metal (which would account for the black color), in the solid formed at the anode (from whose surface the hydrogen gas was evolved), then one-fourth of the calcium lost from the anode would indeed be expected to appear in this material at the end of the electrolysis.

An interesting gradation in V_i values is observed for solutions containing chloride, bromide, and iodide ions. As implied earlier, this variation appears to be related to a change in mechanism, although the reason for the dependence of the mechanism on the presence of a particular halide is not apparent.

A Simple Preparation of Substituted Chlorophosphonium Salts; the Salt FPCl₃SbCl₆[1]

BY JOHN K. RUFF

The reaction of tertiary phosphines with excess antimony pentachloride produced phosphonium salts. Phosphines of the types $RPCl_2$, R_2PCl, and R_3P were employed. Reaction of $FPCl_2$ with antimony pentachloride in the presence of chlorine was found to yield the salt $FPCl_3SbCl_6$. The constitution of these materials is discussed.

The recognition that phosphorus pentachloride possessed an ionic constitution, both in the solid state[2] and in polar solvents,[3] supported the belief that alkyl or aryl halophosphoranes of the types RPX_4, R_2PX_3, and R_3PX_2 were also partially ionized, and that adducts formed between these phosphoranes or phosphorus pentachloride and metal halides capable of forming polyhalo metal anions were actually phosphonium salts.

$$C_6H_{11}PBr_4 + SbBr_3 \longrightarrow C_6H_{11}PBr_3SbBr_4 [4]$$
$$(C_6H_5)_3PCl_2 + SbCl_5 \longrightarrow (C_6H_5)_3PClSbCl_6 [5]$$
$$PCl_5 + MCl_n \longrightarrow PCl_4MCl_{n+1} [6]$$
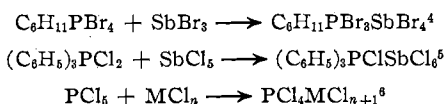
Evidence for the ionic constitution of these adducts was based upon their electrical conductivity in solution and in a few cases on transport measurements. Phosphoranes of the types $(RO)_{4-n}PX_{n+1}$ and $(R_2N)_{4-n}PX_{n+1}$ were also found to be ionic although the exact nature of the ions involved is not known.[7,8] Adduct formation of this type of phosphorane with metal halides is not necessarily indicative of an ionic constitution since for example the complex $R_2NPCl_4 \cdot FCl_5$[9] could also have the covalent structure $Cl_5P \leftarrow N(R_2)$-PCl_4.

As noted above, the general method used for the preparation of the adducts was based on the reaction of a halo-substituted phosphorane with a halide ion acceptor.[4-6] The requisite halophosphoranes were obtained from halogenation of the corresponding phosphines and in some cases were found to be unstable and difficult to purify. A simple method of preparation of a number of substituted chlorophosphonium hexachloroantimonate salts has been developed in which isolation of these intermediates was not necessary.

Results and Discussion

Tertiary phosphines were found to react with antimony pentachloride to produce substituted chlorophosphonium salts according to the stoichiometry

$$R_3P + 2SbCl_5 \longrightarrow R_3PClSbCl_6 + SbCl_3$$

Although the over-all reaction might formally be considered as consisting of two consecutive reactions (chlorination followed by chloride ion abstraction), it was not possible to isolate the intermediate chlorophosphorane (R_3PCl_2), even when an excess of the phosphine was employed. The reaction was found to proceed readily with a number of differently substituted phosphines. The compounds that were prepared are listed in Table I. In general the phosphonium salts precipitated as they formed.

Recrystallization of the initial precipitates was not necessary as they were obtained analytically pure. The antimony trichloride remained in solution and could be isolated in moderate yield. Several of the products were prepared by reaction of equimolar mixtures of antimony pentachloride and the chlorophosphorane. The products obtained by both methods were identical. It was not possible to prepare the trichlorothiophenoxyphosphonium salt ($C_6H_5SPCl_3SbCl_6$) by either method. Chlorination of the sulfur–phosphorus bond occurred and benzenesulfenyl chloride was apparently formed.

(1) This work was performed under Contract Number DA-01-021 ORD 11878.
(2) D. Clarke, H. M. Powell, and A. F. Wells, *J. Chem. Soc.*, 642 (1942).
(3) D. S. Payne, *ibid.*, 1052 (1953).
(4) K. Issleib and W. Seidel, *Z. anorg. allgem. Chem.*, **303**, 155 (1960).
(5) K. Issleib and W. Seidel, *ibid.*, **288**, 201 (1956).
(6) W. L. Groeneveld, *Rec. trav. chim.*, **71**, 1152 (1952).
(7) G. S. Harris and D. S. Payne, *J. Chem. Soc.*, 3038 (1956).
(8) H. N. Rydon and B. L. Tonge, *ibid.*, 3043 (1956).
(9) A. Michaelis, *Ann.*, **326**, 129 (1903).

TABLE I
CHARACTERIZATION OF THE SUBSTITUTED CHLOROPHOSPHONIUM SALT

Compound	M.p., °C.	Yield, %	Method	Found					Calcd.				
				C	H	Sb	Cl	N	C	H	Sb	Cl	N
$C_6H_5PCl_3SbCl_6$	290–292	90	A and B	13.31	1.11	22.4	58.1	...	13.13	0.92	22.2	58.1	...
$(C_6H_5)_2PCl_2SbCl_6$	168–170	67	B	24.27	1.92	20.8	47.9	...	24.40	1.71	20.6	48.0	...
$(C_6H_5)_3PClSbCl_6$	172–173	59	B	34.53	2.66	19.4	38.1	...	34.19	2.39	19.3	39.3	...
$(C_2H_5)_2NPCl_3SbCl_6$	247–249	67	A and B	9.14	2.12	22.3	58.4	2.57	8.83	1.85	22.4	58.7	2.57
$[(C_2H_5)_2N]_3PClSbCl_6$	230–232	91	B	23.68	5.13	20.0	40.8	6.72	23.35	4.90	19.7	40.2	6.81
$C_6H_5OPCl_3SbCl_6$	265–266	81	A and B	13.01	1.23	21.8	56.4	...	12.75	0.84	21.6	56.5	...
PCl_4SbCl_6	>300	84	A and B	...	...	23.9	69.8	...	...	...	24.0	69.9	...
				...	...	24.1	70.1	...	...	...	...	...	...
$FPCl_3SbCl_6$	>300	74		...	3.8ᵃ	25.0	64.7	...	...	3.9ᵃ	24.8	65.0	...
				...	3.8ᵃ	24.9	65.1	...	...	...	...	...	...
$NOSbCl_6$		92		...	...	33.5	58.1	3.72	...	...	33.4	58.3	3.84
				...	...	33.4	58.2	3.89	...	...	...	...	...

ᵃ Fluorine analyses.

The reaction between the phosphines and antimony pentachloride was usually complete in a few minutes. Although it was not possible even qualitatively to observe rate differences between the various phosphines it was evident that phosphorus trichloride was slower to react than the others. Only slight reaction was observed between phosphorus fluoride dichloride and antimony pentachloride under the same conditions. Based on the assumption that chlorination of the phosphine was slower than chloride ion abstraction, elemental chlorine was employed in the reaction with phosphorus fluoride dichloride.

$$FPCl_2 + Cl_2 + SbCl_5 \longrightarrow FPCl_3SbCl_6$$
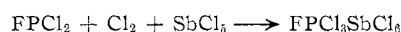
Formation of fluorotrichlorophosphonium hexachloroantimonate occurred rapidly at $-78°$.

An attempt was made to prepare the trifluorochlorophosphonium salt by an analogous reaction employing phosphorus trifluoride. Only a small amount of solid product precipitated from solution and it was found to be the previously prepared fluorotrichlorophosphonium hexachloroantimonate. Phosphorus tribromide was also found to react with antimony pentachloride to produce a white precipitate. Elemental analyses indicated that it had the composition $PSbBr_3Cl_7$. The material was unstable and decomposed readily on melting, during attempted purification, or slowly on standing at ambient temperature. It was therefore not possible to complete characterization of this adduct.

The formulation of the adducts as substituted chlorophosphonium salts is based, in part, on their electrical conductivity in nitrobenzene. The results obtained are presented in Table II. The values determined for the molar conductance of $C_6H_5PCl_3SbCl_6$ are in agreement with those previously reported.[5] The magnitude of the molar conductance for all the salts is in the range (20–30 Λ) attributed to a 1:1 electrolyte in a 10^{-3} M nitrobenzene solution.[10,11] Furthermore the molar conductance reported for tetraethylammonium iodide and trimethylbenzylammonium hexachloroantimonate falls within the same range.[5] Unfortunately it was not possible to obtain conductivity data on $FPCl_3SbCl_6$ as the compound decomposed in either nitrobenzene or

acetonitrile. Some evidence for decomposition of $C_6H_5OPCl_3SbCl_6$ was also observed in nitrobenzene so the values obtained for this salt may be unreliable.

TABLE II
ELECTRICAL CONDUCTANCES IN NITROBENZENE

Compound	Moles/l. $\times 10^3$	Resistance	Λ
$C_6H_5PCl_3SbCl_6$	7.138	2864	25.2
	3.569	5480	26.3
	1.785	10300	28.0
	0.8925	19100	30.2
$(C_6H_5)_2PCl_2SbCl_6$	1.468	4252	27.1
	2.234	8115	28.4
	1.117	15320	30.1
	0.5585	28630	32.2
$(C_6H_5)_3PClSbCl_6$	5.676	3464	26.2
	2.838	6646	27.3
	1.419	12600	28.8
	0.7095	23340	31.1
$(C_2H_5)_2NPCl_3SbCl_6$	7.380	2800	24.9
	3.690	5424	25.5
	1.845	10300	27.1
	0.9225	19650	28.4
$[(C_2H_5)_2N]_3PClSbCl_6$	7.780	3010	22.0
	3.890	5756	23.0
	1.945	10890	24.3
	0.9725	20610	25.7
$C_6H_5OPCl_3SbCl_6$	6.520	3238	24.4
	3.260	6196	25.5
	1.630	11570	27.3
	0.8150	22090	28.6

Although the adducts behave as 1:1 electrolytes in solution no information as to the composition of the ions can be obtained from the conductance data. Two points concerning their composition which must be considered are: (a) which element, phosphorus or antimony, is contained in the cation and (b) did exchange of groups occur between phosphorus and antimony? Complete evidence is lacking for all the adducts but it is probable that the antimony is present in the anion in every case since stibonium salts are considerably less stable than the corresponding phosphonium salts and the stability of the $SbCl_6^-$ ion is greater than the PCl_6^- ion. Thus, when the pentachlorides of phosphorus and antimony are allowed to interact the phosphonium salt, $PCl_4^+SbCl_6^-$, is formed rather than the stibonium salt.[12]

(10) C. M. Harris and R. S. Nyholm, *J. Chem. Soc.*, 4375 (1956).
(11) D. J. Phillips and S. Y. Tyree, Jr., *J. Am. Chem. Soc.*, **83**, 1806 (1961).
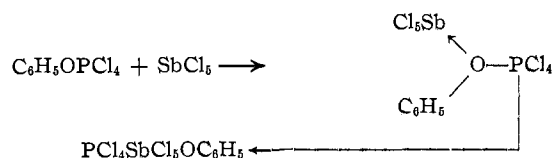(12) I. R. Beattie and M. Webster, *J. Chem. Soc.*, 38 (1963).

TABLE III

INFRARED SPECTRA OF THE SUBSTITUTED CHLOROPHOSPHONIUM SALTS AND RELATED COMPOUNDS

FPCl₂ (gas)[a]	(C₆H₅)-PClSbCl₆	(C₆H₅)₂-PCl₂SbCl₆	C₆H₅-PCl₃SbCl₆	(C₂H₅)₂-NPCl₂SbCl₆	[(C₂H₅)₂N]₃-PClSbCl₆	C₆H₅O-PCl₃SbCl₆
11.06 w[b]	3.45 m, br.	3.45 m, br.	3.43 m	3.41 s	3.42 s	3.40 s
11.95 } s, dbt.	6.32 m	6.35 m	6.34 m	6.87 vs	8.88 s	6.34 w
12.05 }	6.87 m	6.87 m	6.88 m	7.23 m	7.26 s	6.78 s
19.35 vs, br.	6.97 s	6.48 s	6.97 s	7.39 s	7.50 vw	6.87 m
	7.29 m	7.28 m	7.29 m	7.82 w	7.76 w	7.30 w
FSiCl₃ (gas)*	7.50 w	7.48 m	7.45 m	8.35 s	8.28 s	7.80 w
10.52	7.05 vw	7.05 w	7.64 w	8.80 s	8.67 m	8.50 w
10.58 s	8.44 s	8.44 w	8.44 w	9.18 m	8.74 s	8.04 m
10.68 w	8.61 w	8.59 vw	8.57 vw	9.74 vs	9.12 m	8.82 s
15.67 vs, br.	9.00 vs	9.00 vs	8.98 vs	10.80 m	9.45 w	9.36 s
	9.12 s	9.13 s	4.12 s	12.59 s	9.72 vs	9.74 m
PCl₄SbCl₆	10.04 s	10.04 s	10.02 s	14.37 w	10.24 w	9.84 w
15.14 vs	13.42 m	13.38 s	13.30 s	15.22 vs	10.52 w	10.00 s
15.50 vs	13.70 s	13.65 s	13.70 s	16.35 vs	10.83 w	13.00 s
17.03 w	14.30 m	14.00 s	14.50 s	19.50 vw	12.58 s	13.20 w
	14.64 s	14.75 vs	14.85 vs	20.55 w	14.03 w	14.68 w
FPCl₃SbCl₆	16.16 m	15.75 vs	15.60 vs		15.40 s	15.07 s
9.82 vw	16.95 vs, br.	16.00 vs	16.20 m		18.05 vs	15.36 s
10.14 w	19.13 vs, br.	16.50 s	19.29 vs		21.55 w	17.00 w
10.27 s	21.46 vw	17.53 vs	20.89 w			20.60 w
14.35 vs, br.	22.38 vw, br.	20.18 } vs, dbt.	21.07 w			
		20.32 }				
		21.38 w				
		22.40 w				

[a] The infrared spectra of all samples, unless otherwise noted, were obtained in Nujol mulls. The Nujol bands are included in the above tabulation. [b] w, weak; m, medium; s, strong; v, very; br., broad; dbt., doublet.

The possibility of group exchange was felt to be particularly likely when the phosphines $(C_2H_5)_2NPCl_2$, $[(C_2H_5)_2N]_3P$, and $C_6H_5OPCl_2$ were employed because attack of the antimony pentachloride on the unshared pair of electrons on the nitrogen or oxygen could result in abstraction of an amide or a phenoxyl ion instead of a chloride ion.

$$C_6H_5OPCl_4 + SbCl_5 \longrightarrow \begin{matrix} Cl_5Sb \\ \nwarrow \\ O\text{---}PCl_4 \\ \diagup \\ C_6H_5 \end{matrix}$$

$$PCl_4SbCl_5OC_6H_5 \longleftarrow$$

The infrared spectra (see Table III) did not show the presence of the PCl_4^+ ion[12] in any of the substituted phosphonium salts except possibly $[(C_2H_5)_2N]_3PCl$-$SbCl_6$ and $C_6H_5OPCl_3SbCl_6$. Thus no exchange of groups occurred in the monosubstituted adducts $FPCl_3SbCl_6$, $C_6H_5PCl_3SbCl_6$, and $(C_2H_5)_2NPCl_3SbCl_6$. The strong band at 10.27 μ in the infrared spectrum of the fluorotrichlorophosphonium salt probably is attributable to a P–F stretching mode since it is found in this region for other P–F compounds.[13] The observed doublet in the F^{19} n.m.r. spectrum of this material confirms the presence of a P–F bond since no observable coupling would be expected between fluorine and antimony.

The proton n.m.r. spectra of the other adducts demonstrated that no exchange of the organic groups occurred either. Coupling between the protons on the methylene carbon of the ethyl group and phosphorus was observed in the adducts $(C_2H_5)_2NPCl_3SbCl_6$ and

$[(C_2H_5)_2N]_3PClSbCl_6$, indicating that the amino function was still bonded to phosphorus. Similar coupling was observed in the starting materials $(C_2H_5)_2NPCl_2$ and $[(C_2H_5)_2N]_3P$. Since the presence of the tetrachlorophosphonium ion in the material which analyzed for $[(C_2H_5)_2N]_3PClSbCl_6$ could not be eliminated it is possible that this product is a mixture of the tetrasubstituted phosphonium salts. However in the preparation no precipitation of products occurred under conditions where PCl_4SbCl_6 was found to precipitate in high yield. Thus the presence of substantial amounts of the tetrachlorophosphonium salt is felt to be unlikely.

The proton n.m.r. spectrum of $C_6H_5OPCl_3SbCl_6$ consisted of a doublet as did the spectrum of $C_6H_5OPCl_2$ and only a small difference in the chemical shifts of the two bands was noted. The spectra of the phenyl-substituted adducts were less conclusive. However, only one type of phenyl group was present in all the salts so that formulations of the type $C_6H_5PCl_3SbCl_5C_6H_5$, etc., are eliminated. This fact together with the absence of absorption bands due to the PCl_4^+ ion in the infrared spectra of these adducts suggests that no exchange occurred.

It is probable that the formulation of the organosubstituted adducts as phosphonium salts of the hexachloroantimonate anion is correct. However, since no examples of halo-substituted chlorophosphonium cations have been reported, other formulations for the adduct $FPCl_3SbCl_6$ must be considered. Although conductance data are lacking the similarity in physical properties of $FPCl_3SbCl_6$ and $PCl_4^+SbCl_6^-$ (high melting points and solubility characteristics) suggest that the former is also ionic. An alternative ionic formulation for the adduct is $SbCl_4^+PCl_5F^-$ since examples containing both of

(13) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd Ed., John Wiley & Sons, New York, N. Y., p. 324.

TABLE IV

N.M.R. SPECTRA OF THE SUBSTITUTED CHLOROPHOSPHONIUM
SALTS AND RELATED PHOSPHINES

$C_6H_5PCl_3SbCl_6$	Three complex bands, $\phi_1 = 1.80$, $\phi_2 = 1.60$, and $\phi_3 = 1.48$
$C_6H_5PCl_2$	Three complex bands, $\phi_1 = 2.40$, $\phi_2 = 2.23$, and $\phi_3 = 2.08$
$(C_6H_5)_2PCl_2SbCl_6$	Four complex bands, $\phi_1 = 1.86$, $\phi_2 = 1.80$, $\phi_3 = 1.72$, and $\phi_4 = 1.60$
$(C_6H_5)_2PCl$	Two complex bands, $\phi_1 = 2.60$ and $\phi_2 = 2.40$
$(C_6H_5)_3PCl_3SbCl_6$	Three bands, $\phi_1 = 1.90$, $\phi_2 = 1.80$, and $\phi_3 = 1.64$
$(C_6H_5)_3P$	Two bands, $\phi_1 = 2.68$ and $\phi_2 = 2.62$
$(C_2H_5)_2NPCl_3SbCl_6$	Triplet: $\phi = 8.36$, $J_{CH} = 8$ c.p.s. Two quadruplets: $\phi_1 = 6.00$, $J_{CH} = 9$ c.p.s.; $\phi_2 = 5.61$, $J_{CH} = 9$ c.p.s.; $J_{PH} = 23$ c.p.s.
$(C_2H_5)_2NPCl_2$	Triplet: $\phi = 8.77$, $J_{CH} = 9$ c.p.s. Two quadruplets: $\phi_1 = 6.40$, $J_{CH} = 8$ c.p.s.; $\phi_2 = 6.62$, $J_{CH} = 9$ c.p.s.; $J_{PH} = 15$ c.p.s.
$[(C_2H_5)_2N]_3PClSbCl_6$	Triplet: $\phi = 8.66$, $J_{CH} = 8$ c.p.s. Two quadruplets: $\phi_1 = 6.65$, $J_{CH} = 9$ c.p.s.; $\phi_2 = 6.40$, $J_{CH} = 9$ c.p.s.; $J_{PH} = 16$ c.p.s.
$[(C_2H_5)_2N]_3P$	Triplet: $\phi = 9.02$, $J_{CH} = 9$ c.p.s. Two quadruplets: $\phi_1 = 6.96$, $J_{CH} = 9$ c.p.s.; $\phi_2 = 7.10$, $J_{CH} = 9$ c.p.s.; $J_{PH} = 10$ c.p.s.
$C_6H_5OPCl_2$	Two bands, $\phi_1 = 2.04$ and $\phi_2 = 2.26$
$C_6H_5OPCl_3SbCl_6$	Two bands, $\phi_1 = 2.52$ and $\phi_2 = 2.71$
$FPCl_3SbCl_6{}^a$	Doublet $-3395c$ .p.s., -2101 c.p.s. (relative to TFA), $J_{PF} = 1296$ c.p.s.

^{a} F^{19} n.m.r. spectrum. All others are proton spectra.

these ions are known.[14,15] Unfortunately no infrared or F^{19} n.m.r. spectra were reported for the salt PCl_4-PCl_5F so that a direct comparison is not possible. The magnitude of the PF coupling constants of phosphorus trifluoride, phosphorus pentafluoride, and the hexa-fluorophosphate anion (PF_3, $J_{PF} = 1441$; PF_5, $J_{PF} = 916$; and $PF_6{}^-$, $J_{PF} = 710$ c.p.s.) was found to decrease substantially as the degree of s orbital character in the hydridization decreased.[16] The magnitude of the observed PF ($J_{PF} = 1294$ c.p.s.) coupling constant in $FPCl_3SbCl_6$ supports tetrahedral hydridization for the phosphorus as would be expected for a $FPCl_3{}^+$ ion. Furthermore there is a shift to shorter wave length in the infrared for both the P–F and P–Cl stretching modes over those observed in $FPCl_2$ and $PCl_4{}^+SbCl_6{}^-$. In fact a remarkable similarity in the infrared spectrum of the ion $FPCl_3{}^+$ and the isoelectronic species $FSiCl_3$ (see Table IV) was found. While not conclusive it is felt that the infrared data also support the existence of the $FPCl_3{}^+$ ion. The existence of the PCl_5F^- ion was established by transport measurements in acetonitrile solutions of the salt $PCl_4{}^+PCl_5F^-$.[14] The solvated $SbCl_4{}^+$ ion was also found to be stable in acetonitrile.[17] Thus the instability of the adduct in this solvent may perhaps be taken as further evidence in favor of the present formulation.

(14) L. Kolditz, *Z. anorg. allgem. Chem.*, **289**, 128 (1957).

(15) T. Kennedy and D. S. Payne, *J. Chem. Soc.*, 4126 (1960).

(16) E. L. Muetterties and W. D. Phillips, *Advan. Inorg. Chem. Radiochem.*, **4**, 244 (1962).

(17) L. Kolditz and H. Preiss, *Z. anorg. allgem. Chem.*, **310**, 243 (1961).

The use of antimony pentachloride as chlorinating agent has led to a convenient synthesis of substituted chlorophosphonium salts. The extension of this concept to other systems should be of synthetic value. One example of such an extension that was found is the preparation of nitrosonium hexachloroantimonate from nitrogen oxide and antimony pentachloride.

$$2NO + 3SbCl_5 \longrightarrow 2NOSbCl_6 + SbCl_3$$

The products were readily isolated in good yield by sublimation.

Experimental

Materials.—The phosphorus compounds, $C_6H_5PCl_2$, $(C_6H_5)_2$-PCl, PCl_5, PCl_3, and $(C_6H_5)_3P$, and the antimony pentachloride were obtained commercially and used without further purification. The phosphines $(C_2H_5)_2NPCl_2$,[18] $C_6H_5OPCl_2$,[19] and $[(C_2H_5)_2N]_3P$[18] were prepared as described in the literature and purified by distillation. Phosphorus fluoride dichloride and silicon fluoride trichloride were prepared by the method of Wilkins[20] and were shown to be pure after fractionation by their mass spectra. It should be noted that it was necessary to use very dry ammonium fluoride in the preparation of $FPCl_2$ in order to avoid the formation of phosphorus oxyhalides. The phosphoranes C_6H_5-PCl_4, m.p. 79°, $(C_2H_5)_2NPCl_4$, m.p. 215°, and $C_6H_5OPCl_4$, m.p. 128–130°, were prepared by chlorination of the corresponding phosphines. The latter compound was difficult to obtain pure and diethyl ether was found to be the best medium for the chlorination.[21]

Anal. Calcd. for $(C_2H_5)_2NPCl_4$: C, 19.61; H, 4.12; N, 5.72; Cl, 57.9. Found: C, 19.84; H, 3.99; N, 5.58; Cl, 57.5. Calcd. for $C_6H_5PCl_4$: C, 28.80; H, 2.00; Cl, 56.8. Found: C, 28.69; H, 2.13; Cl, 56.4. Calcd. for $C_6H_5OPCl_4$: C, 27.10; H, 1.90; Cl, 53.3. Found: C, 27.51; H, 2.15; Cl, 53.2.

Preparation of the Substituted Chlorophosphonium Salts. Method A.—The organo-substituted chlorophosphonium salts were prepared by slow addition of 10 mmoles of the desired phosphorane (described above) in 15 to 20 ml. of methylene chloride to a solution of 10 mmoles of antimony pentachloride in 10 ml. of the same solvent at 0°.

When phosphorus pentachloride was employed it was necessary to use 50 ml. of methylene chloride. Precipitation of the product occurred in every case and the reaction mixtures were filtered in a vacuum filtration apparatus. The product was dried under high vacuum for several hours prior to removal to the dry-box for handling.

Method B.—This procedure is essentially identical with the one described above except that 10 mmoles of the desired phosphine or phosphorus trichloride was allowed to react with 20 mmoles of antimony pentachloride at 0° in methylene chloride. Precipitation of the product occurred in all cases, except when the phosphine $[(C_2H_5)_2N]_3P$ was employed, and the reaction mixtures were treated as described before. The removal of approximately one-half of the methylene chloride from the reaction mixture $[(C_2H_5)_2$-$N]_3P$–$SbCl_5$ allowed precipitation of the desired product by the addition of diethyl ether. In a similar manner the yield of the salt $(C_6H_5)_3PClSbCl_6$ could be increased.

Preparation of $FPCl_3SbCl_6$.—A 5.06-mmole sample of antimony pentachloride was placed in 10 ml. of methylene chloride and the mixture was cooled to $-78°$. Then 4.97 mmoles of phosphorus fluoride dichloride was allowed to condense into the solution. Finally 5.01 mmoles of chlorine was added slowly. Precipitation of the product began immediately after admitting the chlorine. After stirring the mixture at $-45°$ for 0.5 hr., it was filtered and a 1.72-g. sample of the salt was obtained. When the above

(18) A. Michaelis, *Ann.*, **326**, 129 (1903).

(19) R. Anschütz and W. O. Emery, *ibid.*, **239**, 297 (1887).

(20) C. J. Wilkins, *J. Chem. Soc.*, 2726 (1951).

(21) R. Anschütz and W. O. Emery, *Ann.*, **253**, 105 (1889).

procedure was followed using phosphorus trifluoride instead of phosphorus fluoride dichloride only a 0.26-g. sample of solid was isolated (based on the same amount of starting materials). The solid was shown to be the salt $FPCl_3SbCl_6$ by a comparison of its infrared and F^{19} n.m.r. spectra with those of an authentic sample.

Reaction of PBr_3 with $SbCl_5$.—Phosphorus tribromide, 10.6 mmoles, was allowed to react with 21.0 mmoles of antimony pentachloride in 50 ml. of methylene chloride at $-10°$. Precipitation of a white solid occurred as the components were mixed. The product, 5.07 g., was obtained by filtration. It was not stable and slowly turned first yellow and then red on standing at ambient temperature for several days. The same color changes occurred rapidly on melting, 152–154°, or upon attempted recrystallization from acetonitrile.

Anal. Calcd. for $PBr_3Cl_2 \cdot SbCl_5$: Sb, 20.3; Cl, 36.8; total halogen, 75.1. Found: Sb, 19.9; Cl, 37.6; total halogen, 76.0.

Preparation of $NOSbCl_6$.—Nitrogen oxide was purified by scrubbing with a 2 N NaOH solution and dried over phosphorus pentoxide before being bubbled through a solution containing approximately 20 mmoles of antimony pentachloride in 75 ml. of trimethylene chloride. A yellow precipitate formed after several minutes and the gas stream was shut off after 20 min. Nitrosonium hexachloroantimonate was isolated by filtration, and could be purified by vacuum sublimation.

Analyses.—Carbon, hydrogen, and nitrogen analyses were performed by the normal microcombustion techniques. Antimony was determined by precipitation of antimony(III) sulfide with hydrogen sulfide, followed by dissolution in concentrated hydrochloric acid. The trivalent antimony was titrated with standard potassium bromate solution using a methyl orange indicator.[22] The salt, $FPCl_3SbCl_6$, was analyzed for fluorine by first

degrading the sample with lithium in *n*-propylamine and isolating the fluoride ion by steam distillation.[23] Then the fluorine content was obtained by the conventional thorium nitrate titration procedure. Although hydrolysis of the samples with a saturated KOH–methanol solution was sufficient to remove all of the chlorine as chloride in the salts, fluorine could not be done this way. The liberated chloride ion was determined by the Volhard method. Chlorine in the presence of bromine was determined by the method of Berg[24] after hydrolysis of the sample.

Infrared Spectra.—The infrared spectra in the 2.5 to 25 μ range of the salts and the gases $FPCl_2$ and $FSiCl_3$ were obtained in Nujol mulls or in the gas phase using a Perkin-Elmer Model 21 spectrophotometer equipped with potassium bromide optics.

N.m.r. Spectra.—The proton n.m.r. spectra of the salts and phosphines were obtained on a 10–12% solution using a Varian Model A-60 spectrometer. Nitrobenzene was used as a solvent for the derivatives containing ethyl groups and nitromethane was used for those containing phenyl groups. Tetramethylsilane was used as an internal standard. The F^{19} n.m.r. spectrum was obtained on a saturated solution of $FPCl_3SbCl_6$ in acetonitrile using a Varian Model 4300B spectrometer operating at 40 Mc. Trifluoroacetic acid was used as a standard. This solution was not stable and darkened to a deep brown on standing at room temperature for several hours. Therefore, the solution was stored at $-78°$ until run.

Conductance.—The conductivity of the salts in nitrobenzene was determined at 25.0 $\pm$ 0.05° in a cell of conventional design which had a cell constant of 0.515 cm.$^{-1}$. An oscilloscope equipped with a high gain preamplifier was used to detect the null point in a 2-kc. sine wave signal. Decade load resistors and a variable air capacitor were used to balance the bridge and the cell leads, respectively.

(22) W. W. Scott, "Standard Methods of Chemical Analysis," Vol. II, 5th Edition, D. Von Nostrand Co., New York, N. Y., 1939, p. 74.

(23) R. D. Strahm, *Anal. Chem.*, **31**, 615 (1959).

(24) I. M. Kolthoff and V. A. Stenger, "Volumetric Analysis," Vol. II, 2nd Ed., Interscience Publishers, Inc., New York, N. Y., 1947, p. 264.

# The Structure, Spectra, and Magnetic Properties of Certain Iron Halide Complexes

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The magnetic susceptibilities, optical spectra, and Mössbauer spectra of the compounds $(pyH)_3Fe_2Cl_9$ and $(pyH)_3Fe_2Br_9$ indicate that they do not contain the μ-trihalo dimeric anion $(Fe_2X_9)^{3-}$ as suggested by several authors, but rather that the iron is entirely present as tetrahedral FeX_4^-. Two forms of $Cs_3Fe_2Cl_9$ have been prepared. One is probably like the pyridinium compounds, *i.e.*, $[CsFeCl_4]_2 \cdot CsCl$, while the other contains the μ-trichloro dimeric anion. Low temperature electronic spectra of the pyridinium iron halides are reported and the assignments of the bands are discussed.

During the course of an investigation of metal–metal interactions in polynuclear transition metal complexes we examined the compounds $(pyH)_3Fe_2Cl_9$ and $(pyH)_3$-Fe_2Br_9 (py = pyridine). As a result of this work we came to the conclusion, surprising in the light of earlier work, that the iron in these compounds is present entirely as a tetrahedrally coördinated monomeric anion. The enneachloride was first described by Weinland and Kissling,[1] who at the same time reported the compounds $(QH)_4Fe_2Cl_{10}$ (Q = quinoline) and $(pyH)_5Fe_2Cl_{11}$ and, on the basis of the stoichiometry, proposed that these

(1) R. F. Weinland and A. Kissling, *Z. anorg. allgem. Chem.*, **120**, 209 (1922).
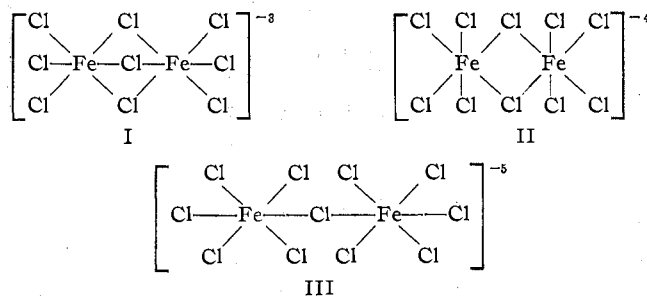
substances contain the binuclear complex anions I, II, and III, respectively. In the above complexes, each iron is presumably surrounded octahedrally