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Adducts of Organoselenium and -tellurium Trichlorides with Antimony Pentachloride

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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 $[\text{RMCl}_2^+][\text{SbCl}_6^-]$, where $\text{M} = \text{Se}, \text{Te}$. Proton magnetic resonance data on these compounds are discussed.

Introduction

The preparation of compounds containing chloro-organosulfur(IV) cations of the type RSCl_2^+ and R_2SCl^+ has been reported by Peach,¹ while triorgano-sulfonium salts $\text{R}_3\text{S}^+\text{X}^-$ have long been known. Compounds containing SeCl_3^+ ,² $(\text{CH}_3)_2\text{SeCl}^+$,^{1,3} and $(\text{CH}_3)_3\text{Se}^+$ ⁴ cations have also been characterized, but an attempt to prepare the $\text{CH}_3\text{SeCl}_2^+$ cation was not successful.⁴ Less structural information is available on compounds containing $\text{R}_n\text{TeX}_{3-n}^+$ cations, although the TeCl_3^+ ion⁵ has been found to exist in a number of compounds. It is generally assumed that R_3TeX compounds⁶ are ionic although no definitive structural data are available. In this connection it is interesting that the reaction of $(\text{CH}_3)_2\text{TeCl}_2$ with BCl_3 ¹ and of $(\text{CH}_3)_2\text{TeBr}_2$ 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, $[(\text{CH}_3)_2\text{TeBr}_2]_2\text{BBr}_3$ formed from $(\text{CH}_3)_2\text{TeBr}_2$ 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 $(\text{CH}_3)_2\text{TeCl}_2 \cdot \text{BCl}_3$ adduct¹ 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*- $\text{CH}_3\text{OC}_6\text{H}_4\text{TeCl}_3$ 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 $132\text{--}134^\circ$, lit.¹² mp $133\text{--}134^\circ$.

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, $J_{\text{HCH}_3-\text{HCH}_2} = 9$ Hz; triplet δ 1.60). The density of $(\text{C}_2\text{H}_5)_2\text{Te}_2$ was found to be 2.5 g/ml. Generally, $(\text{C}_2\text{H}_5)_2\text{Te}_2$ was used directly after preparation without isolation.

Chlorination of 5.0 g of $(\text{C}_2\text{H}_5)_2\text{Te}_2$ in 350 ml of CH_2Cl_2 followed by cooling to -20° yielded 6.3 g (75% yield) of ethyltellurium trichloride, mp $114\text{--}115^\circ$. *Anal.* Calcd for $\text{C}_2\text{H}_5\text{TeCl}_3$: 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, $J_{\text{HCH}_3-\text{HCH}_2} = 8$ 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.

$\text{CH}_3\text{SeCl}_3 \cdot \text{SbCl}_5$.—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.

$\text{C}_2\text{H}_5\text{SeCl}_3 \cdot \text{SbCl}_5$.—Because of the instability of $\text{C}_2\text{H}_5\text{SeCl}_3$ the $\text{C}_2\text{H}_5\text{SeCl}_3 \cdot \text{SbCl}_5$ adduct was prepared by generating ethylselenium trichloride *in situ*. Diethyl diselenide (5.0 g, 24.2

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TABLE I

Compound	Yield, ^a %	Color and form	Mp, ^b °C	Soly ^c	Analyses, %					
					C		H		Cl	
					Calcd	Found	Calcd	Found	Calcd	Found
CH ₃ SeCl ₃ ·SbCl ₅	88.0	Yellow plates	114–117	2.7	2.41	2.32	0.601	0.58	56.80	55.97
C ₂ H ₅ SeCl ₃ ·SbCl ₅	84.5	Yellow needles	94–95	4.7	4.68	4.85	0.982	0.99	55.25	51.13
C ₆ H ₅ SeCl ₃ ·SbCl ₅	65.5	Yellow plates	85–87	6.0	12.86	12.53	0.898	1.10	50.25	50.82
CH ₃ TeCl ₃ ·SbCl ₅	68.5	White needles	125–127	7.0	2.19	2.26	0.552	0.79	51.76	51.44
C ₂ H ₅ TeCl ₃ ·SbCl ₅	61.0	White needles	86–88	8.0	4.27	4.11	0.897	1.01	50.46	50.39
<i>p</i> -CH ₃ OC ₆ H ₄ TeCl ₃ ·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 RMCl₃. ^b Uncorrected. ^c Grams per 100 ml of CH₂Cl₂ at 25°.

mmol) was dissolved in 300 ml of CH₂Cl₂ in a 500-ml three-necked flask. A pressure equalizing dropping funnel was loaded with SbCl₅ (7.47 g, 25.0 mmol) and 15 ml of CH₂Cl₂. 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 SbCl₅ solution was then added dropwise while maintaining a slow stream of chlorine. As the last few drops of the SbCl₅ 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 (C₂H₅)₂Se. Physical properties and analytical results are shown in Table I.

Reaction of Diisopropyl Diselenide with Chlorine and SbCl₅.—Diisopropyl diselenide (5 g, 20 mmol) was dissolved in 250 ml of CH₂Cl₂ and chlorine was passed through as described in the above preparation of C₂H₅SeCl₃·SbCl₅. When the solution lightened in color, SbCl₅ (6.0 g, 20.0 mmol) in 20 ml of CH₂Cl₂ was added and a crystalline precipitate formed. Analysis indicated the compound to be the previously reported¹⁵ SeCl₄·SbCl₅ (subl pt 200°). *Anal.* Calcd; Cl, 61.4. Found: Cl, 60.70.

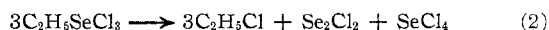
We attempted to prepare AlCl₃, PCl₅, and FeCl₃ adducts of CH₃SeCl₃ but only recovered starting materials. We also attempted to prepare a methyltellurium trichloride–boron trichloride adduct without success.

Results and Discussion

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



where M = Se, R = CH₃, C₂H₅, C₆H₅; M = Te, R = CH₃, C₂H₅, *p*-CH₃OC₆H₄. 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 SbCl₅. This latter method proved the only way possible to isolate C₂H₅SeCl₃·SbCl₅, as our efforts to prepare C₂H₅SeCl₃ from (C₂H₅)₂Se₂ and chlorine in CH₂Cl₂ led to the isolation of SeCl₄ as the only solid product. Presumably ethylselenium trichloride decomposes rapidly in solution at ambient temperature *via* the equation



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 CH₃SeCl₃⁴ which is readily isolable and recrystallizable from CH₂Cl₂.

Under conditions similar to those used for the preparation of C₂H₅SeCl₃·SbCl₅, the reaction of (*i*-C₃H₇)₂Se₂, Cl₂, and SbCl₅ gave only SeCl₄·SbCl₅. This suggests

that *i*-C₃H₇SeCl₃ is even less stable than C₂H₅SeCl₃ and may decompose *via* an analogous route. Supporting this, a proton nmr spectrum of the reaction solution showed *i*-C₃H₇Cl to be present. The SeCl₄ produced directly *via* the decomposition of *i*-C₃H₇SeCl₃ and by the reaction of excess chlorine with Se₂Cl₂ evidently reacted with SbCl₅ to give the observed product.

One of the surprising aspects of this study was the stability of phenylselenium and *p*-methoxyphenyl-tellurium trichloride–antimony pentachloride adducts. It has been found that (C₆H₅)₂SeCl₂·BCl₃ decomposes at room temperature.¹ In addition we have found that BF₃ causes the decomposition of (C₆H₅)₂SeF₂,¹¹ perhaps through the intermediate formation of (C₆H₅)₂SeF₂·BF₃. It seemed possible in these cases that the (C₆H₅)₂SeX⁺ ion was acting as an electrophile and attacking the phenyl group on (C₆H₅)₂SeX⁺ or (C₆H₅)₂SeX₂ leading to the formation of a polymer. The unexpected stability of ArMX₂·SbCl₅– compounds remains unexplained, but it is possible that these unusual electrophiles could be synthetically useful for the introduction of the ArMX₂ 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 RMCl₃·SbCl₅ adducts together with those for SeOCl₂¹⁶ are listed in Table II. The infrared spectra of CH₃SeCl₃ and its SbCl₅ adduct are shown in Figure 1.

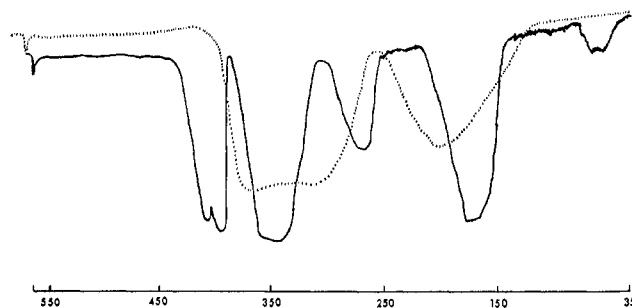


Figure 1.—The infrared spectra of CH₃SeCl₃ (·····) and CH₃SeCl₃·SbCl₅ (—), 33–570 cm^{–1}.

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 RSeCl₃·SbCl₅ adducts to “Sb–Cl” modes. These have been found fairly invariant in SbCl₅–X species

(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).

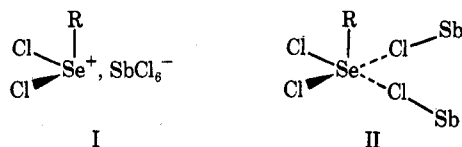
TABLE II
 INFRARED ABSORPTIONS (CM⁻¹) AND ASSIGNMENTS FOR RSeCl₃·SbCl₅ AND RTeCl₃·SbCl₅^{a,b} ADDUCTS AND SeOCl₂^c

CH ₃ SeCl ₃ · SbCl ₅	C ₂ H ₅ SeCl ₃ · SbCl ₅	SeOCl ₂	C ₆ H ₅ SeCl ₃ · SbCl ₅	CH ₃ TeCl ₃ · SbCl ₅	C ₂ H ₅ TeCl ₃ · SbCl ₅	<i>p</i> -CH ₃ OC ₆ H ₄ · TeCl ₃ ·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	340 s	330 s	SbCl ₆ ⁻ , ν ₃
283 w-m	280 m	279	282 w-m	325	275	310 sh, w	
180 m-s	185 m	255		265		265	M-Cl bending, ν ₁ , ν ₈ (A', A'')
42 w	65 w	161	178	175 w-m	185 m-s	185 m-s	SbCl ₆ ⁻ , ν ₄ ν ₃ , bending Lattice mode?
					50 w-m		

^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 C₆H₅SeCl₃. ^e Compare to 328 cm⁻¹ (s) in *p*-CH₃OC₆H₄TeCl₃.

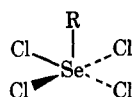
whether X = Cl or a nitrogen donor.¹⁷ In addition it is likely that absorptions at 60 cm⁻¹ are due to lattice vibrations; therefore the remaining peaks are assigned to Se-C or Se-Cl modes.

Now considering particular structural models, two are of special interest for the RSeCl₃·SbCl₅ 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 SeF₄¹⁸ 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 RMCl₃·SbCl₅ adducts.

We will consider first the structural implications of the ir spectrum of CH₃SeCl₃·SbCl₅, for, in addition to separate Se-Cl and Sb-Cl absorptions, the parent trichloride is stable⁴ 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 CH₃SeCl₃·SbCl₅, 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 CH₃SeCl₃ to the adduct. It is important to note that our current view for the structure of RSeCl₃ compounds in the solid state is somewhat different from that originally suggested for CH₃SeCl₃.⁴ Consistent with our recent proposed theory⁸ we believe the immediate environment of Se in RSeCl₃ 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 CH₃SeCl₃·SbCl₅, 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 XeF₂¹⁹ are at 550 and 560 cm⁻¹, the terminal frequencies in the Xe₂F₃⁺ 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 XeF₂ to represent the case of "strongest coordination" of F⁻ to XeF⁺. The increase in the highest Xe-F stretching frequency in going from XeF₂ 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 CH₃SeCl₃·SbCl₅ is among the highest ever observed but close to that for SeCl₃⁺ at 417 cm⁻¹² and (CH₃)₂SeCl⁺ at 405 cm⁻¹.^{1,3} This high Se-Cl stretching frequency suggests little bridging occurs between Cl⁻ and CH₃SeCl₂⁺ 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 CH₃SeCl₃·SbCl₅ is 68 cm⁻¹ higher²¹ (Figure 1) than

(19) J. L. Weeks, C. L. Chernick, and M. S. Matheson, *J. Amer. Chem. Soc.*, **84**, 4612 (1962).

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

(21) The original report⁴ on the infrared spectrum of solid CH₃SeCl₃ 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.

(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).

(18) A. J. Edwards and G. R. Jones, *ibid.*, **A**, 1891 (1970).

for CH_3SeCl_3 where Cl bridging has been postulated.^{4,8} Lastly, the frequencies assigned to the $\text{CH}_3\text{SeCl}_2^+$ ion are in reasonable agreement with those observed for CH_3AsCl_2 .²²

Virtually identical far-infrared spectra were recorded for both $\text{CH}_3\text{SeCl}_3 \cdot \text{SbCl}_5$ and $\text{C}_2\text{H}_5\text{SeCl}_3 \cdot \text{SbCl}_5$. Using arguments identical to those above we believe that formulation I best represents the structure of $\text{C}_2\text{H}_5\text{SeCl}_3 \cdot \text{SbCl}_5$. The spectrum of $\text{C}_6\text{H}_5\text{SeCl}_3 \cdot \text{SbCl}_5$ 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 $\text{RSeCl}_3 \cdot \text{SbCl}_5$ 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 ($\text{CH}_3\text{TeCl}_3 \cdot \text{SbCl}_5$).

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 $\sim 340\text{ cm}^{-1}$, while the peaks at ~ 370 and $\sim 270\text{ cm}^{-1}$ 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 $\text{RSeCl}_3 \cdot \text{SbCl}_5$ adducts. Our evidence favoring the $\text{RTeCl}_2^+ \cdot \text{SbCl}_6^-$ formulation is not strong and it is

(22) G. P. Van der Kelen and M. A. Herman, *Bull. Soc. Chim. Belg.*, **65**, 350 (1956).

(23) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," Wiley, New York, N. Y., 1968, p 90.

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 $\text{RTeCl}_3 \cdot \text{SbCl}_5$ 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 $\text{CH}_3\text{TeCl}_3 \cdot \text{SbCl}_5$ 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 $\text{RSeCl}_3 \cdot \text{SbCl}_5$ 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 $\text{RSeCl}_3 \cdot \text{SbCl}_5 \rightarrow \text{RSeCl}_3 + \text{SbCl}_5$. Also consistent with a high degree of dissociation are nmr spectral data in CD_2Cl_2 on freshly prepared solutions of $\text{RSeCl}_3 \cdot \text{SbCl}_5$ 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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The Reaction of Fluorosulfuryl Isocyanate with Alkali Metal Fluorides¹

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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 $\text{FSO}_2\text{NCO}:\text{MF}$ close to 1:1. Chemical and physical evidence indicates that these compounds may be formulated as the salts of fluoroformylfluorosulfonylimide, $\text{M}^+[\text{N}(\text{SO}_2\text{F})\text{C}(\text{O})\text{F}]^-$.

Redwood and Willis² have described the preparation of the alkali metal trifluoromethoxides MOCF_3 (where $\text{M} = \text{K}, \text{Rb}, \text{Cs}$) 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).