorosulfates. Any trends in the region of the deformation modes are less pronounced and are not discussed in any detail.

TABLE V

REPORTED INTERATOMIC DISTANCES (Å) AND SELECTED BOND ANGLES (DEG) FOR SOME FLUOROSULFATES

Bond parameter[a]	KSO_3F[25]	$(CH_3)_2Sn(SO_3F)_2$[4]
R_{S-F}	1.58	1.50
R_{S-O}	1.43	1.42
R_{Sn-O}		2.30
$2 \times R_{S-O'}$[b]	1.43	1.43
O–S–O (av)	112.9	111.1
O–S–F (av)	105.8	106.4

[a] Denotes uncorrected for thermal motion, (av) denotes average. [b] O′ denotes the oxygen atom bonded to both S and Sn.

A similar argument in favor of a bidentate SO_3CF_3 group in the reported trifluoromethanesulfonates can be presented in good agreement with our proposals for $(CH_3)_3SnSO_3CF_3$.[2] The structural similarity between this group and the fluorosulfates will become more apparent from the ^{119}Sn Mössbauer data, discussed in the following section.

Finally the assigned tin–carbon and tin–chlorine stretching modes are listed in Table VI. The reported vibrational spectra of the methyltin(IV) chlorides[25] provide good precedents for these assignments. As can be seen, the tin–carbon and tin–chlorine stretching modes fall into a rather narrow range. A linear or nearly linear carbon–tin–carbon group is suggested for $(CH_3)_2Sn(SO_3X)_2$, with X = F and CF_3, since the mutual exclusion of infrared and Raman active Sn–C stretching modes is observed. Using the same criteria, bent $Sn-Cl_2$ or SnC_2 grouping appears to be present in $CH_3SnCl_2SO_3F$ and $(CH_3)_2SnClSO_3F$, respectively.

The fact that $\nu(Sn-Cl)$ is found to vary somewhat from 345 cm^{-1} in $(CH_3)_2SnClSO_3F$ to ~385 cm^{-1} in the methyltin(IV) chlorobissulfonates may conceivably be interpreted in terms of the presence or absence of weak chlorine bridging as has been detected recently in $(CH_3)_2SnCl_2$.[26] Simple electroinductive effects can be invoked when a methyl group is formally replaced by the more electronegative SO_3X group.

III. Mössbauer Spectra.—^{119}Sn Mössbauer parameters at 80°K for the methyltin(IV) fluorosulfates and trifluoromethanesulfonates are given in Table VII, along with results for some related compounds. In every case the Mössbauer results are consistent with the presence of one and only one environment for the tin atom. With the exception of $(CH_3)_3SnSO_3X$ (X = F, CF_3, CH_3), all the derivatives reported show Mössbauer absorption at room temperature. We consider this to be good evidence for the existence of polymeric structures in these compounds, as suggested by the vibrational spectra and confirmed[4] in the case of $(CH_3)_2Sn(SO_3F)_2$. However, the absence of room-temperature absorption in the trimethyltin(IV) sulfonates does not rule out a similar polymeric structure here, as we have pointed out elsewhere.[2] Since the isomer shifts (δ) and quadrupole splittings (Δ) at

---

(23) A. M. Qureshi, H. A. Carter, and F. Aubke, *Can. J. Chem.*, **49**, 35 (1971).

(24) K. O'Sullivan, R. C. Thompson, and J. Trotter, *J. Chem. Soc. A*, 2024 (1967).

(25) W. F. Edgell and C. H. Ward, *J. Mol. Spectrosc.*, **8**, 343 (1962), and references to earlier work.

(26) A. G. Davies, H. J. Milledge, D. C. Puxley, and P. J. Smith, *J. Chem. Soc. A*, 2862 (1970).

TABLE VI

TIN–CARBON AND TIN–CHLORINE STRETCHING MODES IN THE METHYLTIN(IV) CHLOROSULFONATE COMPOUNDS

Compound		ν(Sn–C)	ν_a(Sn–C)	ν_{sym}(Sn–C)	ν(Sn–Cl)	ν_a(Sn–Cl)	ν_{sym}(Sn–Cl)
$(CH_3)_2Sn(SO_3F)_2$	Ir		576				
	RA			531			
$(CH_3)_2Sn(SO_3CF_3)_2$	Ir		584				
	RA			530			
$(CH_3)_3SnSO_3F$[2]	Ir		580				
	RA			523			
$CH_3SnCl_2SO_3F$	Ir	576				384	366
	RA					387	368
$(CH_3)_2SnCl(SO_3F)$	Ir		578	527	345		
	RA		582	535	345		
$(CH_3)SnCl(SO_3F)_2$	Ir	578			385		
	RA	585			390		
$(CH_3)SnCl(SO_3CF_3)_2$	Ir	575			384		

TABLE VII

^{119}Sn MÖSSBAUER PARAMETERS FOR SOME METHYLTIN(IV) SULFONATES AT 80°K

No.	Compound	δ, mm sec^{-1a}	Δ, mm sec^{-1}	Γ, mm sec^{-1}		R^b
1	$(CH_3)_2Sn(SO_3F)_2$	1.82	5.54	0.82	0.82	0.09
2	$(CH_3)_2Sn(SO_3CF_3)_2$	1.79	5.51	0.96	0.96	0.13
3	$(CH_3)_2Sn(SO_3Cl)_2$	1.75	5.20	0.92	0.93	0.20
4	$(CH_3)_2Sn(SO_3CH_3)_2$	1.52	5.05	0.98	1.00	0.13
5	$(CH_3)_2Sn(SO_3C_2H_5)_2$	1.52	4.91	0.86	0.89	0.12
6	$(CH_3)_2Sn(SO_3C_6H_4CH_3)_2$	1.51	4.85	1.01	1.01	0.18
7	$CH_3ClSn(SO_3F)_2$	1.23	3.77	1.02	1.14	0.12
8	$CH_3ClSn(SO_3CF_3)_2$	1.19	3.70	1.01	1.16	0.20
9[f]	$Br_2Sn(SO_3F)_2$	0.58	2.42	1.33	1.37	0.53
10[c]	$Cl_2Sn(SO_3F)_2$	0.34	2.29	1.35	1.38	0.46
11[d]	$F_2Sn(SO_3F)_2$	−0.23	1.96	1.07	1.22	0.36
12[c]	$Sn(SO_3F)_4$	−0.27	1.34	1.05	1.32	0.42
13[e]	$(CH_3)_3SnSO_3F$	1.52	4.61	0.99	1.04	
14[e]	$(CH_3)_3SnSO_3CF_3$	1.52	4.57	1.07	1.08	
15[e]	$(CH_3)_3SnSO_3CH_3$	1.43	4.21	1.03	1.06	
16	$(CH_3)_2ClSnSO_3F$	1.58	4.69	1.19	1.16	0.05
17	$CH_3Cl_2SnSO_3F$	1.14	3.25	1.29	1.12	0.55
18[d]	$(CH_3)_2SnF_2$	1.23	4.52	1.08	1.20	
19[d]	CH_3SnF_3	0.76	3.24	1.70	1.81	0.74
20[d]	CH_3SnCl_2F	1.08	2.69	1.30	1.25	0.50
21[d]	$(CH_3)_2SnClF$	1.32	3.80	1.05	1.10	0.53

[a] Relative to SnO_2 at 80°K. [b] Ratio of the Mössbauer absorption intensities at 295 and 80°K. [c] Reference 5. [d] Reference 6. [e] Reference 2. [f] D. Klett, J. R. Sams, and F. Aubke, unpublished results.

295°K are not appreciably different from those at 80°K, only the latter are considered here.

The hexacoordinate bis(sulfonate) derivatives show a very wide range of isomer shifts and quadrupole splittings, depending both on the nature of X in the SO_3X group and on the nature of the ligands occupying trans octahedral positions. For $(CH_3)_2Sn(SO_3X)_2$ with X = F, Cl, CF_3, $\delta \geqslant 1.75$ mm sec^{-1}, values which are among the highest yet observed in organotin(IV) compounds. It was suggested above that the bonding in these compounds is highly ionic, with essentially linear $(CH_3)_2Sn$ cations interacting covalently with SO_3X anions. If we describe the tin–methyl bonds in terms of sp_z hybrid orbitals on tin, then we can think of the cation–anion interaction as involving the p_x and p_y orbitals of tin in the formation of rather weak polar 3-center 4-electron bonds, a view consistent with the observed Sn–O bond distances for $(CH_3)_2Sn(SO_3F)_2$.[4] The observed distance of 2.30 Å is considerably longer than previous values for hexacoordinated tin, *e.g.*, in $SnCl_4 \cdot 2SeOCl_2$[27] (2.12 Å), and the sum of the covalent radii, according to Schomaker and Stevenson.[28] The great electronegativity of the SO_3X groups will lead to a strong withdrawal of p-electron density in the equatorial plane, with concomitant deshielding of the tin 5s electrons resulting in the high δ values observed. At the same time, a large imbalance in the p-orbital charge density on tin will result, accounting for the exceptionally large Δ values. On this picture we would expect that a decrease in the electronegativity of X, which will reduce the acceptor ability of the SO_3X group, will result in an increased p-electron density in the Sn–O region reducing both isomer shift and quadrupole splitting. This is in fact observed for X = CH_3, C_2H_5, and C_6H_4–CH_3, where δ is constant at 1.52 mm sec^{-1} and Δ is in the range 4.85–5.05 mm sec^{-1}. These values are very similar to those found for $(CH_3)_2SnSO_4$ and $(CH_3)_2SnSeO_4$.[29]

Likewise, reductions in δ and Δ occur when one of the axial methyl groups is replaced by chlorine in $CH_3ClSn(SO_3X)_2$ (X = F, CF_3), where now $\delta \simeq 1.2$ mm sec^{-1} and $\Delta \simeq 3.7$ mm sec.$^{-1}$ This can be explained in terms of a reduction of the electron donor ability of the CH_3ClSn moiety resulting in increased covalency of the Sn–O bonds, leading to increased shielding of the s-electron density on tin and a smaller imbalance of charge in the p orbitals. When both axial positions are occupied by electronegative groups, as in $Y_2Sn(SO_3F)_2$ (Y = Br, Cl, F, SO_3F), the isomer shift drops to the range $-0.3 \leqslant \delta \leqslant +0.6$ mm sec^{-1}, decreasing with increasing electronegativity of Y, and approaching the value of -0.43 mm sec^{-1} calculated for a Sn^{4+} ion with $5s^0$-electron configuration.[30] As shown in Figure 1, a linear trend is observed for the δ values of the hexacoordinated SO_3F derivatives when plotted against Pauling electronegativities for the axial ligands. However, a simple ionic structure in these compounds is precluded by the vibrational spectra,[5,6] the sizable quadrupole splittings observed, and other physicochemical data.[5,6] As suggested above, the large splitting of the E mode of the SO_3F^- ion in these derivatives indicates an increased covalency of the Sn–SO_3F bonds. This could account for the substantial increase in the *R* factor for these four compounds compared with, *e.g.*, that for $(CH_3)_2Sn(SO_3F)_2$. High *R* values (which imply a small temperature dependence of the recoil-free fraction) might not be inconsistent with an ionic model, if it is assumed that the optical modes dominate the lattice phonon spectrum.[31,32] If this were the case,

---

[27] Y. Hermodsson, *Acta Crystallogr.*, **13**, 656 (1960).

[28] V. Schomaker and D. P. Stevenson, *J. Amer. Chem. Soc.*, **63**, 37 (1941).

[29] B. F. E. Ford, J. R. Sams, R. G. Goel, and D. R. Ridley, *J. Inorg. Nucl. Chem.*, **33**, 23 (1971).

[30] J. K. Lees and P. A. Flinn, *J. Chem. Phys.*, **48**, 882 (1968).

[31] Yu. Kagan, *Sov. Phys. JETP*, **14**, 472 (1962).

[32] Yu. Kagan and V. A. Maslov, *ibid.*, **14**, 922 (1962).

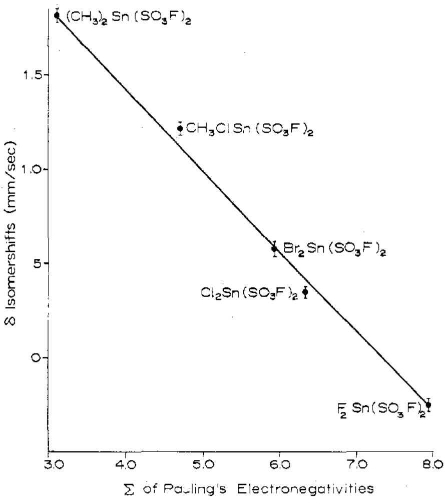

Figure 1.—Correlation between the sum of the Pauling electronegativities for axial ligands and the isomer shift in the series $X_2Sn(SO_3F)_2$ with X = CH_3, F, Cl, and Br. Electronegativity values used: F, 3.98; Cl, 3.16; Br, 2.98 (F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," Interscience, New York, N. Y., 2nd ed, 1966, p 103); CH_3, 1.57 (E. Constantinides, *Proc. Chem. Soc., London*, 290 (1964)).

however, the R value for $Sn(SO_3F)_4$ should be the largest of the four,[32] which it is not.

Quite similar trends in δ and Δ values are found for the $(CH_3)_3SnSO_3X$ derivatives (X = F, CF_3, CH_3) and a similar bonding scheme can be proposed. That is, we assume planar trimethyltin cations with sp^2 hybridization of the tin bonding orbitals interact covalently with bridging SO_3X anions *via* the tin $5p_z$ orbital. The δ values of 1.52 mm sec^{-1} for X = F and CF_3 are exceptionally high for trigonal-bipyramidal organotin(IV) compounds, as are the quadrupole splittings, but this is not unexpected on the basis of the bonding ideas above. The highly polar nature of the 3-center 4-electron O–Sn–O bonds will produce the large p-orbital imbalance required to give the observed splittings and simultaneously deshield the s-electron density, leading to the high isomer shifts. By the same reasoning as for the bis(sulfonates), replacement of F or CF_3 in SO_3X by CH_3 leads to smaller values of both δ and Δ.

It will be noted that the isomer shifts for the trimethyltin derivatives, while considerably smaller than those for the corresponding dimethyltin compounds, are still quite a bit larger than those for tetraorganotin compounds (*e.g.*, tetramethyltin, δ = 1.22 mm sec^{-1}). This trend is consistent with a reduction in the per cent s character in the tin bonding orbitals directed toward carbon from ~50% (sp hybridization) to ~33% (sp^2) to ~25% (sp^3).

Somewhat unusual behavior is noticed when one of the equatorial methyl groups in $(CH_3)_3SnSO_3F$ is replaced by chlorine to give $(CH_3)_2ClSnSO_3F$. There is an apparent small increase in δ, whereas on the basis of the data for $(CH_3)_2Sn(SO_3F)_2$ and $CH_3ClSn(SO_3F)_2$ we might have expected to find $\delta \sim 1.3$ mm sec^{-1}. The quadrupole splitting also seems anomalously high, in comparison with other data in Table VII. We shall return to this point later. For $CH_3Cl_2SnSO_3F$, δ is lowered to ~1.1 mm sec^{-1} and Δ to ~3.2 mm sec^{-1}, and at the same time there is a large increase in R.

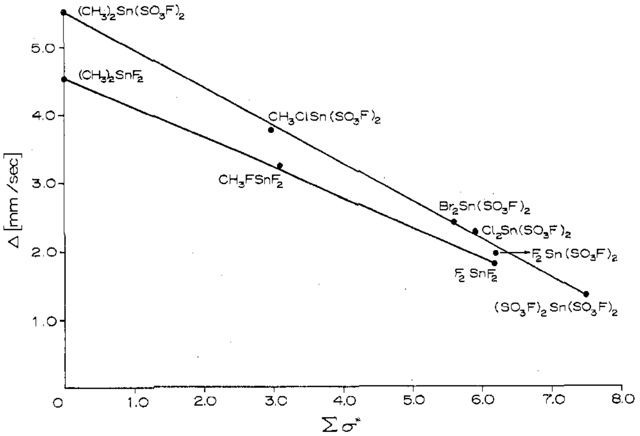

Figure 2.—Correlation between the sum of the Taft inductive constant (σ^*) for axial ligands and the quadrupole splitting (Δ) in the series $X_2Sn(SO_3F)_2$ and X_2SnF_2 with X = CH_3, F, Cl, Br, and SO_3F. σ^* values used: F, 3.08; Cl, 2.94; Br, 2.80; CH_3, 0 (R. W. Taft, Jr., "Steric Effects in Organic Chemistry," M. S. Newman, Ed., Wiley, New York, N. Y., 1956, p 615); SO_3F, 3.68 (this work).

These results suggest that the presence of two chlorine atoms in the equatorial plane increases the covalency of the Sn–O bonds, thereby producing a much stronger polymeric association.

The sign of the quadrupole interaction in the present compounds is also of interest, as this determines the shape of the charge distribution about the tin nucleus. When the principal component of the electric-field gradient V_{zz} is negative for ^{119}Sn, then the $\pm{}^3/_2$ nuclear spin state lies above the $\pm{}^1/_2$ state in energy, and the charge distribution about tin is prolate (excess electron density along the z axis over that in the xy plane). From magnetic perturbation and Gol'danskii–Karyagin effect studies on compounds of the same symmetry types,[33-37] it seems entirely safe to assume V_{zz} is negative for the $(CH_3)_2Sn(SO_3X)_2$ derivatives and positive for the $(CH_3)_3SnSO_3X$ compounds. Moreover, from the fact that in the series $Y_2Sn(SO_3F)_2$ (Y = CH_3, Br, Cl, F, SO_3F) the quadrupole splitting is linearly dependent upon the sum of the Taft inductive factors for the axial substituents (see Figure 2), we were able to show that V_{zz} must have the same sign for all members of the series.[6] A similar correlation (Figure 2) led us to conclude that $V_{zz} < 0$ also for CH_3SnF_3 and SnF_4.[6]

For compounds 16, 17, 20, and 21 in Table VII, where methyl and chlorine groups are both thought to be in equatorial positions, the signs of V_{zz} are not so easily deduced. Point-charge calculations,[38] based either on the Parish and Platt[39] partial quadrupole splitting values or on self-consistent values[38] obtained from data on other methyltin fluorides and fluorosulfates, predict $V_{zz} > 0$ for all four compounds. However, Parish and Johnson[35] have found that while V_{zz} is positive for $Me_3SnCl_2^-$, it is negative for $Me_2SnBr_3^-$, and the possibility of a similar sign reversal in the present cases cannot be ruled out. Furthermore, both $(CH_3)_2ClSnF$

---

[33] N. E. Erickson, *Chem. Commun.*, 1349 (1970).

[34] B. W. Fitzsimmons, *J. Chem. Soc. A*, 3235 (1970).

[35] R. V. Parish and C. E. Johnson, 1906 (1971).

[36] R. H. Herber and S. Chandra, *J. Chem. Phys.*, **52**, 6045 (1970); **54**, 1847 (1971).

[37] B. A. Goodman and N. N. Greenwood, *J. Chem. Soc. A*, 1862 (1971).

[38] P. A. Yeats, J. R. Sams, and F. Aubke, unpublished results.

[39] R. V. Parish and R. H. Platt, *Inorg. Chim. Acta*, **4**, 65 (1970).

and $(CH_3)_2ClSnSO_3F$ have unexpectedly large Δ values. For the former it has been suggested[6] that the large splitting and the position of ν(Sn–Cl) may indicate the presence of weak chlorine bridging. For the latter, the occurrence of ν(Sn–Cl) in the same region as found for $(CH_3)_2ClSnF$ tempts us to suggest the possibility of some chlorine bridging here as well. If chlorine bridging *is* present in these compounds, leading to quasi-octahedral structures, there could well be a reorientation of the z axis of the field-gradient tensor. Thus, determination of the signs of the quadrupole coupling constants in these two derivatives would be of considerable interest, and we hope to report such measurements in the near future.

Acknowledgments.—The financial support of this study by the National Research Council of Canada is gratefully acknowledged. We are indebted to Professor J. Trotter for making the results of the structure analysis for $(CH_3)_2Sn(SO_3F)_2$ available to us prior to publication, to Mrs. A. Sallos for technical assistance, and to the 3M Company for a gift of $Ba(SO_3CF_3)_2$.

CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY, KANSAS STATE UNIVERSITY,
MANHATTAN, KANSAS 66506, AND NORTHEASTERN UNIVERSITY, BOSTON, MASSACHUSETTS 02115

The Reaction of Fluorosulfuric Acid with Xenon Fluorides. Synthesis of Pentafluoroxenon Fluorosulfate

BY DARRYL D. DESMARTEAU* AND M. EISENBERG

Received June 20, 1972

No evidence was obtained for a xenon(IV) fluorosulfate and only the previously reported xenon(II) fluorosulfates $FXeOSO_2F$ and $Xe(OSO_2F)_2$ are formed on reaction with XeF_4. Xenon hexafluoride forms only XeF_5OSO_2F on reaction with fluorosulfuric acid. Pentafluoroxenon fluorosulfate is a stable white solid at 22° which melts with decomposition above 73°. Raman and ^{19}F nmr spectra have been used to characterize the compound.

Introduction

The ability of xenon to form chemical compounds is now well established.[1] Until recently, the known compounds were of three general types: (1) fluorides formed by reaction of xenon with strong oxidative fluorinating reagents, (2) oxides and oxyfluorides formed from reactions of the xenon fluorides, and (3) a variety of complex compounds formed by the xenon fluorides and oxyfluorides with various fluoride donors and acceptors.

Recently several investigators have reported compounds of xenon(II) formed by substitution with xenon difluoride[2–6] and there have been two reports of xenon(IV) and -(VI) compounds formed by analogous reactions.[7,8] The latter claims have recently been questioned[9,10] and this work was undertaken to identify the species formed in reactions of xenon hexafluoride and xenon tetrafluoride with fluorosulfuric acid.

Experimental Section

General.—Volatile compounds were handled in a 316SS-Kel-F vacuum system or a glass system equipped with glass–Teflon valves. Pressures were measured with a precision Heise Bourdon gauge in the metal system and in a Wallace and Tiernan differential pressure gauge in the glass system. All-metal Kel-F, FEP, and Teflon equipment was preconditioned with ClF_3 before handling XeF_6 and XeF_4.

All reactions involving XeF_6 and XeF_4 were carried out in ~6-ml Kel-F reactors fitted with 316 SS or Teflon diaphragm valves. Amounts of all reactants and products were determined by weight or *PVT* measurements. Molecular weights of gases were determined by *PVT* measurements employing a Wallace and Tiernan differential pressure gauge. Identification of volatile products was made by infrared spectra, physical properties, and vapor density molecular weight.

Infrared spectra were recorded on a Perkin-Elmer 337 spectrometer with a 10-cm Monel or glass cell fitted with silver chloride windows. Raman spectra were taken on a Spex 4001 argon laser instrument using the 465.8 nm line for excitation. Samples were prepared and run in $^1/_4$ in. o.d. FEP tubes directly.

Fluorine nmr spectra were taken on a Varian XL-100 instrument using internal $HOSO_2F$ as a reference and proton lock source. Samples were contained in $^3/_8$ in. o.d. Kel-F tubes prepared as described above for the Raman spectra. The Kel-F sample tubes were inserted into standard glass nmr tubes to record the spectra.

Reagents.—Xenon hexafluoride was prepared by heating a 30:1 fluorine–xenon mixture at 230° for 5 days. The calculated pressure assuming ideal gas behavior was 300 atm. The XeF_6 was collected in a Monel–Kel-F U-trap cooled to −25°. The ir spectrum at 25 mm showed no $XeOF_4$. Under these conditions the amount of XeF_4 contamination was assumed to be small.[11]

Xenon tetrafluoride was obtained by heating a 7:1 ratio of fluorine to xenon in a 150 ml Monel reactor for 3 hr at 400°. The total pressure at 400° was calculated to be 7 atm assuming ideal gas behavior. The XeF_4 was collected at −5° in Monel–Kel-F U-trap. The ir at the equilibrium vapor pressure of XeF_4 at 28° showed only XeF_4.

Fluorosulfuric acid was doubly distilled in an all-glass apparatus and a middle fraction boiling at 163.0° was collected in a vessel fitted with a glass–Teflon valve. After collection the storage vessel was flamed off from the distillation setup and evacuated. Sulfur trioxide was obtained from the General

---

* Author to whom correspondence should be addressed at Kansas State University.

(1) For a recent authoritative review on xenon compounds, see J. G. Malm and E. G. Appelman, *At. Energy Rev.*, **8**, 3 (1969).

(2) N. Bartlett, M. Wechsberg, F. O. Sladky, P. A. Bulliner, S. R. Jones, and R. D. Burbank, *Chem. Commun.*, 703 (1969).

(3) M. Eisenberg and D. D. DesMarteau, *Inorg. Nucl. Chem. Lett.*, **6**, 29 (1970).

(4) J. I. Musher, *J. Amer. Chem. Soc.*, **90**, 7371 (1968).

(5) F. Sladky, *Monatsh. Chem.*, **101**, 1559 (1970).

(6) F. Sladky, *ibid.*, **101**, 1571 (1970).

(7) M. Eisenberg and D. D. DesMarteau, *J. Amer. Chem. Soc.*, **92**, 4759 (1970).

(8) A. Iskraut, R. Taubenest, and E. Schumacker, *Chimia*, **18**, 188 (1964).

(9) R. J. Gillespie, First Winter Fluorine Conference, St. Petersburg, Fla., Jan 24–28, 1972.

(10) Reference 1, p 38.

(11) B. Weinstock, E. E. Weaver, and C. P. Knop, *Inorg. Chem.*, **5**, 2189 (1966).