for CH_3SeCl_3 where Cl bridging has been postulated.[4,8] Lastly, the frequencies assigned to the $CH_3SeCl_2^+$ ion are in reasonable agreement with those observed for CH_3AsCl_2.[22]

Virtually identical far-infrared spectra were recorded for both $CH_3SeCl_3 \cdot SbCl_5$ and $C_2H_5SeCl_3 \cdot SbCl_5$. Using arguments identical to those above we believe that formulation I best represents the structure of $C_2H_5SeCl_3 \cdot SbCl_5$. The spectrum of $C_6H_5SeCl_3 \cdot SbCl_5$ was similar to that of the methyl- and ethylselenium trichloride adducts suggesting an ionic formulation best represents the solid-state structure of this adduct also. Frequency assignments for these three adducts have therefore been made assuming the presence of an $RSeCl_2^+$ ion of C_s symmetry and an $SbCl_6^-$ ion of O_h symmetry. We have assigned the higher and lower Se–Cl stretching frequencies to $\nu_2(A')$ and $\nu_5(A'')$, respectively, by analogy with the assignment for $SeOCl_2$[16] and a number of other XYZ_2 molecules of C_s symmetry.[23]

The ν_3 vibration observed in $SeOCl_2$ at 161 cm^{-1} was not observed in any of the $RSeCl_3 \cdot SbCl_5$ adducts and may be coincident with strong ν_5 absorption of $SbCl_6^-$ at 180 cm^{-1}. In addition it appears that ν_4 and ν_6 are degenerate and appear at 280 cm^{-1}. In contrast these frequencies are well separated in one tellurium analog ($CH_3TeCl_3 \cdot SbCl_5$).

Turning to the organotellurium trichloride–antimony pentachloride adducts we find that in the critical Te–Cl and Sb–Cl stretching regions there is considerable overlap of peaks. However, it appears that "Sb–Cl" absorptions are once again found at ~180 and ~340 cm^{-1}, while the peaks at ~370 and ~270 cm^{-1} are assignable to Te–Cl modes. We have assigned peaks in these regions assuming the presence of $RTeCl_2^+$ and $SbCl_6^-$ ions by analogy with the structure favored for $RSeCl_3 \cdot SbCl_6$ adducts. Our evidence favoring the $RTeCl_2^+SbCl_6^-$ formulation is not strong and it is possible that halogen bridging is more important in the solid-state structure of these adducts than in their selenium analogs. However, the highest Te–Cl stretch in the $RTeCl_3 \cdot SbCl_5$ adducts is found 35 cm^{-1} higher than in CH_3TeCl_3.[8] If one again assumes that a higher terminal stretching frequency may be correlated with decreased bridging, then the 35-cm^{-1} difference is evidence in support of an ionic formulation. It should also be noted that the increase in the Te–Cl bending frequencies in $CH_3TeCl_3 \cdot SbCl_5$ adduct relative to those found for CH_3TeCl_3[8] (103, 140, and 200 cm^{-1}) is also evidence tending to favor an ionic model.

We examined the solution spectra of the $RSeCl_3 \cdot SbCl_5$ adducts in chloroform. No peaks were observed above 400 cm^{-1}, but a strong broad absorption due to $CHCl_3$, Se–Cl, and Sb–Cl modes was found centered at 375 cm^{-1}. This suggests the adducts are mainly dissociated in solution according to the equation $RSeCl_3 \cdot SbCl_5 \rightarrow RSeCl_3 + SbCl_5$. Also consistent with a high degree of dissociation are nmr spectral data in CD_2Cl_2 on freshly prepared solutions of $RSeCl_3 \cdot SbCl_5$ adducts. The proton chemical shifts are essentially unchanged from those observed in the parent trichlorides.[4,8]

A study of the nmr spectra *vs.* time showed substantial decomposition of the alkylchalcogen trichloride–antimony pentachloride adducts took place over an 8-hr period, one of the main products being the alkyl chloride. This relatively rapid decomposition is responsible for the limited solution data as it was impossible to obtain reliable molecular weight or conductivity data on any of the adducts. The nmr spectra of the aryl derivatives were not studied *vs.* time but solutions turned dark indicating decomposition after 24 hr.

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(23) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," Wiley, New York, N. Y., 1963, p 90.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
WAKE FOREST UNIVERSITY, WINSTON-SALEM, NORTH CAROLINA 27109

The Reaction of Fluorosulfuryl Isocyanate with Alkali Metal Fluorides(1)

BY JOSEPH A. RODERIGUEZ AND RONALD E. NOFTLE*

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Fluorosulfuryl isocyanate reacts with cesium, potassium, and sodium fluorides in acetonitrile solvent at 25° to form stable, solid adducts having a molar ratio $FSO_2NCO{:}MF$ close to 1:1. Chemical and physical evidence indicates that these compounds may be formulated as the salts of fluoroformylfluorosulfurylimide, $M^+[N(SO_2F)C(O)F]^-$.

Redwood and Willis[2] have described the preparation of the alkali metal trifluoromethoxides $MOCF_3$ (where M = K, Rb, Cs) by the reversible reaction of carbonyl fluoride with the appropriate alkali metal fluoride in acetonitrile solvent.

Fawcett, *et al.*,[3] have reported that addition of carbonyl fluoride across the carbon–nitrogen double

(1) Presented in part at the Summer Symposium on Fluorine Chemistry Honoring Professor G. H. Cady, Milwaukee, Wis., June 1970.

(2) M. E. Redwood and C. J. Willis, *Can. J. Chem.*, **43**, 1893 (1965).

(3) F. S. Fawcett, C. W. Tullock, and D. D. Coffman, *J. Amer. Chem. Soc.*, **84**, 4275 (1962).

bond of $CF_3N{=}CF_2$ is brought about by the catalytic action of CsF, presumably[4] through the formation of an intermediate addition product of CsF across the carbon–nitrogen double bond, $Cs^+[N(CF_3)_2]^-$.

In view of this work, it was of interest to examine the reaction of fluorosulfuryl isocyanate, FSO_2NCO, with various alkali metal fluorides to determine whether addition products would form. When a slight excess of FSO_2NCO was allowed to contact a slurry of CsF and acetonitrile, the CsF dissolved exothermally. Upon removal of the solvent, a white crystalline solid of composition $CsF \cdot FSO_2NCO$ was isolated. Similar results were observed with NaF and KF. Physical and chemical data supported formulation of these adducts as $M^+[N(SO_2F)C(O)F]^-$.

Experimental Section

Materials.—FSO_2NCO was prepared by the method of Roesky and Hoff.[5] It was found that addition of a small amount of $SbCl_5$ increased the rate of the reaction. Purity was determined by infrared analysis[6] and determination of molecular weight: calcd, 125; found, 124.

Acetonitrile (Baker Chemical Co., reagent grade) was stored over calcium hydride to ensure dryness. It was freshly distilled prior to use.

Cesium fluoride was obtained from the American Potash and Chemical Corp. It was handled in a drybox and samples for reaction were flamed under high vacuum to ensure complete absence of moisture. Weight loss data on such samples showed that a negligible amount of moisture was present.

Sodium and potassium fluorides were obtained from Baker Chemical Co. and dried by heating to redness in a Pt crucible prior to use. The materials were handled in a drybox thereafter.

$S_2O_6F_2$ was prepared and purified according to Dudley.[7]

Nitryl chloride was prepared by the method of Haplan and Schechter,[8] purified by repeated fractional condensation, and checked for purity by infrared analysis[9] and molecular weight determination.

Preparation of $Cs^+[N(SO_2F)C(O)F]^-$.—In a typical preparation, a weighed amount of dry CsF was held in a 30-ml Pyrex reaction vessel equipped with a 4-mm Fisher and Porter threaded glass valve and a Teflon-covered stirbar. Dry CH_3CN was condensed into the weighed vessel at −196° and the vessel was reweighed after warming it to room temperature. A weighed excess of FSO_2NCO was condensed onto the suspension by cooling the vessel to −196°. Upon warming to room temperature with stirring, all of the CsF dissolved exothermally to form a clear solution.

All of the volatile material remaining after the reaction was removed by pumping at room temperature through a collection trap held at −196°. As the liquid phase was removed, the product mixture in the reaction vessel became very viscous until, on prolonged pumping, a white solid remained. This solid was identified as a 1:1 addition product of FSO_2NCO and CsF, $Cs^+[N(SO_2F)C(O)F]^-$. The volatile materials were shown to consist only of FSO_2NCO and CH_3CN by comparison of their infrared spectra with published spectra.[5,10]

Characterization.—Preliminary characterization was accomplished by comparing the weight of CsF present initially with the weight of the solid residue remaining after reaction. Data from four runs are presented in Table I. As can be seen from the table, the molar ratio of FSO_2NCO to CsF varied with each run. The ratio most closely approached 1:1 for runs in which the solvent and unreacted FSO_2NCO were removed quickly from the product (see Discussion). The volatile materials (CH_3CN and FSO_2NCO) removed were not separated but a combined weight was obtained.

Samples of $Cs^+[N(SO_2F)C(O)F]^-$ which weight uptake data indicated to be of high quality were submitted to A. Bernhardt, Mikroanalytisches Laboratorium, Elbach, West Germany, for elemental analysis. *Anal.* Calcd for $Cs^+[N(SO_2F)C(O)F]^-$: C, 4.34; F, 13.72; N, 5.06; S, 11.58. Found: C, 4.13, 4.20; F, 13.71, 13.71; N, 5.24; 5.20; S, 11.63, 11.75.

TABLE I

WEIGHT UPTAKE DATA (GRAMS) FOR THE REACTION: $CsF + FSO_2NCO = Cs^+[N(SO_2F)C(O)F]^-$

CsF (reactant)[a]	FSO_2NCO (reactant)[a]	CH_3CN	$FSO_2NCO + CH_3CN$ (recovered)	FSO_2NCO (combined)[a]	Molar combining ratio FSO_2NCO/CsF
2.3712 (15.61)	2.3625 (18.89)	8.2608	8.7691	1.8609 (14.88)	0.9532
6.4144 (42.23)	6.6000 (52.77)	12.9783	14.4237	5.1644 (41.29)	0.9777
2.3332 (15.36)	3.5500 (28.38)	6.5153	8.1778	1.8875 (15.09)	0.9824
1.6264 (10.71)	1.5500 (12.39)	17.2158	17.4433	1.3327 (10.65)	0.9943

[a] Corresponding number of millimoles in parentheses.

The ^{19}F nmr spectrum of $Cs^+[N(SO_2F)C(O)F]^-$ was taken in CH_3CN solution using a Varian A-56/60 nmr spectrometer. CCl_3F was used as an external reference. Two resonances of equal intensity were observed which upon high resolution split into doublets. The low-field doublet (−47.4 ppm) was assigned to the fluorine atom attached to the sulfuryl group ($-SO_2F$),[5,6] and the high-field doublet (−4.7 ppm) was assigned to the fluorine atom attached to the carbonyl group ($-C(O)F$).[6] The fluorine–fluorine coupling constant was observed to be 16 Hz.

A sample of $Cs^+[N(SO_2F)C(O)F]^-$ was hydrolyzed in base qualitatively and the resulting solution was tested for the presence of SO_4^{2-}, CO_3^{2-}, F^-, and NH_3.[11] All were found to be present. A weighed sample of $Cs^+[N(SO_2F)C(O)F]^-$ (2.0687 g, 7.469 mmol) was allowed to react with a known excess of 0.2000 *N* NaOH for 1 week at 100°. The unconsumed base was back-titrated with standard HCl after first adding an exact quantity of $BaCl_2$ solution to prevent end point interference by CO_3^{2-}. The titration showed that 37.18 mequiv of OH^- had been consumed. These results indicated that hydrolysis of the compound could be represented by the equation

$$Cs^+[N(SO_2F)C(O)F]^- + 5OH^- = SO_4^{2-} + NH_3 + 2F^- + CO_3^{2-} + Cs^+ + H_2O$$

where the following data apply: calcd, 5.000 mequiv of OH^-/mmol of $Cs^+[N(SO_2F)C(O)F]^-$; found, 4.978 mequiv of OH^-/mmol of $Cs^+[N(SO_2F)C(O)F]^-$.

Samples of $Cs^+[N(SO_2F)C(O)F]^-$ from a number of different preparations were sealed into Pyrex capillaries under vacuum. Melting points of these samples were obtained. Some individual melting point ranges were 70–74, 74–77.5, and 80.5–83.4° for samples whose ratios of FSO_2NCO to CsF were 0.9532, 0.9824, and 0.9943, respectively. It is seen that the highest melting point range corresponded to the sample with the highest ratio of FSO_2NCO to CsF. This result is consistent with the fact that there is less CsF present as an impurity in samples with combining ratios close to 1:1.

A sample of $Cs^+[N(SO_2F)C(O)F]^-$ (0.2772 g) was heated to 90° under high vacuum for 1.5 hr. The solid was observed to melt and volatile material (0.0081 g) was collected in a trap held at −196°. Infrared analysis identified the volatile material as FSO_2NCO.[5] The small amount of decomposition observed under these conditions demonstrates the stability of $Cs^+[N(SO_2F)C(O)F]^-$.

Attempts to record infrared spectra were generally unsuccessful owing to the hygroscopic nature of the compound.

Preparation of $K^+[N(SO_2F)C(O)F]^-$.—In one of a series of preparations, dry KF (0.6119 g, 10.53 mmol) and CH_3CN (1.7937 g) were placed in a 30-ml Pyrex vessel equipped with a Teflon stopcock. FSO_2NCO (1.8297 g, 14.63 mmol) was added, and the KF dissolved slowly to give a clear colorless solution. Complete dissolution required several hours. As soon as all of the KF dissolved, the volatile material was quickly removed leaving a glassy, viscous residue. The volatile material was shown to consist of CH_3CN and FSO_2NCO by infrared analysis.[5,10] The remainder of FSO_2NCO and CH_3CN was removed with great

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[4] R. E. Banks, "Fluorocarbons and Their Derivatives," Oldburne Press, London, 1964, p 91.

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difficulty, leaving a crystalline solid weighing 1.9063 g which had a ratio of FSO_2NCO to KF equal to 0.9826. In some cases, several days of pumping under high vacuum was required to achieve constant weight. The glassy residue did not form stable crystals until the ratio of FSO_2NCO to KF was close to 1.0000 or slightly lower. Other preparations gave similar results: $FSO_2NCO:KF = 0.9972, 1.0049$.

Characterization.—The ^{19}F nmr spectrum of an acetonitrile solution of $K^+[N(SO_2F)C(O)F]^-$ showed two resonances of equal intensity at −46.0 and −3.9 ppm relative to CCl_3F. Under high resolution, each of these resonances split into a doublet with a coupling constant of 16.5 Hz. These values are in good agreement with those observed for $Cs^+[N(SO_2F)C(O)F]^-$. *Anal.* Calcd for $K^+[N(SO_2F)C(O)F]^-$: K, 21.35; S, 17.50. Found: K, 21.00; S, 18.78.

A sample of $K^+[N(SO_2F)C(O)F]^-$ (0.6809 g) which weight uptake data indicated to be of good quality ($FSO_2NCO:KF = 0.9923$) was held at 90° for 1 hr under dynamic vacuum. Volatile material (0.0087 g) was collected in a trap at −196° during this time and was shown to be FSO_2NCO and a trace of CH_3CN by infrared analysis.[5,10] This result indicated that $Cs^+[N(SO_2F)C(O)F]^-$ and $K^+[N(SO_2F)C(O)F]^-$ are of comparable stability. When a sample of $K^+[N(SO_2F)C(O)F]^-$ was held at 150° under dynamic vacuum, COF_2 was observed as a product in addition to FSO_2NCO.

Preparation of $Na^+[N(SO_2F)C(O)F]^-$.—The procedure previously described was followed. In a typical reaction, NaF (0.2386 g, 5.68 mmol) combined with FSO_2NCO in CH_3CN solution to yield a white crystalline product (0.9472 g) having a ratio of $FSO_2NCO:NaF$ equal to 0.9972. No difficulty was experienced in removing the solvent and excess FSO_2NCO. Other runs yielded products having ratios of $FSO_2NCO:NaF$ equal to 0.9672 and 0.9989.

Characterization.—*Anal.* Calcd for $Na^+[N(SO_2F)C(O)F]^-$: Na, 13.76; S, 19.19. Found: Na, 13.77; S, 20.29. The ^{19}F nmr spectrum of $Na^+[N(SO_2F)C(O)F]^-$ in CH_3CN solution showed two resonances of equal intensity which were resolved into doublets under high resolution: δ_{S-F} −47.7 ppm, δ_{C-F} −3.9 ppm; $J_{F-F} = 15$ Hz.

A sample of $Na^+[N(SO_2F)C(O)F]^-$ was sealed in a capillary under vacuum and heated slowly to 170°. The material did not melt but instead appeared to undergo decomposition. This result was confirmed by a quantitative measurement of weight loss (0.0908 g) when a fresh sample (0.9293 g) of $Na^+[N(SO_2F)C(O)F]^-$ was held at 70° for 30 min. The volatile product was shown to be FSO_2NCO by infrared analysis.[5] These data showed that 13% decomposition had occurred. When a sample of $Na^+[N(SO_2F)C(O)F]^-$ (0.8413 g) was held at 90° for 1 hr, FSO_2NCO (0.5081 g) was recovered indicating that 81% decomposition had occurred. These results show that the sodium salt is the least stable of the adducts prepared in this work.

Reactions of $Cs^+[N(SO_2F)C(O)F]^-$.—A sample of $Cs^+[N(SO_2F)C(O)F]^-$ (1.0608 g, 3.83 mmol) was placed in a 30-ml Pyrex reaction vessel equipped with a Fisher and Porter 4-mm Labcrest valve and a Teflon stirbar. Cl_2 (dried over P_4O_{10}) (0.3888 g, 5.45 mmol) was added and the vessel was allowed to stand at 25° with stirring for 24 hr. After this time the volatile material was removed. The weight of the residue in the reaction vessel was 1.0708 g. Infrared analysis of the volatile materials showed that no absorbing species were present indicating that no reaction had taken place.

Using a vessel similar to that above, NO_2Cl (0.8626 g, 10.59 mmol) was condensed onto a sample of $Cs^+[N(SO_2F)C(O)F]^-$ (2.3467 g, 8.47 mmol) at −196°. The mixture was warmed to 25° and allowed to stand in the dark for 6 days. After this time the volatile products were removed, separated into two fractions (−78, −196°) by fractional condensation, and identified by infrared spectroscopy. Each fraction was weighed and by using *PVT* measurements and Regnault's method of molecular weight determination, the whole amount of each component present was estimated. The −78° fraction consisted of FSO_2Cl^{12} (3.0 mmol) and FSO_2F^{13} (0.2 mmol). The fraction condensing at −196° consisted of CO_2^{14} (8.2 mmol) which was separated from the other components by absorption on Ascarite, N_2O^{14} (7.3 mmol), and $SO_2F_2^{13}$ (0.9 mmol). The weight of the solid residue was 1.9329 g. Since this weight was higher than would be expected if complete reaction of $Cs^+[N(SO_2F)C(O)F]^-$ with NO_2Cl had taken place, an additional amount of NO_2Cl (0.5326 g, 6.54 mmol) was added to determine if further reaction would occur. This additional portion brought the total molar ratio of NO_2Cl to $Cs^+[N(SO_2F)C(O)F]^-$ to a value slightly greater than 2:1. The reactants were allowed to stand in the dark for 3 days. The volatile products were removed leaving a yellow solid residue behind in the reaction vessel. The residue was hydrolyzed for spot test determinations, and the presence of F^-, Cl^-, NO_3^-, SO_4^{2-}, and a small amount of NO_2^- was confirmed.[11] No CO_3^{2-} was observed to be present.[11] The volatile products were separated into two fractions by fractional condensation. The fraction condensing at −78° was shown by infrared analysis and *PVT* measurements to consist of $NOCl^{14}$ (7.2 mmol) and $ClSO_2F^{12}$ (2.0 mmol). The fraction condensing at −196° was worked up as previously described and consisted of CO_2^{14} (0.5 mmol), N_2O^{14} (0.9 mmol), and $ClSO_2F^{12}$ (0.1 mmol). The total quantity of each volatile product recovered from the reaction was as follows: SO_2ClX (where X = F, Cl), 6.2 mmol; CO_2, 8.7 mmol; N_2O, 8.2 mmol; NOCl, 7.2 mmol. The presence of F^-, Cl^-, NO_3^-, SO_4^{2-}, and a trace of NO_2^- in the hydrolyzed solid residue showed that the reaction had been a complex one forming more than one set of products. The data above indicate that the most important reaction can be represented by the equation

$$Cs^+[N(SO_2F)C(O)F]^- + 2NO_2Cl = NOCl + SO_2ClF + SO_2F_2 + N_2O + CO_2 + \text{Cs salts}$$

Reaction of $Na[N(SO_2F)C(O)F]$ with $S_2O_6F_2$.—A sample of $Na[N(SO_2F)C(O)F]$ (0.5500 g, 3.29 mmol) was prepared in a 30-ml Pyrex vessel equipped with a Fisher and Porter Teflon threaded glass valve. $S_2O_6F_2$ (0.7485 g, 3.78 mmol) was condensed into the vessel and the mixture was heated to 70° for 12 hr. After this time the volatile material was removed and separated by fractional condensation. A small amount of noncondensable gas (O_2) was present. The fraction which passed a trap cooled to −78° consisted of small amounts of COF_2 and SO_2F_2 with traces of SiF_4. The fraction retained at −78° consisted of $S_2O_6F_2$, FSO_2NCO, and a small amount of $S_2O_5F_2$. The fraction retained at −20° was identified as $FSO_2N(OSO_2F)C(O)F$,[6] the expected product (0.1386 g, 0.57 mmol, 17%). The solid residue in the reaction vessel dissolved smoothly in water and gave a positive test for $^-OSO_2F$ when tested with nitron reagent. On the basis of this evidence the main reaction may be written

$$NaN(SO_2F)C(O)F + S_2O_6F_2 = FSO_2N(OSO_2F)C(O)F + NaOSO_2F$$

$CsN(SO_2F)C(O)F$ reacted with $S_2O_6F_2$ at 70° in a similar fashion to give a 21% yield of $FSO_2N(OSO_2F)C(O)F$.

Discussion

Fluorosulfuryl isocyanate reacts with alkali metal fluorides MF (where M = Cs, K, Na) in acetonitrile solution to form the corresponding salts of fluoroformylfluorosulfurylimide according to the equation

$$FSO_2N{=}C{=}O + MF \overset{CH_3CN}{\underset{25°}{=}} M[N(SO_2F)C(O)F]$$

It was observed that a slight excess of FSO_2NCO was always required in order to effect complete dissolution of the metal fluoride. Furthermore, the combining ratios of FSO_2NCO with MF were closest to 1:1 for samples prepared by removing the CH_3CN and excess FSO_2NCO quickly after final dissolution of the metal fluoride had taken place. Samples isolated by removing the excess FSO_2NCO and solvent slowly had combining ratios less than 1:1. These results suggest that the reaction in which $M[N(SO_2F)C(O)F]$ is formed is an equilibrium and excess FSO_2NCO is required to drive the reaction to the right. Removal of the excess FSO_2NCO allows the equilibrium to shift in the direction of undissociated adduct as long as acetonitrile is present. The dry salts are stable at 25°. Similar

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(12) H. W. Roesky and A. Hoff, *Chem. Ber.*, **98**, 2429 (1965).

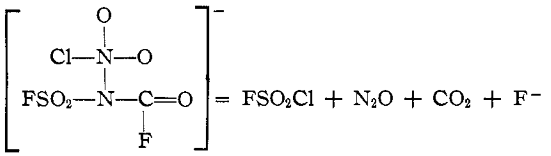
(13) D. G. Weiblen in "Fluorine Chemistry," J. H. Simons, Ed., Vol. II, Academic Press, New York, N. Y., 1954, pp 472–493.

(14) R. H. Pierson, A. N. Fletcher, and E. St. Clair Gantz, *Anal. Chem.*, **28**, 1218 (1956).

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.



$$\left[\begin{array}{l} \qquad\quad O \\ \qquad\quad | \\ Cl-N-O \\ \qquad\quad | \\ FSO_2-N-C=O \\ \qquad\qquad\quad | \\ \qquad\qquad\quad F \end{array}\right]^- = FSO_2Cl + N_2O + CO_2 + F^-$$

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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[15] C. W. Tullock and D. D. Coffman, *J. Org. Chem.*, **25**, 2016 (1960).

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

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

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

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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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