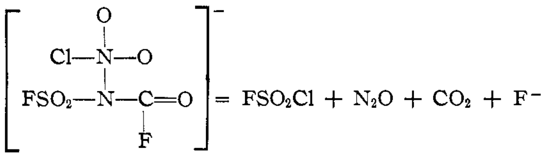
results were observed by Redwood and Willis[2] in a study of the reaction of COF_2 with alkali metal fluorides in acetonitrile solution.

Hydrolysis data and ^{19}F nmr spectra provide evidence in support of the proposed structure. The ^{19}F resonances were broadened at room temperature for $K[N(SO_2F)C(O)F]$ and $Na[N(SO_2F)C(O)F]$ indicating that exchange was taking place. A study of this exchange is in progress.

Further evidence for the proposed structure is obtained from a study of the reactions of $M[N(SO_2F)C(O)F]$ with NO_2Cl and $S_2O_6F_2$. The reaction of $Cs[N(SO_2F)C(O)F]$ with NO_2Cl yields primarily N_2O, SO_2ClF, and CO_2. Traces of SO_2F_2 are also produced. When an excess of NO_2Cl is added, NOCl is observed as a product. These results may be explained by assuming initial formation of a complex containing NO_2Cl and $Cs[N(SO_2F)C(O)F]$ which immediately undergoes decomposition by attack of an oxygen atom of the nitryl group on the carbonyl carbon atom with formation of CO_2 and elimination of F^-. Attack of chlorine on sulfur results in the formation of SO_2ClF and N_2O.



$$\left[\mathrm{FSO_2{-}}\overset{\overset{\mathrm{Cl{-}}\overset{\mathrm{O}}{\overset{|}{\mathrm{N}}}\mathrm{{-}O}}{|}}{\mathrm{N}}\mathrm{{-}}\underset{\mathrm{F}}{\underset{|}{\mathrm{C}}}\mathrm{{=}O}\right]^- = \mathrm{FSO_2Cl} + \mathrm{N_2O} + \mathrm{CO_2} + \mathrm{F^-}$$

SO_2F_2 is thought to arise by halogen exchange[15] of SO_2ClF with CsF formed during the reaction. The reason for the appearance of NOCl as a product after the second addition of NO_2Cl to the reaction mixture is not apparent, but NO_2 is known to react with CsCl to produce NOCl and $CsNO_3$.[16]

The reaction of $S_2O_6F_2$ with $M[N(SO_2F)C(O)F]$ (where M = Na, Cs) yields $FSO_2N(OSO_2F)C(O)F$.[16] This product was expected to arise by attack of the fluorosulfate group on the negative nitrogen atom of $M[N(SO_2F)C(O)F]$. FSO_2NCO appeared as a product in reactions involving both $Na[N(SO_2F)C(O)F]$ and $Cs[N(SO_2F)C(O)F]$ indicating that thermal decomposition of the adduct was probably not solely responsible for its formation. Small amounts of O_2, SO_2F_2, COF_2, and $S_2O_5F_2$ are frequently observed as byproducts in reactions involving $S_2O_6F_2$ with oxidizable substances.

The thermal decomposition data indicate that the Cs and K adducts are of comparable stability. The Na adduct is much less stable.

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The Synthesis and Mössbauer and Vibrational Spectra of Some Trimethyltin(IV) Sulfonates

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Two new trimethyltin(IV) sulfonates of the type $(CH_3)_3SnSO_3X$ with X = F and CH_3 are synthesized *via* acid solvolysis of $(CH_3)_4Sn$ in a simple one-step procedure. Detailed vibrational assignments for the SO_3X groups are presented. In both compounds and in the previously reported $(CH_3)_3SnSO_3CF_3$, bridging SO_3X groups are present, resulting in polymeric structures with pentacoordination around tin. These conclusions are confirmed by the ^{119}Sn Mössbauer spectra, where unusually high isomer shifts and wide quadrupole splittings are found. The Mössbauer data are found to be affected by the nature of X in the same manner as observed for the series $(CH_3)_2Sn(SO_3X)_2$. Attempts to identify a solvated $(CH_3)_3Sn^+$ ion by solvolysis of $(CH_3)_3SnSO_3F$ in HSO_3F were unsuccessful due to incomplete breakdown of the polymeric structures at low concentration and to further cleavage of the tin–carbon bond at higher solute concentrations.

Introduction

A number of trimethyltin(IV) salts of monobasic inorganic acids, of the type $(CH_3)_3SnX$, are known.[1-5] Their synthesis, except that for the heavier halogen compounds where ligand redistribution is feasible, has been generally accomplished *via* the silver salt method according to $(CH_3)_3SnHal + AgX \rightarrow (CH_3)_3SnX + AgHal$.

A simple alternative method has been found recently in the acid solvolysis of methyltin(IV) derivatives[6] resulting in the formation of dimethyltin(IV) bis(sulfonates) of the type $(CH_3)_2Sn(SO_3X)_2$ with X = F, CF_3, Cl, CH_3, and C_2H_5. Shortly thereafter the preparation of $(CH_3)_3SnSO_3CF_3$ was reported by the same route.[7]

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

The present communication reports the synthesis of $(CH_3)_3SnSO_3F$ and $(CH_3)_3SnSO_3CH_3$.

Structural studies of these compounds consist of the X-ray diffraction studies on $(CH_3)_3SnF$[8] and (CH_3)-SnCN[9] and vibrational spectroscopy.[2,3b,10] The absence of ν_{sym}(Sn–C) at approximately 520–530 cm^{-1} in the infrared spectrum is taken as evidence for planarity of the SnC_3 skeleton, and a lowering of symmetry for the anion, indicated by the removal of degeneracies and the breakdown of the mutual exclusion rule for ir- and Raman-active vibrations, has been explained by a bridging arrangement for the anion. It is generally concluded that pentacoordination is the rule rather than the exception,[11] resulting in polymeric structures. For the sulfonates discussed here a symmetry lowering from C_{3v} for the SO_3X in the unperturbed ion to C_s for the bidentate bridging group is expected. Detailed vibrational assignments are published only for the bridging SO_3F group.[12,13]

Further confirmation of a pentacoordinated structure is expected from the ^{119}Sn Mössbauer data. The dimethyltin(IV) bis(sulfonates), where hexacoordination for the SO_3F derivative has been confirmed by X-ray diffraction,[14] had exhibited unusually high isomer shifts and very wide quadrupole splittings. A similar situation is expected for the trimethyltin(IV) sulfonates.[6]

The trimethyltin(IV) fluorosulfate should also be a very suitable solute for solution studies in HSO_3F where established techniques exist,[15] and simple ionization should lead to a solvated trimethyltin(IV) cation. Such a species has been found to exist in H_2SO_4.[16] Organometallic cations of the type R_3Sn^+ are claimed to exist in solution in solvated form,[17] but in the solid state polymeric structures are preferred.[18]

Experimental Section

Tetramethyltin(IV) was obtained from Peninsular Chem-Research and purified before use by distillation. Fluorosulfuric acid (Allied Chemicals) was doubly distilled before use as described previously.[19] Methanesulfonic acid was purchased from Eastman Organic Chemicals and used without further purification. Chlorosulfonic acid (Matheson Coleman and Bell) was also used without purification as recommended earlier.[20] Trifluoromethanesulfonic acid was prepared by solvolysis of the barium salt with H_2SO_4. We are grateful to the 3M Co. for a gift of $Ba(SO_3CF_3)_2$. Trimethyltin chloride and $AgSbF_6$ (both Alfa Inorganics) were used for the preparation of $(CH_3)_3SnSbF_6$.

All preparations were carried out in a 100-ml two-part reaction flask with a magnetic stirring bar. The acid was added *via* a buret while the reactor with the $(CH_3)_4Sn$ was cooled in a clear-view dewar. The mixture was slowly allowed to warm up over several hours while being vigorously stirred. The course of the reaction could be followed by the methane release. The trimethyltin(IV) sulfonates were formed as white, flaky solids. The excess of tetramethyltin(IV) was recovered after the reaction.

Instrumentation.—Infrared spectra were recorded on a Perkin-Elmer 457 spectrophotometer. Silver chloride and KRS-5 (Harshaw Chemicals) were used either with Nujol as mulling agent or without any mulling agent at all.

The Mössbauer spectrometer has been described previously.[12] Measurements were made with the absorber at 80°K and the $Ba^{119m}SnO_3$ source at room temperature. All isomer shifts are reported relative to SnO_2 absorber at 80°K. The confidence limit of the Mössbauer parameter is ±0.03 mm/sec.

A Wayne-Kerr universal bridge, No. B-221A, was used for the conductometric studies. The conductivity cells and the cell constant determination are described elsewhere.[19] A Sargent thermometer, Model ST, with a circulating and heating unit was used in a constant-temperature oil bath.

Analyses and Physical Properties.—(a) *Anal.* Calcd for $(CH_3)_3SnSO_3CH_3$: C, 18.15; H, 4.67. Found: C, 18.59; H, 4.48. Mp 144–145°; subl pt 75–80° (10^{-2} mm). (b) *Anal.* Calcd for $(CH_3)_3SnSO_3F$: S, 12.20; F, 7.23. Found: S, 12.29; F, 7.04. Mp 109–111°; subl pt 70–75° (10^{-2} mm).

Results and Discussion

The new trimethyltin(IV) sulfonates are prepared in a simple straightforward manner by allowing a three- to fivefold excess of tetramethyltin(IV) to react with the corresponding acid, as reported previously for the preparation of $(CH_3)_3SnSO_3CF_3$. It is important to cool the reactants in order to get a smooth reaction and to avoid side reactions such as the formation of the dimethyltin(IV) bis(sulfonates). Reaction occurs after warming up the reaction mixture according to $(CH_3)_4Sn + HSO_3X \rightarrow (CH_3)_3SnSO_3X + CH_4$, whereby the reaction temperature seems to depend on the acid strength. Tetramethyltin reacts with HSO_3F and HSO_3CF_3 at approximately −50° and with HSO_3CH_3 at +15°. Ethanesulfonic acid reacts with $(CH_3)_4Sn$ only after warming to about 50°, and only oily, incompletely reacted materials could be obtained. An additional synthetic route to $(CH_3)_3SnSO_3CH_3$ was found inadvertently. Solvolysis of $(CH_3)_4Sn$ in HSO_3Cl was found to lead to $(CH_3)_3SnSO_3CH_3$ and $(CH_3)_3SnCl$, presumably *via* the intermediate $(CH_3)_3SnSO_3Cl$, which could not be isolated since immediate methylation on sulfur takes place. The obtained product was identified by its ir and Mössbauer spectra and by chemical analysis.

These trimethyltin(IV) compounds are found to be white, moderately hygroscopic solids. They are obtained when the excess $(CH_3)_4Sn$ is removed *in vacuo.* The melting points agree well with values reported for other trimethyltin salts.

The infrared spectral frequencies from 2000 to 250 cm^{-1} are listed in Table I. Only very fragmentary Raman data could be obtained due to strong scattering over the whole spectral range. The vibrational frequencies due to the anion do, as expected, disagree with previous reports for the alkali metal sulfonates.[21,22] This observation is in marked contrast to the report by Schmeisser, *et al.*,[7] where, even though no infrared data are published for $(CH_3)_3SnSO_3CF_3$, the claim of agreement with spectra of ionic compounds[22] is made. We have therefore reinvestigated the infrared spectrum but are unable to confirm the claim.

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TABLE I[a]

VIBRATIONAL FREQUENCIES FOR $(CH_3)_3Sn(SO_3X)$ IN CM^{-1} FROM 200 CM^{-1}

KSO_3F[b]	$(CH_3)_3SnSO_3F$	$(CH_3)_3SnSO_3CF_3$	$(CH_3)_3SnSO_3CH_3$
	1408 wm, CH_3 asym def	1400 w, CH_3 asym def	1418 w, 1405 w, sh, CH_3 asym def
	1355 s, SO_3 str (A'')	1319 vs, b, SO_3 str (A'')	1345 m, sh, 1337 m, CH_3 sym def
1285 $\nu(SO_3)$ (E)	1335 m, CH_3 sym def		
		1226 vs, CF_3 str (E)	1266 s, SO_3 str (A'')
1079 $\nu(SO_3)$ (A_1)	1218 s 1196 vs} SO_3 str (A')	1179 s, b, CF_3 str (A_1)	1254 vs
			1207 vw
			1196 vw
745 ν(SF) (A_1)			
	1123 w, 2 × 555	1145 s, SO_3 str (A')	1112 vs, SO_3 str (A')
594 $\delta(SO_3)$ (E)			
586	1068 vs, SO_3 str (A')	1026 s, SO_3 str (A')	1035 s, SO_3 str (A')
570 $\delta(SO_3)$ (A_1)	820 s, sh, SF str (A')	796 s, CH_3 rock	968 w
			810 s, sh, CH_3 rock
407 rock(SO_3F) (E)	778 vs, CH_3 rock	771 m, CF_3 def (E)	783 s, CH_3 rock
	630 m, SO_3 def (A'')	633 ms, SO_3 def (A'')	562 s, SO_3 def (A'')
	596 s, SO_3 def (A')	577 ms, SO_3 def (A')	550 vs, Sn–C asym str
	578 s, SO_3 def (A')	555 s, Sn–C asym str	531 s, SO_3 def (A')
			516 ms, SO_3 def (A')
	555 s, Sn–C asym str	530 m, sh, SO_3 def (A')	425 mw, S–C str
			352 m, sh 346 m} SO_3CH_3 rock (A'')
	410 ms, SO_3F rock (A'')	517 ms, CF_3 def (A_1)	
		356 ms, SO_3CF_3 def (A'')	
	370 ms, SO_3F rock (A')	347 s, S–C str (A')	330 m, Sn–O str
		330 m, sh, SnO str	
	298 m, b, Sn–O str	317 m, SO_3CF_3 rock (A')	275 m, sh, SO_3CH_3 rock (A')

[a] Key: vw, very weak; w, weak; m, medium; s, strong; vs, very strong; sh, shoulder; b, broad; def, deformation; rock, rocking. [b] Raman spectrum of ref 22.

All anion frequencies indicate the presence of only one type of SO_3X group and are best rationalized by assuming a lowering of the symmetry of SO_3X from C_{3v} to C_s. As a consequence, the number of fundamentals will increase from 6 for the SO_3X ion (3 A_1 and 3 E modes, all ir and Raman active) to 9 for the covalently bonded SO_3X group (6 A' and 3 A'' modes).

Covalent interaction, of course, is not the only possible explanation for the observed splitting of the E modes. Alternative arguments could involve site symmetry lowering and anion polarization by the nonspherical cation. These alternatives can be dismissed for the following reasons. (a) Site symmetry and polarization effects are expected to lead to small splittings of the E modes—typical values are found between 10 and 30 cm^{-1} for $NOSO_3F$ and NO_2SO_3F,[23] compounds with nonspherical, polarizing cations. (b) For SO_3F compounds no effect on the S–F stretching mode (A_1) should be found if no interaction took place, but the spectrum indicates a strong shift of ν(S–F) to higher wave numbers. (c) Excellent agreement is found for the anion spectra of the trimethyltin(IV) sulfonates and the corresponding dimethyltin(IV) bis(sulfonates), where proof for the bridging SO_3F group is obtained from X-ray diffraction.[14] The observed Sn–O distance is at 2.27 Å only slightly longer than the single-bond distance of approximately 2.12 Å as *e.g.*, in $SnCl_4 \cdot 2SeOCl_2$.[24] The observed symmetry lowering is also expected for a monodentate SO_3X group; however, argument c and the fact that at least two SO stretching modes are found at higher frequencies[12,13] rule this possibility out.

The nine frequencies can best be described in the following way: three S–O stretching modes (2 A' and A''), one S–X stretch (A'), three S–O deformation modes (2 A' and 1 A''), and two rocking modes (A' and A''). Frequencies for the ionic SO_3F group in KSO_3F are listed as a guide in Table I.

Complications are found for the SO_3CF_3 groups, where an accurate vibrational assignment for the $SO_3CF_3^-$ has been hampered by the fact that S–O and C–F vibrations of identical symmetry (A' and E) are found in the same spectral range,[22] resulting in extensive coupling. Symmetry lowering due to covalent bridge bonding will remove the degeneracy for the S–O stretching and deformation modes and should lead to a clearer distinction as is found in our case. Tentative assignment for all modes except for some very weak combination modes is presented in Table I. Some small splittings of various modes can be attributed to crystalline field effects and spatially different orientations of the SO_3X groups.

Vibrational modes for the SO_3CF_3 group are found at lower wave numbers than the corresponding ones for SO_3F, the difference being about 40 cm^{-1}. Similar effects are reported for the S–O stretching frequencies of the pairs CF_3SO_2F *vs.* FSO_2F and CF_3SO_2Cl *vs.* FSO_2Cl.[25] The CF_3 modes are assigned in agreement with previous work on $SO_3CF_3^-$.[22]

Vibrational modes assigned to the trimethyltin group are in good agreement with previous reports.[1,2] Again the symmetric Sn–C stretching mode, found usually in the Raman spectrum at 520 cm^{-1}, is missing in the ir spectrum. The CH_3 stretching modes, not listed, are generally very weak and found at 3000–2900 cm^{-1}. It is interesting that all CH_3 modes in the methanesulfonate are split, as expected.

All assignments in the very low-frequency range are tentative, in particular where the tin–oxygen stretches are concerned. Far-infrared work is needed to arrive at a better assignment in this part of the spectrum.

The ^{119}Sn Mössbauer parameters at 80°K are listed in Table II, together with those for some related compounds. The spectrum of $(CH_3)_3SnSO_3CH_3$ is repro-

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TABLE II

^{119}Sn MÖSSBAUER DATA FOR SOME TRIMETHYLTIN(IV) COMPOUNDS AT 80°K[a]

Compound	Isomer shift[b]	Quad-rople splitting[c]	Γ_1	Γ_2
$(CH_3)_3SnSO_3F$	1.52	4.61	0.99	1.04
$(CH_3)_3SnSO_3CF_3$	1.52	4.57	1.07	1.08
$(CH_3)_3SnSO_3CH_3$	1.43	4.21	1.03	1.06
$(CH_3)_3SnSbF_6$	1.47	4.75	1.20	1.22
$(CH_3)_3SnCO_2CF_3$[d]	1.38	4.22		
$[(CH_3)_3Sn]_2SO_4$[e]	1.37	4.06		
$(CH_3)_3SnF$[f]	1.18	3.47		
$(CH_3)_2Sn(SO_3F)_2$[g]	1.82	5.54		
$(CH_3)_4Sn$[f]	1.22	0		

[a] All values in mm/sec, ±0.03 mm/sec. [b] Relative to SnO_2 at 80°K. [c] The signs are those predicted in the text. [d] C. Poder and J. R. Sams, *J. Organometal. Chem.*, **19,** 67 (1969). [e] B. F. E. Ford, J. R. Sams, R. G. Goel, and D. R. Ridley, *J. Inorg. Nucl. Chem.*, in press. [f] R. H. Herber and G. I. Parisi, *Inorg. Chem.*, **5,** 769 (1966). [g] Reference 6a.

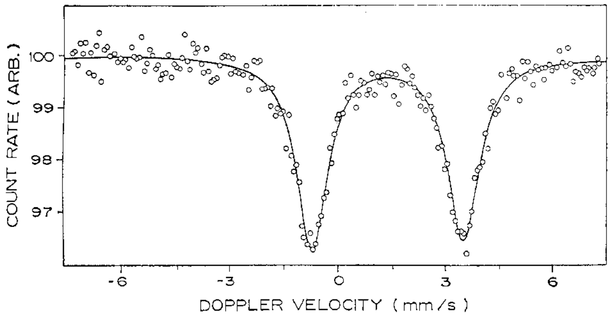

Figure 1.—The ^{119}Sn Mössbauer spectrum of $(CH_3)_3SnSO_3CH_3$ at 80°K.

duced in Figure 1. Except for $(CH_3)_3SnSbF_6$, which was measured for reference purposes, no resolvable Mössbauer spectra could be obtained at room temperature. This by no means rules out the polymeric structure indicated by the vibrational spectra. Many triorganotin(IV) carboxylates, where polymeric structures are doubtlessly present, do not appear to exhibit a room-temperature effect.[26] Furthermore, room-temperature absorption in the $R_2Sn(SO_3X)_2$ series, where two bridging groups are present instead of one, is not strong.[6a]

The molecular structure best suited to describe the observed vibrational and Mössbauer spectra is analogous to the one first proposed by Clark[1] for $(CH_3)_3SnClO_4$: planar $(CH_3)_3Sn$ groups are linked by bidentate bridging SO_3X groups resulting in chain-type polymers with a possibly distorted trigonal-bipyramidal configuration about tin. This is not unexpected since the ClO_4 and SO_3F groups are isoelectronic.

Structural similarity within this group of compounds is indicated by the Mössbauer parameters, and the same trends noted for compounds of the type $R_2Sn(SO_3X)_2$ are again observed.[6a] Both isomer shift and quadrupole splitting increase with increasing electronegativity of X, both parameters being identical for X = F and CF_3 within the accuracy of the measurements. The isomer shifts show a fairly small spread from 1.43 to 1.52 mm/sec relative to SnO_2 and are higher than any previously reported values for trimethyltin(IV) compounds except those for $(CH_3)_3SnSbF_6$. This is indicative of a high s-electron density around tin. The quadrupole splittings (Δ) are larger than those found for trimethyltin(IV) haloacetates[27] and sulfates[28] but are considerably smaller than those for the dimethyltin(IV) bis(sulfonates).[6a] The Δ values range from 4.21 to 4.61 mm/sec and are exceeded only by the value for $(CH_3)_3SnSbF_6$. A detailed discussion of the Mössbauer parameters for the trimethyltin(IV) sulfonates and a discussion of the bonding in these and related compounds will be presented in a forthcoming publication.[29]

It became interesting to see whether trimethyltin(IV) fluorosulfate would dissociate in HSO_3F under quantitative formation of solvated trimethyltin(IV) cations in analogy to the reported findings in H_2SO_4.[16] This is clearly not borne out by the conductivity results in HSO_3F. The specific conductivity values κ, together with the values for $(CH_3)_2Sn(SO_3F)_2$[6b] and the standard base KSO_3F,[19] are listed in Table III. The plot of the conductance *vs.* the molality is shown in Figure 2.

TABLE III

SPECIFIC ELECTRIC CONDUCTANCE OF $(CH_3)_2SnSO_3F$ AND $(CH_3)_2Sn(SO_3F)_2$ IN HSO_3F AT 25°

Concn, *m*	$(CH_3)_3SnSO_3F$[a] $10^4\kappa$, $ohm^{-1}\ cm^{-1}$	$(CH_3)_3SnSO_3F$[b] $10^4\kappa$, $ohm^{-1}\ cm^{-1}$	$(CH_3)_2Sn(SO_3F)_2$ $10^4\kappa$, $ohm^{-1}\ cm^{-1}$
2.5×10^{-3}	4.82	4.65	4.15
5.0×10^{-3}	8.26	7.80	6.18
7.5×10^{-3}	11.22	10.64	8.75
1.0×10^{-2}	14.20	13.30	10.50
1.25×10^{-2}	17.01	15.74	12.40

[a] Measured immediately after addition. [b] Measured after 30 min.

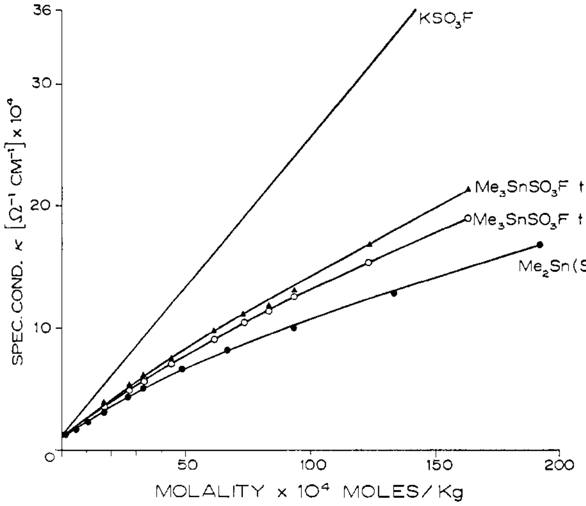

Figure 2.—Specific conductivities in HSO_3F at 25.0°.

The observed κ values are less than expected for complete solvolysis, even at very low concentration. Furthermore a small drift of the measured conductance to lower values is noticed in the first 30 min after solute addition, accompanied by a small amount of gas evolution. This drift is only noticed at concentrations above 10^{-3} *m*. A stable equilibrium is reached after 30 min.

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(27) C. Poder and J. R. Sams, *J. Organometal. Chem.*, **19,** 67 (1969).

(28) B. F. E. Ford, J. R. Sams, R. G. Goel, and D. R. Ridley, *J. Inorg. Nucl. Chem.*, in press.

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

This behavior justifies the conclusion that a monomeric $(CH_3)_3Sn^+{}_{solv}$ is not a stable species in HSO_3F. The low conductance in the early stages of the measurement indicates an incomplete breakdown of the polymeric structure, because the amount of SO_3F^- ions, the main contributor to the electrical conductance for basic solvolysis, is less than expected. This does not rule out the possibility that some $(CH_3)_3Sn^+{}_{solv}$ may be formed, but it is clearly not the sole tin species as is the case in H_2SO_4.

At higher concentrations, two effects are noticed. Dissociation decreases further and the curve of κ *vs.* molality shows some inflection. In addition further solvolysis of the tin–carbon bond occurs giving rise to dimethyltin(IV) derivatives in solution. The quantitative conversion of $(CH_3)_3SnSO_3F$ into $(CH_3)_2Sn(SO_3F)_2$ has been accomplished at higher solute to solvent ratios and is described together with the detailed solvolysis studies of the latter compound elsewhere.[6b]

Due to limited stability of the incomplete electrolytic dissociation, intended studies such as Raman, nmr, and frozen-solution Mössbauer were found not too meaningful. It must be concluded that weaker protonic solvents may be more suited as solvent systems for organotin cations.

The work presented allows a very good insight into the structure and bonding of the trimethyltin(IV) sulfonates. We hope to verify some of the structural proposals by X-ray diffraction.

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The Oxidation of Halates to Perhalates by Xenon Difluoride in Aqueous Solution[1]

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Xenon difluoride oxidizes chlorate, bromate, and iodate to the respective perhalates. The maximum yield of perchlorate and periodate is about 93% of the initial XeF_2. The maximum yield of perbromate is only about 12%. In the oxidation of iodate, the maximum yield is obtained at iodate concentrations above 0.001 *M*, while in the oxidation of chlorate and bromate the maximum yield is only approached at halate concentrations in excess of 1 *M*. The oxidation of chlorate and bromate is brought about by an intermediate in the oxidation of water by XeF_2. The same is true of the oxidation of low concentrations of iodate. At high iodate concentrations, however, a direct reaction between XeF_2 and IO_3^- takes place. These reactions have been interpreted in terms of oxidation of the halate to an intermediate that either can go on to form stable perhalate or else can react with water to give back halate. The latter reaction predominates in the case of bromate. Experiments in the chlorine and bromine systems with ^{18}O-enriched water show that during the course of the reaction there is no gross exchange of oxygen between solvent water and halate or perhalate. However, in the bromate case, reversion of the oxidized intermediate to BrO_3^- leads to ^{18}O enrichment of the unreacted bromate. Substantial reduction of periodate by XeF_2 is observed. This reduction can be suppressed, however, if a sufficient excess of iodate is present.

Introduction

The formation of the perhalate ion by chemical oxidation of halate becomes increasingly more difficult as one goes from periodate to perchlorate to perbromate. The only oxidants known to form perbromate from bromate are XeF_2 in acid solution[2] and F_2 in alkaline solution.[3] That this increasing difficulty of oxidation is a kinetic rather than a thermodynamic effect is evident from consideration of the standard electrode potentials of the halate–perhalate couples. For iodate–periodate the potential is 1.64 V,[4] for chlorate–perchlorate it is 1.23 V,[4] and for bromate–perbromate it is 1.74 V.[5]

In this paper we have attempted to shed light on the nature of the activation barrier to the formation of perhalate by examining the reaction between aqueous xenon difluoride and each of the halate ions. We hope in the future to be able to carry out a similar study using molecular F_2 in place of XeF_2.

Xenon difluoride dissolves in water to the extent of about 0.15 *M* at 0°, and the solution appears to contain discrete XeF_2 molecules.[6,7] The standard electrode potential of the reaction

$$Xe(g) + 2HF = XeF_2 + 2H^+ + 2e^-$$

has been calculated to be 2.64 V,[8] making XeF_2 one of the most potent oxidants known in aqueous solution. Aqueous XeF_2 oxidizes water with a half-time of about 27 min at 25°.[9] The reaction is catalyzed by bases and by fluoride acceptors; this fact suggests that the rate-determining step may be hydrolysis to form a xenon oxy compound as an intermediate.[9]

There is good evidence that the reaction between

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[1] Work performed under the auspices of the U. S. Atomic Energy Commission.

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