Liquid hydrogen chloride solvent system. XII. Reactions of some sulfur, selenium, and tellurium compounds¹

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The ions Me_2SCl^+ and $MeSCl_2^+$ have been prepared in hydrogen chloride solution from the oxidation of dimethyl sulfide and methanesulfenyl chloride with chlorine, or from methyl sulfur trichloride $(MeSCl_2^+)$, and characterized as their tetrachloroborates and hexafluorophosphates. $Et_2SCl^+BCl_4^-$ and $EtSCl_2^+BCl_4^-$ have been prepared analogously. Dimethyl selenium and dimethyl tellurium solutions were oxidized with chlorine to dimethyl selenium dichloride and dimethyl tellurium dichloride. Methanesulfenyl chloride colution was ionized due to the protonation of sulfur and not to the loss of

Methanesulfenyl chloride solution was ionized due to the protonation of sulfur, and not to the loss of a chloride ion. Methylchlorosulfonium hexafluorophosphate has been characterized. Methane- and ethane-sulfenyl chloride solutions reacted with boron trichloride giving (RSCl)₂BCl₃. Sulfur tetrachloride, selenium tetrachloride, and tellurium tetrachloride were sparingly soluble and

sulfur tetrachloride, selenium tetrachloride, and tellurium tetrachloride were sparingly soluble and showed no acidic or basic properties in the solvent. Sulfur monochloride, sulfur dichloride, selenium monochloride, and tellurium dichloride were non-basic in solution.

The new compounds, Me₂S₂.BCl₃ and Me₂Te.BCl₃, have been prepared and characterized.

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Introduction

The reactions of some sulfur compounds in solvent liquid hydrogen chloride have been described previously. Thiols and sulfides act as solvobases of varying strengths, and when treated with the solvoacid boron trichloride, form boron trichloride adducts in solution (1)

 $Me_2S + 2HCl \rightarrow Me_2SH^+ + HCl_2^-$

 $Me_2SH^+ + BCl_3 \rightarrow Me_2S.BCl_3 + H^+$

The properties of compounds containing a double sulfur oxygen bond, R_2SO , R_2SO_2 , RSO_2Cl , SO_2Cl_2 , $SOCl_2$, SO_2 , H_2SO_4 , $MeSO_3H$, CF_3SO_3H , and $CISO_3H$ have been studied as potential acids and bases (2). This paper extends the previous work on divalent sulfur compounds by considering the oxidation of certain compounds in solution with chlorine and stabilization of the products as tetrachloroborates or hexafluorophosphates. Analogous reactions have been studied with some selenium and tellurium compounds. The properties of the sulfur, selenium, and tellurium chlorides in solution have also been examined.

Results and Discussion

The dialkylsulfonium ion, R_2SH^+ , can only be isolated from hydrogen chloride solution as an unstable hexafluorophosphate (3). The S—H bond formed in solution by protonation of dialkyl sulfides and alkanesulfenyl chlorides has been oxidized with chlorine to form the dialkylchlorosulfonium and alkyldichlorosulfonium ions in solution.

$$R_2SH^+ + Cl_2 \rightarrow R_2SCl^+ + HCl$$

The use of the halogens as oxidizing agents in solvent liquid hydrogen chloride has been studied (4). Dialkyl sulfur dichlorides could not be isolated as stable materials from the oxidation of the sulfide solutions, but the reaction of a solution of the dialkylchlorosulfonium ion with boron trichloride or phosphorus pentafluoride resulted in the formation of dimethyl- and diethylchlorosulfonium tetrachloroborates and dimethylchlorosulfonium hexafluorophosphate. Phosphorus pentafluoride acts as a solvoacid and reacts with solvobases, such as tetramethylammonium hydrogendichloride, according to the equation

 $2Me_4N^+HCl^- + 3PF_5 \rightarrow 2Me_4N^+PF_6^-$

$$+ PF_3Cl_2 + 2HCl$$

Methyl sulfur trichloride was formed in the chlorine oxidation of methanesulfenyl chloride. Methyl and ethyl sulfur trichlorides and trimethylsulfonium iodide acted as solvobases, forming stable tetrachloroborates, $RSCl_2^+BCl_4^-$ and $Me_3S^+BCl_4^-$, with boron trichloride and an unstable methyldichlorosulfonium hexafluorophosphate with phosphorus pentafluoride. Tri-*n*-butylsulfonium tetrachloroborate has been prepared from tri-*n*-butyl sulfur chloride and boron trichloride, and its properties investigated (5).

¹For Part XI, see ref. 21.

The methods described here represent a good method of preparing the previously unknown ions R_2SCl^+ and $RSCl_2^+$.

Chlorine oxidation of solutions of alkanethiols or dialkyl disulfides caused a fracture of the S—S bond (formed initially in the alkanethiol reaction) and the formation of the alkanesulfenyl chloride in solution. Methane- and ethane-sulfenyl chlorides both act as solvobases, forming good conducting solutions. These compounds may ionize in either of two ways

[1]
$$RSCl + 2HCl \rightarrow [R-S-Cl]^+ + HCl_2^-$$

 \downarrow
H

 $[2] \qquad RSCI + HCI \rightarrow RS^+ + HCl_2^-$

The scant evidence for the existence of the sulfenium ion, RS^+ , in other media (6) and the observation that sulfenyl chlorides are protonated in strong sulfuric acid (7) both suggest that the ionization may be due to protonation, as in reaction [1]. The reactions of methanesulfenyl chloride in solution with phosphorus pentafluoride, which gave methylchlorosulfonium hexafluorophosphate and not methanesulfenyl hexafluorophosphate, and its oxidation with chlorine to methyl sulfur trichloride, are further evidence in favor of ionization caused by protonation.

Dimethyl selenium and dimethyl tellurium were found to be strong solvobases which were oxidized with chlorine in solution to dimethyl selenium dichloride and dimethyl tellurium dichloride. Dimethyl selenium dichloride reacted with boron trichloride in solution giving dimethylchloroselonium tetrachloroborate, previously prepared from dimethyl selenium dichloride and boron trichloride at -25° in methylene dichloride (8). A solution of dimethyl tellurium dichloride reacted with boron trichloride to give a dimethyl tellurium dichloride boron trichloride adduct of unknown structure, which lost boron trichloride very readily on pumping at room temperature. Diphenyl selenium dichloride reacted with boron trichloride to form diphenylchloroselonium tetrachloroborate in solution, but this decomposed on warming to room temperature.

The reactions of solutions of diethyl sulfide, dimethyl selenium, and dimethyl tellurium with boron trichloride yielded the corresponding adducts at room temperature.

$$\begin{split} Me_2Se+ 2HCl \rightarrow Me_2SeH^+ + HCl_2^- \\ Me_2SeH^+ + BCl_3 \rightarrow Me_2SeBCl_3 + H^+ \end{split}$$

although dimethyl telluronium tetrachloroborate was formed in solution. The diethyl sulfide boron trichloride adduct has been prepared by the reaction of boron trichloride with diethyl sulfide in ligroin (9) and the dimethyl selenium - boron trichloride adduct prepared by the direct interaction of dimethyl selenium and boron trichloride (8). Dimethyl and diethyl disulfides reacted in solution with boron trichloride to form the somewhat unstable boron trichloride adducts, R_2S_2 . BCl₃. Methane- and ethane-sulfenyl chlorides reacted with boron trichloride to form an ionic compound in solution of stoichiometry (RSCl)₂BCl₃; the methanesulfenyl chloride compound has been characterized (10). Various structures have been suggested for the compound (MeSCl)₂BCl₃



of which 3 is favored (10).

The potentially amphoteric chlorides SeCl₄ and TeCl₄, and SCl₄ were examined; ions of the type MCl_3^+ (11) and $SeCl_6^{2-}$ and $TeCl_6^{2-}$ (12) are all well known. It has very recently been shown that SeCl₄ and TeCl₄ both dissolve in chlorosulfuric acid to form the ions SeCl₃⁺ and $TeCl_3^+$ (13). Sulfur, selenium, and tellurium tetrachlorides were all sparingly soluble and did not show any basic properties in solution, failing to react with boron trichloride, although sulfur tetrachloride is known to form an unstable adduct with boron trichloride in the absence of a solvent; this adduct decomposes at -20° (14). Selenium and tellurium tetrachlorides did not react with boron trichloride in the absence of a solvent. The acidic properties, if any, of selenium and tellurium tetrachlorides, dimethyl and diphenyl selenium dichlorides, and dimethyl tellurium dichloride were investigated by mixing them with stoichiometric amounts of tetramethylammonium chloride in the solvent. From the increase in weight observed and the infrared (i.r.) spectrum of the product, it was inferred that tetramethylammonium hydrogen dichloride had

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been formed, and that none of these chlorides had any acidic properties in liquid hydrogen chloride solution. Sulfur dichloride, sulfur monochloride, selenium monochloride, and tellurium dichloride did not react with boron trichloride in liquid hydrogen chloride or without a solvent.

Comparison of the conductivities of dimethyl sulfide, dimethyl selenium, and dimethyl tellurium shows that for solutions of approximately the same concentration, the basicities are of the same order of magnitude and that changing the Group VI element has little effect on the ease of protonation of Me₂M to form Me₂MH⁺. A much greater change in conductivities is observed in changing the methyl group for chlorine; in the series Me_xSCl_{3-x}⁺ it is observed that the basic strengths are

$Me_3S^+ > Me_2SCl^+ > MeSCl_2^+$

The derivatives of tetravalent sulfur, R_2SCl_2 and $RSCl_3$, are considerably less stable than R_2SeCl_2 and R_2TeCl_2 and are comparable to the relative stabilities of sulfur, selenium, and tellurium tetrachlorides. The ions $MeSCl_2^+$, Me_2SCl^+ , and Me_2SeCl^+ could be stabilized as tetrachloroborates, but the ion Me_2TeCl^+ could not be stabilized analogously, suggesting that Me_2TeCl_2 may react with boron trichloride to form a nonionized adduct $Me_2Cl_2Te.BCl_3$ containing a Te—B bond.

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Experimental

The apparatus and techniques have been described previously (15). Volatile reactants were distilled into the conductivity cell from a calibrated volume at a known pressure and temperature; by the use of liquid nitrogen, quantitative transfer was possible. Measured volumes of liquids were obtained using a syringe and solids were weighed directly into the cell. The products were very hydrolytically sensitive and were therefore handled in a dry box. Chloride was analyzed gravimetrically and boron acidimetrically as the mannitol-borate complex. Infrared spectra were recorded on a Perkin-Elmer 457 spectrophotometer.

All the reagents were available commercially, unless their preparation is described.

The conductivities of the materials studied are shown in Table I.

Reactions with Chlorine (and Boron Trichloride)

Dimethyl and diethyl sulfide solutions were both separately titrated against chlorine, the titration showing a break when the mole ratio of $R_2S:Cl_2$ was 1.0:1.0, see Fig. 1. No stable products were isolated at room temperature, both products decomposing with partial chlorination of the alkyl groups. Titration of a solution of a mixture of 1 mole of dimethyl or diethyl sulfide and 1 mole of chlorine against boron trichloride showed end points when the mole ratios $R_2SCl_2:BCl_3$ were 1.0:1.05

ΤA	BL	E	I

Specific and molar conductances of compounds in liquid hydrogen chloride at -95°

Compound	Concen- tration (mole/l)	Specific conductance $(\mu\Omega^{-1} \text{ cm}^{-1})$	Molar conductance $(\Omega^{-1} \text{ cm}^2 \text{ mole}^{-1})$
Me ₂ S	0.29	3 165	10.8
Et ₂ S	0.39	6 4 3 0	16.6
(CeFe) S	Saturated	7.8	
EtSH	0.34	68.0	0.200
Me ₂ S ₂	0.40	168	0.415
Et ₂ S ₂	0.42	285	
MeSCl	0.43	3 778	8.80
EtSCl	0.59	7 010	11.9
MeSCl ₃	0.46	4 780	10.5
EtSCl ₃	0.40	4 360	10.9
Me ₂ SČl ₂	0.29	6 180	21.1
Et ₂ SCl ₂	0.42	12 800	30.8
Me ₃ SI	0.39	10 500	27.3
S_2Cl_2	Saturated	0.33	
SCl ₂	0.40	1.44	0.004
SC14	Saturated	1.97	_
Me ₂ Se	0.34	5 490	16.0
Me ₂ SeCl ₂	0.34	30.7	0.090
Ph ₂ SeCl ₂	0.26	1 500	5.71
SeCl ₄	Saturated	1.30	—
Se_2Cl_2	Saturated	1.83	_
SeOCl ₂	Saturated	0.75	_
Me₂Te	0.32	3 123	9.64
Me ₂ TeCl ₂	Saturated	20.7	_
TeCl₄	Saturated	0.22	_
TeCl ₂	Saturated	0.86	_





 (Me_2SCl_2) and 1.0:1.10 (Et₂SCl₂), see Fig. 1. The high conductivity at the end points in all these titrations indicates the formation of the ions R_2SCl^+ in solution.

White solids dimethylchlorosulfonium tetrachloroborate, m.p. 172-173° and diethylchlorosulfonium tetrachloroborate, m.p. 35-36° were isolated. Anal. Calcd. for $C_2H_6BCl_5S$: B, 4.32; Cl, 70.8. Found: B, 4.24: Cl, 70.3.

Anal. Calcd. for C₄H₁₀BCl₅S: B, 3.94; Cl, 64.6. Found: B, 3.92; Cl, 64.4.

The i.r. spectra of the products showed frequencies characteristic of the RS group, the BCl_4^- ion (16), and S—CI frequencies at 521(m) cm⁻¹ (Me₂SCl.BCl₄) and at 536(m) and 516(m) cm⁻¹ (Et₂SCl.BCl₄).

A solution of methanesulfenyl chloride was oxidized with chlorine to methyl sulfur trichloride; on treatment with boron trichloride, methyldichlorosulfonium tetrachloroborate was formed, which was isolated and characterized by its m.p. and i.r. spectrum.

The reactions of solutions of dimethyl disulfide and ethanethiol with chlorine gave ill-defined products both of which were shown by their i.r. spectra to contain C—Cl and S—Cl bonds. The reaction of 1 mole of dimethyl disulfide solution, after equilibration at -95° and treatment with 1 mole of chlorine and then 1 mole of boron trichloride yielded the same product as the reaction of MeSCl and BCl₃.

Sulfur dichloride was not oxidized in solution with chlorine to sulfur tetrachloride.

Dimethyl selenide formed a colorless solution; titration with chlorine caused precipitation and the end point was not sharp. Dimethyl selenium dichloride was isolated, m.p. $60-62^{\circ}$ (lit. 61° (8)). A suspension of dimethyl selenium dichloride was prepared in situ and treated with boron trichloride, to form dimethylchloroselenonium tetrachloroborate, m.p. $81-82^{\circ}$ (lit. 58° decomp. (8)).

Anal. Calcd. C₂H₆BCl₅Se: B, 3.64; Cl, 59.7. Found: B, 3.56; Cl, 59.6, 58.6.

The i.r. spectrum differs from that reported previously in that distinct tetrachloroborate ion peaks are found at 695, 671, and 663 cm⁻¹ (10).

Dimethyl tellurium formed a colorless solution which when titrated with chlorine showed a break at a mole ratio 1.0:1.0 and the very low conductivity indicated the formation of a non-conducting species. White dimethyl tellurium dichloride, m.p. 94–95°, was isolated.

Anal. Calcd. for C₂H₆Cl₂Te: Cl, 30.9. Found: Cl, 31.0.

Reaction of a suspension of dimethyl tellurium dichloride, prepared in situ, with boron trichloride, gave an adduct Me_2TeCl_2 . BCl_3 which decomposed on warming from -80° to room temperature with the quantitative evolution of boron trichloride, leaving solid dimethyl tellurium dichloride.

Reactions of Sulfur Compounds with Boron Trichloride

Methane- and ethane-sulfenyl chlorides, prepared in situ by allowing 1 mole of dialkyl disulfide and 1 mole of chlorine to equilibrate at -20° for $\frac{1}{2}$ h (17), when titrated against boron trichloride, showed sharp breaks at mole ratio RSCI:BCl₃ of 2.3:1.0 (MeSCl) and 2.0:1.0 (EtSCl), see Fig. 2, indicating the formation of an ionic species (RSCl)₂BCl₃. A white solid (MeSCl)₂BCl₃, m.p. 159° decomp., and a yellow liquid (EtSCl)₂BCl₃ were isolated at room temperature.

Anal. Calcd. for $C_2H_6BCl_5S_2$: B, 3.84; Cl, 62.8. Found: B, 3.81; Cl, 62.5.

Anal. Calcd. for $C_4H_{10}BCl_5S_2$: B, 3.48; Cl, 57.1. Found: B, 3.49; Cl, 57.0.

Both products decomposed on standing. In the i.r. spectra RS peaks, B--Cl peaks at 682(s), 655(s) cm⁻¹ ((MeSCl)₂BCl₃); 656(s), 688(s) cm⁻¹ ((EtSCl)₂BCl₃); and



FIG. 2. Conductimetric titrations in liquid hydrogen chloride. A, 0.59 *M* EtSCl and BCl₃ (0–1.5 scale); B, 0.56 *M* MeSCl and PF₅ (0–3 scale); C, 0.51 *M* MeSCl and BCl₃ (0–1.5 scale).

S—Cl peaks at 494(m), 470(m), 460(m) cm⁻¹ ((MeSCl)₂-BCl₃); and 509(m), 466(m), 452(sh) cm⁻¹ ((EtSCl)₂BCl₃) were observed.

Methyl and ethyl sulfur trichlorides, prepared in situ from 1 mole of the dialkyl disulfide and 3 moles of chlorine at -20° (18), both reacted with boron trichloride to form the corresponding alkyldichlorosulfonium tetrachloroborate. White methyldichlorosulfonium tetrachloroborate, m.p. 155–156°, precipitated from solution.

Anal. Calcd. for CH₃BCl₆S: B, 3.99; Cl, 78.6. Found: B, 3.91; Cl, 79.6.

The conductiometric titration of ethyl sulfur trichloride against boron trichloride showed a break at mole ratio 1.0:1.0, EtSCl₃:BCl₃, see Fig. 3, indicating the formation of the ionic species $EtSCl_2^+BCl_4^-$ in solution, which was isolated as a white solid, m.p. $101-104^\circ$.

Anal. Calcd. for C₂H₆BCl₆S: B, 4.57; Cl, 69.6. Found: B, 4.17; Cl, 69.9.

The i.r. spectra showed peaks characteristic of the RS group, the BCl₄⁻ ion (10), and S—Cl frequencies at 522(m) and 496(m) cm⁻¹ (MeSCl₂⁺) and 541(m) and 508(m) cm⁻¹ (EtSCl₂⁺).

Solutions of dimethyl and diethyl disulfide reacted with boron trichloride to form the boron trichloride adducts; no sharp break was observed in the conductiometric titration, both products being colorless liquids which fumed readily in moist air. The diethyl disulfide boron trichloride adduct was also formed by mixing diethyl disulfide with an excess of boron trichloride in a sealed tube, which was opened after standing for 4 days at room temperature. From the amount of boron trichloride recovered it was deduced that an adduct of composition Et_2S_2 .BCl₃ had been formed, but the colorless fuming

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FIG. 3. Conductimetric titrations in liquid hydrogen chloride. A, 0.26 M Ph₂SeCl₂ and BCl₃ (0–3 scale); B, 0.40 M EtSCl₃ and BCl₃ (0–6 scale); C, 0.34 M Me₂Se and BCl₃ (0–6 scale).

liquid readily decomposed in a glove box to a brown liquid, and could not be analyzed satisfactorily.

Anal. Calcd. for $C_2H_6BCl_3S_2$: B, 5.11; Cl, 50.3. Found: B, 5.26; Cl, 50.6.

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The i.r. spectra showed peaks characteristic of the RS group B—Cl frequencies at 760(vs), 751(vs), 691(m), and 584(s) cm⁻¹ (Me₂S₂.BCl₃); 759(vs), 750(vs), 696(m), and 582(s) cm⁻¹ (Et₂S₂.BCl₃); and B—S peaks at 960(m) cm⁻¹ (Me₂S₂.BCl₃); 1054(m) cm⁻¹ (Et₂S₂.BCl₃).

Titration of diethyl sulfide solution against boron trichloride showed a sharp break at mole ratio 1.0:1.0 (Et₂S:BCl₃), see Fig. 1, the low conductivity at the end point indicating the formation of the undissociated adduct in solution. Colorless liquid diethyl sulfide – boron trichloride adduct was isolated.

Anal. Calcd. for $C_2H_{10}BCl_3S$: B, 5.55; Cl, 51.7. Found: B, 5.29; Cl, 51.2.

The i.r. spectrum showed peaks characteristic of the EtS group, B—Cl peaks at 743(vs) and 616(s) cm⁻¹, and a possible B—S frequency at 1054(m) cm⁻¹.

Trimethylsulfonium iodide formed a highly conducting solution; titration with boron trichloride showed an end point at mole ratio Me₃SI:BCl₃ of 1.0:1.2. A white solid, trimethylsulfonium tetrachloroborate, decomp. 300°, was isolated.

Anal. Calcd. for C₃H₉BCl₄S: B, 4.70; Cl, 61.7. Found: B, 4.60; Cl, 60.4.

This formula was confirmed by the i.r. spectrum which contained only Me_3S^+ ion and BCl_4^- ion frequencies (19, 10).

The compounds sulfur monochloride, sulfur dichloride, sulfur tetrachloride (prepared by allowing 1 mole of sulfur dichloride and 1 mole of chlorine to equilibrate at -60°), and bis(pentafluorophenyl)sulfide formed very poorly conducting solutions and did not react with boron truchloride.

Reactions of Selenium Compounds with Boron Trichloride Dimethyl selenium solution showed a break at mole ratio 1.0:1.0, Me₂Se:BCl₃, when titrated against boron trichloride, see Fig. 3, the low conductivity at the equivalence point indicating the formation of the undissociated dimethyl selenium – boron trichloride adduct in solution, which was isolated as a white solid, $93-95^{\circ}$ (lit. 101–102° (5)).

Anal. Calcd. for $C_2H_6BCl_3Se: B, 4.78; Cl, 47.0.$ Found: B, 4.79; Cl, 47.4.

The i.r. spectrum agrees with that reported previously (5).

Diphenyl selenium dichloride when titrated against boron trichloride gave an equivalence point when the ratio $Ph_2SeCl_2:BCl_3$ was 1.0:1.0, see Fig. 3, the high conductivity indicating the formation of an ionic species, probably $Ph_2SeCl^+BCl_4^-$. After removal of the solvent, the white solid product decomposed on warming to room temperature.

Selenium monochloride and selenium tetrachloride both formed poorly conducting solutions which did not react with boron trichloride.

Reactions of Tellurium Compounds with Boron Trichloride

The reaction of boron trichloride with a solution of dimethyl tellurium produced a white precipitate. After removal of the solvent and pumping at -80° for 2 h, 0.98 mole of hydrogen chloride per mole of dimethyl tellurium was evolved and the white dimethyl tellurium boron trichloride adduct, m.p. 231–233°, remained.

Anal. Calcd. for $C_2H_6BCl_3Te$: B, 3.93; Cl, 38.7. Found: B, 3.81; Cl, 38.6.

The almost quantitative evolution of hydrogen chloride suggests that dimethyl telluronium tetrachloroborate, $Me_2TeH^+BCl_4^-$, had precipitated from solution and decomposed on warming to room temperature, forming the dimethyl tellurium boron trichloride adduct. The dimethyl tellurium boron trichloride adduct decomposed to a black material, probably tellurium, in a dry box within a day. The i.r. spectrum showed frequencies characteristic of the MeTe group and B—Cl frequencies at 750(sh), 712(vs), and 662(s) cm⁻¹.

Tellurium dichloride and tellurium tetrachloride were both sparingly soluble and did not react with boron trichloride.

Reactions with Phosphorus Pentafluoride

A solution of dimethylchlorosulfonium chloride reacted with phosphorus pentafluoride and white dimethylchlorosulfonium hexafluorophosphate, m.p. 182–184°, was isolated.

Anal. Calcd. for C₂H₆ClF₆PS: Cl, 14.6. Found: Cl, 14.6.

The i.r. spectrum is consistent with its structure as $Me_2SCl^+PF_6^-$, showing only peaks characteristic of the Me_2SCl^+ and PF_6^- ions (3).

Methanesulfenyl chloride solution was titrated against phosphorus pentafluoride, see Fig. 2; the equivalence point was found at mole ratio 1.3:1.0, PF₅:MeSCl, indicating that the reaction,

probably had occurred. White methylchlorosulfonium hexafluorophosphate, m.p. 132-133° decomp., was isolated.

Anal. Calcd. for CH₄ClF₆PS: Cl, 15.5. Found: Cl, 15.5.

In the i.r. spectrum PF_6^- ion peaks (3), MeS group peaks and possible S—Cl frequencies at 496(m) and 479(m) cm⁻¹ were observed. The S-H frequency would be expected to be very weak and no peak can be assigned with certainty, although there may be one at 2270(vw) cm⁻¹

An unstable white methyldichlorosulfonium hexafluorophosphate could be isolated from the reaction of a solution of methyl sulfur trichloride and phosphorus pentafluoride. The solid decomposed with loss of PF5; its i.r. spectrum showed the presence of the ions MeSCl2⁺ and PF_6^- (3).

Potential Acids

Solutions were prepared of approximately 2 moles of Me₄NCl and 1 mole of SeCl₄, Me₂SeCl₂, Ph₂SeCl₂, TeCl₄, and Me₂TeCl₂. After removal of the solvent the increase in weight showed that Me₄NCl had formed Me₄NHCl₂ and not (Me₄N)₂MCl₆. The i.r. spectra of the products of the reactions with Me₂SeCl₂, Ph₂SeCl₂, and Me₂TeCl₂ showed the presence of the HCl₂- ion (20). When 2 moles of Me₄NHCl₂ and 1 mole of SeCl₄ or TeĆl₄ were ground up in Nujol, the i.r. peaks corresponding to the HCl₂⁻ ion had disappeared, indicating that in the grinding process the HCl2⁻ ion had decomposed and the hexachloroselenate and hexachlorotellurate ions had probably been formed. The HCl2- ion would not be expected in the i.r. spectra of the Me₄NCl and SeCl₄ or TeCl₄ reaction products. It can be concluded that none of these chlorides exhibit acidic properties in liquid hydrogen chloride solution.

Reactions with Boron Trichloride without a Solvent

Sulfur monochloride, sulfur dichloride, sulfur tetrachloride, selenium monochloride, selenium tetrachloride, tellurium dichloride, and tellurium tetrachloride were each sealed in a tube under vacuum with an excess of boron trichloride and shaken at room temperature for a week. In all cases, except for sulfur tetrachloride, no reaction occurred and the reactants were recovered. A white solid formed in the sulfur tetrachloride reaction, but after removal of the excess boron trichloride at -60° ,

it started to decompose at about -20° and decomposed too rapidly at room temperature to be analyzed.

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