CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
THE UNIVERSITY OF GEORGIA, ATHENS, GEORGIA 30601

Adducts of Organoselenium and -tellurium Trichlorides with Antimony Pentachloride

BY KENNETH J. WYNNE* AND PHILIP S. PEARSON

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The preparation of a series of 1:1 adducts of organoselenium and -tellurium trichlorides with antimony pentachloride is reported. These compounds are colorless or pale yellow moisture-sensitive crystalline solids. The adducts are soluble in CH_2Cl_2, insoluble in nonpolar organic solvents, and rapidly decomposed by donor organic media. The solid-state infrared spectra are interpreted in terms of the formulation $[RMCl_2^+][SbCl_6^-]$, where M = Se, Te. Proton magnetic resonance data on these compounds are discussed.

Introduction

The preparation of compounds containing chloroorganosulfur(IV) cations of the type $RSCl_2^+$ and R_2SCl^+ has been reported by Peach,[1] while triorganosulfonium salts $R_3S^+X^-$ have long been known. Compounds containing $SeCl_3^+$,[2] $(CH_3)_2SeCl^+$,[1,3] and $(CH_3)_3Se^+$ [4] cations have also been characterized, but an attempt to prepare the $CH_3SeCl_2^+$ cation was not successful.[4] Less structural information is available on compounds containing $R_nTeX_{3-n}^+$ cations, although the $TeCl_3^+$ ion[5] has been found to exist in a number of compounds. It is generally assumed that R_3TeX compounds[6] are ionic although no definitive structural data are available. In this connection it is interesting that the reaction of $(CH_3)_2TeCl_2$ with BCl_3[1] and of $(CH_3)_2TeBr_2$ with BBr_3[7] led to quite different results. In the former instance a 1:1 adduct formed at low temperature but was completely dissociated at room temperature. In contrast, $[(CH_3)_2TeBr_2]_2BBr_3$ formed from $(CH_3)_2TeBr_2$ and BBr_3 is stable at ambient temperature in the solid state. The structure of both these adducts is unknown.

The lack of reaction of CH_3SeCl_3 with BCl_3[4] and the instability of the $(CH_3)_2TeCl_2 \cdot BCl_3$ adduct[1] suggested that cations arising from chloride ion transfer from organoselenium and -tellurium trichlorides might be generated only with the strongest of chloride ion acceptors. We therefore examined the reaction of $RSeCl_3$ and $RTeCl_3$ compounds with $SbCl_5$, one of the strongest chloride ion acceptors, in order to establish if $RSeCl_2^+$ and $RTeCl_2^+$ cations could be generated in this manner. The results of our study are reported below.

Experimental Section

General Information.—The extreme moisture sensitivity of the compounds dealt with in this study made the use of dry atmosphere (N_2) and standard vacuum-line techniques necessary. Infrared spectra were obtained using Perkin-Elmer Model 621 and Beckman IR-11 spectrophotometers. Infrared spectra on solutions were recorded with samples in 0.5-mm polyethylene cells, while solid-state spectra were obtained with samples in Nujol mulls between polyethylene or AgCl plates. Proton magnetic resonance data were obtained using a Perkin-Elmer Hitachi Model R-20 nuclear magnetic resonance spectrometer. Chemical shifts were measured *vs.* internal tetramethylsilane.

Chemicals.—Reagent grade chlorine (Matheson) was purified by passage through sulfuric acid and phosphorus(V) oxide traps prior to use. Antimony pentachloride (Baker and Adamson) was fractionally distilled *in vacuo* and stored in an airtight container. Methylene chloride was refluxed over anhydrous P_2O_5 and fractionally distilled onto Linde 5A Molecular Sieves which had previously been pumped on at 300° for 24 hr.

Preparation of Organochalcogen Trichlorides.—CH_3SeCl_3,[4] CH_3TeCl_3,[8] and p-$CH_3OC_6H_4TeCl_3$[9] were prepared as previously described in the literature.

We have found that diphenyl diselenide is a by-product in the preparation of diphenyl selenide.[10,11] Diphenyl diselenide was chlorinated in methylene chloride to give phenylselenium trichloride as hygroscopic, pale yellow crystals, mp 132–134°, lit.[12] mp 133–134°.

Diethyl ditelluride was prepared in a manner analogous to that for dimethyl ditelluride.[13,14] Because of its exceedingly vile odor, instability, and toxic character we have little data on this compound. A reasonable proton nmr spectrum was observed (quartet δ 3.00, $J_{HCH_3-HCH_2} = 9$ Hz; triplet δ 1.60). The density of $(C_2H_5)_2Te_2$ was found to be 2.5 g/ml. Generally, $(C_2H_5)_2Te_2$ was used directly after preparation without isolation.

Chlorination of 5.0 g of $(C_2H_5)_2Te_2$ in 350 ml of CH_2Cl_2 followed by cooling to −20° yielded 6.3 g (75% yield) of ethyltellurium trichloride, mp 114–115°. *Anal.* Calcd for $C_2H_5TeCl_3$: C, 9.1; H, 1.9; Cl, 40.4. Found: C, 9.84; H, 2.0; Cl, 42.2. Proton nmr spectrum: quartet δ 4.05, $J_{HCH_3-HCH_2} =$ 8 Hz; triplet δ 2.15.

Preparation of Organochalcogen Trichloride–Antimony Pentachloride Adducts.—The antimony pentachloride adducts of methyl- and phenylselenium trichloride and methyl-, ethyl-, and p-methoxyphenyltellurium trichloride were prepared by mixing together CH_2Cl_2 solutions of the parent trichloride and $SbCl_5$. A typical preparation is given below for the methylselenium trichloride–antimony pentachloride adduct. These adducts could also be prepared by generating the desired trichloride *in situ* by chlorination of the appropriate diselenide with subsequent addition of $SbCl_5$. Table I shows analytical data, yields, and physical properties for these compounds.

$CH_3SeCl_3 \cdot SbCl_5$.—To a solution of methylselenium trichloride (5.01 g, 25.0 mmol) in 150 ml of CH_2Cl_2 was added dropwise a solution of $SbCl_5$ (7.48 g, 25.0 mmol) in 30 ml of CH_2Cl_2. During this time the solution gradually changed from pale to bright yellow. The solution was filtered to remove some small bits of solid and the filtrate was cooled to −20°. The pale yellow crystals which formed were filtered and pumped on *in vacuo*, yield 9.5 g. Concentration and cooling the filtrate yielded another 1.0 g for a net 88% yield. Solubility in CH_2Cl_2 and analytical data are given in Table I.

$C_2H_5SeCl_3 \cdot SbCl_5$.—Because of the instability of $C_2H_5SeCl_3$ the $C_2H_5SeCl_3 \cdot SbCl_5$ adduct was prepared by generating ethylselenium trichloride *in situ*. Diethyl diselenide (5.0 g, 24.2

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[2] H. Gerding, *Recl. Trav. Chim. Pays-Bas*, **75**, 589 (1969).

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[14] K. J. Wynne and P. S. Pearson, *Inorg. Syn.*, in press.

TABLE I

					Analyses, %					
					C		H		Cl	
Compound	Yield,[a] %	Color and form	Mp,[b] °C	Soly[c]	Calcd	Found	Calcd	Found	Calcd	Found
$CH_3SeCl_3 \cdot SbCl_5$	88.0	Yellow plates	114–117	2.7	2.41	2.32	0.601	0.58	56.80	55.97
$C_2H_5SeCl_3 \cdot SbCl_5$	84.5	Yellow needles	94–95	4.7	4.68	4.85	0.982	0.99	55.25	51.13
$C_6H_5SeCl_3 \cdot SbCl_5$	65.5	Yellow plates	85–87	6.0	12.86	12.53	0.898	1.10	50.25	50.82
$CH_3TeCl_3 \cdot SbCl_5$	68.5	White needles	125–127	7.0	2.19	2.26	0.552	0.79	51.76	51.44
$C_2H_5TeCl_3 \cdot SbCl_5$	61.0	White needles	86–88	8.0	4.27	4.11	0.897	1.01	50.46	50.39
p-$CH_3OC_6H_4TeCl_3 \cdot SbCl_5$	67.5	White plates	131–133	5.0	13.14	12.55	1.102	1.25	44.31	44.20

[a] Based on $RMCl_3$. [b] Uncorrected. [c] Grams per 100 ml of CH_2Cl_2 at 25°.

mmol) was dissolved in 300 ml of CH_2Cl_2 in a 500-ml three-necked flask. A pressure equalizing dropping funnel was loaded with $SbCl_5$ (7.47 g, 25.0 mmol) and 15 ml of CH_2Cl_2. The dropping funnel was attached to the flask which was immersed in an ice bath. While stirring magnetically, chlorine was rapidly passed through the solution. The initially pale red solution turned dark red, lighter red, then abruptly clear. The $SbCl_5$ solution was then added dropwise while maintaining a slow stream of chlorine. As the last few drops of the $SbCl_5$ solution were added, a small quantity of white solid formed. The mixture was filtered and placed at −20°. Upon filtration 10.0 g of pale yellow crystalline product was obtained. Concentration and cooling the filtrate yielded another 0.5 g for an overall 84.5% yield based on $(C_2H_5)_2Se$. Physical properties and analytical results are shown in Table I.

Reaction of Diisopropyl Diselenide with Chlorine and $SbCl_5$.— Diisopropyl diselenide (5 g, 20 mmol) was dissolved in 250 ml of CH_2Cl_2 and chlorine was passed through as described in the above preparation of $C_2H_5SeCl_3 \cdot SbCl_5$. When the solution lightened in color, $SbCl_5$ (6.0 g, 20.0 mmol) in 20 ml of CH_2Cl_2 was added and a crystalline precipitate formed. Analysis indicated the compound to be the previously reported[15] $SeCl_4 \cdot SbCl_5$ (subl pt 200°). *Anal.* Calcd; Cl, 61.4. Found: Cl, 60.70.

We attempted to prepare $AlCl_3$, PCl_5, and $FeCl_3$ adducts of CH_3SeCl_3 but only recovered starting materials. We also attempted to prepare a methyltellurium trichloride–boron trichloride adduct without success.

Results and Discussion

The reaction of organoselenium and -tellurium trihalides with antimony pentachloride yields 1:1 adducts according to the equation

$$RMCl_3 + SbCl_5 \xrightarrow{CH_2Cl_2} RMCl_3 \cdot SbCl_5(s) \qquad (1)$$

where M = Se, R = CH_3, C_2H_5, C_6H_5; M = Te, R = CH_3, C_2H_5, *p*-$CH_3OC_6H_4$. The general physical properties of these highly moisture-sensitive compounds are outlined in Table I. The adducts could also be prepared by generating the desired organochalcogen trichlorides *in situ* from the chlorination of the appropriate diselenide and subsequent addition of $SbCl_5$. This latter method proved the only way possible to isolate $C_2H_5SeCl_3 \cdot SbCl_5$, as our efforts to prepare $C_2H_5SeCl_3$ from $(C_2H_5)_2Se_2$ and chlorine in CH_2Cl_2 led to the isolation of $SeCl_4$ as the only solid product. Presumably ethylselenium trichloride decomposes rapidly in solution at ambient temperature *via* the equation

$$3C_2H_5SeCl_3 \longrightarrow 3C_2H_5Cl + Se_2Cl_2 + SeCl_4 \qquad (2)$$

Our observation of peaks due to chloroethane in the nmr spectrum of the reaction solution supports this view. Ethylselenium trichloride is much less stable than CH_3SeCl_3[4] which is readily isolable and recrystallizable from CH_2Cl_2.

Under conditions similar to those used for the preparation of $C_2H_5SeCl_3 \cdot SbCl_5$, the reaction of $(i\text{-}C_3H_7)_2Se_2$, Cl_2, and $SbCl_5$ gave only $SeCl_4 \cdot SbCl_5$. This suggests that $i\text{-}C_3H_7SeCl_3$ is even less stable than $C_2H_5SeCl_3$ and may decompose *via* an analogous route. Supporting this, a proton nmr spectrum of the reaction solution showed $i\text{-}C_3H_7Cl$ to be present. The $SeCl_4$ produced directly *via* the decomposition of $i\text{-}C_3H_7SeCl_3$ and by the reaction of excess chlorine with Se_2Cl_2 evidently reacted with $SbCl_5$ to give the observed product.

One of the surprising aspects of this study was the stability of phenylselenium and *p*-methoxyphenyltellurium trichloride–antimony pentachloride adducts. It has been found that $(C_6H_5)_2SeCl_2 \cdot BCl_3$ decomposes at room temperature.[1] In addition we have found that BF_3 causes the decomposition of $(C_6H_5)_2SeF_2$,[11] perhaps through the intermediate formation of $(C_6H_5)_2SeF_2 \cdot BF_3$. It seemed possible in these cases that the $(C_6H_5)_2SeX^+$ ion was acting as an electrophile and attacking the phenyl group on $(C_6H_5)_2SeX^+$ or $(C_6H_5)_2SeX_2$ leading to the formation of a polymer. The unexpected stability of $ArMX_2{}^+SbCl_6{}^-$ compounds remains unexplained, but it is possible that these unusual electrophiles could be synthetically useful for the introduction of the $ArMX_2$ group. It is also noteworthy that the arylselenium and -tellurium trichloride–antimony pentachloride adducts prepared in this study were somewhat less moisture sensitive than the alkyl derivatives.

Frequencies and assignments for the $RMCl_3 \cdot SbCl_5$ adducts together with those for $SeOCl_2$[16] are listed in Table II. The infrared spectra of CH_3SeCl_3 and its $SbCl_5$ adduct are shown in Figure 1.

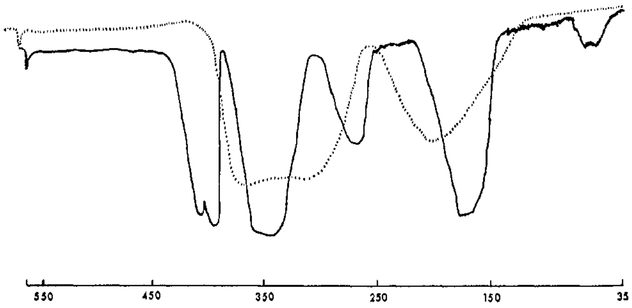

Figure 1.—The infrared spectra of CH_3SeCl_3 (······) and $CH_3SeCl_3 \cdot SbCl_5$ (——), 33–570 cm^{-1}.

Infrared spectral data were especially useful in elucidating the solid-state structure of the methyl-, ethyl-, and phenylselenium trichloride–antimony pentachloride adducts because little overlap appeared to take place between Sb–Cl and Se–Cl absorption frequencies.

Without reference to any particular structural model one can assign absorptions at 340 and 185 cm^{-1} in all $RSeCl_3 \cdot SbCl_5$ adducts to "Sb–Cl" modes. These have been found fairly invarient in $SbCl_5$–X species

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(15) J. R. Masaguer, *An. Real Soc. Espan. Fis. Quim., Ser. B*, **53**, 518 (1957).

(16) J. A. Rolfe and L. A. Woodward, *Trans. Faraday Soc.*, **51**, 779 (1955).

TABLE II

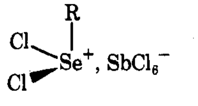
INFRARED ABSORPTIONS (CM^{-1}) AND ASSIGNMENTS FOR $RSeCl_3 \cdot SbCl_5$ AND $RTeCl_3 \cdot SbCl_5$[a,b] ADDUCTS AND $SeOCl_2$[c]

$CH_3SeCl_3 \cdot SbCl_5$	$C_2H_5SeCl_3 \cdot SbCl_5$	$SeOCl_2$	$C_6H_5SeCl_3 \cdot SbCl_5$	$CH_3TeCl_3 \cdot SbCl_5$	$C_2H_5TeCl_3 \cdot SbCl_5$	p-$CH_3OC_6H_4$-$TeCl_3 \cdot SbCl_5$	Assignments
558 w	489 w	995 w	458 w	526 w	. . .	418 w	M–C or M–O str (M = Se, Te), ν_1 (A′)
424 s	424 s	388	425 m[d]	375 s	370 s	373 s[e]	Sym M–Cl str, ν_2 (A′)
413 s	415 s	347	393 m[d]				Asym M–Cl str, ν_5 (A″)
335 s	337 s		346 m–w	350 s 325	340 s	330 s 310 sh, w	$SbCl_6^-$, ν_3
283 w–m	280 m	279 255	282 w–m	283 w 265	275	265	M–Cl bending, ν_1, ν_6 (A′, A″)
180 m–s	185 m		178	175 w–m	185 m–s	185 m–s	$SbCl_6^-$, ν_4
		161					ν_8, bending
42 w	65 w				50 w–m		Lattice mode?

[a] Key: w, weak; m, medium; s, strong; br, broad; sh, shoulder. [b] Not listed are the higher frequency alkyl deformation modes nor characteristic phenyl modes. These are essentially unchanged from those observed in the parent trichloride. [c] See ref 16. [d] Compare to 320 cm^{-1} (s, br) in $C_6H_5SeCl_3$. [e] Compare to 328 cm^{-1} (s) in p-$CH_3OC_6H_4TeCl_3$.

whether X = Cl or a nitrogen donor.[17] In addition it is likely that absorptions at 60 cm^{-1} are due to lattice vibrations; therefore the remaining peaks are assigned to Se–C or Se–Cl modes.

Now considering particular structural models, two are of special interest for the $RSeCl_3 \cdot SbCl_5$ adducts. These are an ionic formulation (I) and a halogen-bridged structure (II) of which a number of different types are possible in addition to the one shown. Previous evidence which has shown diorganoselenium dihalides,[3] triorganoselenium halides,[4] and SeF_4[18] to be halide ion donors strongly militates against a coordinate bond arrangement utilizing the unshared electron pair on selenium being seriously considered as a possible structural model for the $RMCl_3 \cdot SbCl_5$ adducts.



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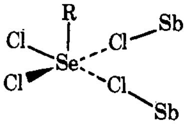
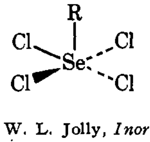


II

We will consider first the structural implications of the ir spectrum of $CH_3SeCl_3 \cdot SbCl_5$, for, in addition to separate Se–Cl and Sb–Cl absorptions, the parent trichloride is stable[4] so that ir data are available for comparison with those of the adduct. In trying to decide whether structure I or II best represents the solid-state structure of $CH_3SeCl_3 \cdot SbCl_5$, two features of the infrared spectrum must be considered. One must take into account the number of Se–Cl and Sb–Cl absorptions together with the shift in the Se–Cl frequencies in going from CH_3SeCl_3 to the adduct. It is important to note that our current view for the structure of $RSeCl_3$ compounds in the solid state is somewhat different from that originally suggested for CH_3SeCl_3.[4] Consistent with out recent proposed theory[8] we believe the immediate environment of Se in $RSeCl_3$ compounds in the solid state is represented by the approximately square-pyramidal arrangement of atoms shown in



Terminal chlorines are connected to Se by solid lines and bridging chlorines by dashed lines.

Returning to the discussion of the structure of $CH_3SeCl_3 \cdot SbCl_5$, it is likely that if the adduct had structure II, the bridging Se–Cl bonds would be longer than the terminal Se–Cl bonds leading to C_s site symmetry for Se–Cl bonds and to C_s site symmetry for Se. Twelve ir-active "Se" modes are expected for this model while only four are observed. This suggests that if bridging occurs, the interaction is not sufficiently strong to perturb the environment around Se and generate a spectrum consistent with a set of six atoms of C_s symmetry.

Pertinent to this discussion has been the observation that within a particular valence state there appears to be a correlation in the frequency of terminal M–X_n vibrations with the degree of coordination of X'_m groups to M, where m and n are the number of X and X′ groups bound to M. Although the highest XeF vibrations in XeF_2[19] are at 550 and 560 cm^{-1}, the terminal frequencies in the $Xe_2F_3^+$ ion which has a bridging fluorine are at 593 and 580 cm^{-1}. Finally in the XeF^+ cation absorptions are found at 602 and 608 cm^{-1}.[20]

For purposes of this discussion we will consider XeF_2 to represent the case of "strongest coordination" of F^- to XeF^+. The increase in the highest Xe–F stretching frequency in going from XeF_2 to XeF^+ is easily correlated with decreasing length and increasing strength of the "terminal" bond. This shift to higher energy may also be correlated with decreased interaction of F^- with XeF^+, that is, with decreasing fluorine bridging. It is therefore notable that the 424-cm^{-1} Se–Cl frequency in $CH_3SeCl_3 \cdot SbCl_5$ is among the highest ever observed but close to that for $SeCl_3^+$ at 417 cm^{-1} [2] and $(CH_3)_2SeCl^+$ at 405 cm^{-1}.[1,3] This high Se–Cl stretching frequency suggests little bridging occurs between Cl^- and $CH_3SeCl_2^+$ in the solid state and strongly supports structure I.

Also consistent with a structure where little bridging occurs is the fact that the highest Se–Cl frequency in $CH_3SeCl_3 \cdot SbCl_5$ is 68 cm^{-1} higher[21] (Figure 1) than

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[17] (a) K. J. Wynne and W. L. Jolly, *Inorg. Chem.*, **6**, 107 (1967); (b) I. R. Beattie, T. Gilson, K. Livingston, V. Fawcett, and G. A. Ozin, *J. Chem. Soc. A*, 712 (1967).

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[20] F. O. Sladky, P. A. Bulliner, N. Bartlett, B. G. DeBoer, and A. Zalkin, *Chem. Commun.*, 1048 (1968).

[21] The original report[4] on the infrared spectrum of solid CH_3SeCl_3 listed one peak at 340 cm^{-1}. We have observed that in dilute, finely ground mulls this peak may barely be resolved into what is apparently at least two peaks at 356 and 293 cm^{-1}. The absorption in this region is quite broad and it is frequently difficult to pick out these two maxima.

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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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

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[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).