# **149.** *The Liquid Hydrogen Chloride Solvent System. Part VII.*[1] *Reactions of Some Non-metallic Fluorides.*

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The acidic properties of some Group IV fluorides and Group V trifluorides and pentafluorides have been studied in an attempt to prepare the ions $M^{IV}F_4Cl_2^{2-}$, $M^{III}F_3Cl^-$, and $M^{V}F_5Cl^-$; none of these ions was formed quantitatively. Phosphorus pentafluoride was found to act as a source of fluorophosphoric acid, and several new hexafluorophosphates have been prepared.

THIS paper describes attempts to prepare the mixed chlorofluoro-anions of elements in Groups IV and V by using the parent fluoride as a solvoacid in liquid hydrogen chloride. Salts of chlorotrifluoroboric acid, $HBF_3Cl$, can be prepared when boron trifluoride acts as a solvoacid in liquid hydrogen chloride.[2] The reaction of nitrosyl chloride with antimony pentafluoride in liquid hydrogen chloride produced nitrosyl chloropentafluoroantimonate, $NOSbF_5Cl$, but this may not be an ionic compound containing the $SbF_5Cl^-$ ion.[3] The chloropentafluoroantimonate ion has been detected among the reaction products of antimony pentachloride and liquid hydrogen fluoride: it is the most stable mixed chlorofluoroantimonate ion formed, but is slowly solvolysed by the hydrogen fluoride to a hexafluoroantimonate.[4] The only monosubstituted fluoro-anion of arsenic pentafluoride known is $AsF_5(OH)^-$,[5] which would be analogous to the unknown $AsF_5Cl^-$ ion.

## EXPERIMENTAL

The apparatus and techniques used have been described previously.[6] As all the fluorides discussed in this paper are readily hydrolysed to hydrogen fluoride and consequently attack

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[1] Part VI, Peach and Waddington, *J.*, 1963, 69.
[2] Waddington and Klanberg, *J.*, 1960, 2332.
[3] Waddington and Klanberg, *Z. anorg. Chem.*. 1960, **304**, 185.
[4] Kolditz and Daunicht, *Z. anorg. Chem.*, 1959, **302**, 230.
[5] Kolditz and Rohnusch, *Z. anorg. Chem.*, 1957, **293**, 168.
[6] Peach and Waddington, *J.*, 1962, 2680.

glass, the apparatus was well flamed out before use, and quartz conductivity and reaction cells were used to minimise any attack by hydrogen fluoride in the solution.

Gaseous compounds were usually kept frozen in a trap connected to a storage bulb: liquids and solids, except antimony pentafluoride, were stored in Polythene bottles. The purity of gaseous compounds was determined by molecular-weight measurements and, as it is extremely difficult to remove silicon tetrafluoride, the main impurity, a percentage purity was calculated. Aliquot parts of gases were measured in the gas phase, and of liquids by using an Agla syringe fitted with a well-dried glass needle. Antimony pentafluoride was too viscous to be handled with a syringe, and aliquot parts were distilled from a weighing vessel fitted with a tap.[7]

Chloride was determined either gravimetrically, or by the Volhard method and fluoride volumetrically, *via* lead chloride fluoride: carbon, hydrogen, and nitrogen were determined by combustion. Phosphorus was determined colorimetrically by graphical comparison with solutions of known phosphorus content.[8] Arsenic was determined gravimetrically as uranous uranate. Most of the compounds were hydrolysed readily, but hexafluorophosphates had to be fused with sodium hydroxide in a Parr bomb at 350—400° for 0·5 hr.

Infrared measurements were made on a Perkin-Elmer model 21 double-beam continuously recording spectrophotometer with rock-salt or potassium bromide optics.

Silicon and germanium tetrafluoride, respectively, were prepared by the decomposition of barium hexafluorosilicate and hexafluorogermanate at 500° and 700°, *in vacuo*.[9] Phosphorus trifluoride was prepared from phosphorus trichloride and zinc fluoride.[10] Phosphorus pentafluoride was formed in *ca.* 90—95% purity on decomposition of benzenediazonium hexafluorophosphate, available as " Phosfluorogen A," at *ca.* 130°: [11] the reaction of arsenic trifluoride and phosphorus pentachloride was found to give a poor yield of relatively impure phosphorus pentafluoride.[12] Arsenic trifluoride was prepared by reaction of arsenious oxide, fluorite, and concentrated sulphuric acid, and was purified by fractional distillation at atmospheric pressure.[13] Arsenic and antimony pentafluorides were prepared by the direct fluorination of the elements.[14,15]

*Conductances.*—These results are shown in Table 1.

TABLE 1.

Specific and molar conductances in liquid hydrogen chloride at $-95°$: all colourless solutions.

| Compound | Concn. (mole/l.) | Spec. conductance ($\mu$mho cm.$^{-1}$) | Molar conductance (mho cm.$^2$ mole$^{-1}$) | Compound | Concn. (moie/l.) | Spec. conductance ($\mu$mho cm.$^{-1}$) | Molar conductance (mho cm.$^2$ mole$^{-1}$) |
|---|---|---|---|---|---|---|---|
| $SiF_4$ ... | 0·13 | 0·98 | 0·0077 | $SbF_3$ ... | Satd. | 1·3 | — |
| $GeF_4$ ... | Satd. | 0·56 | — | $PF_5$ ... | 0·25 | 1·9 | 0·0075 |
| $PF_3$ * ... | 0·12 | 0·22 | 0·0018 | $AsF_5$ ... | Satd. | 56·7 | — |
| $AsF_3$ ... | Satd. | 1·5 | — | $SbF_5$ ... | 1·98 | 30 | 0·017 |

* Value at $-111·6°$.

*Group IV Fluorides.*—Silicon tetrafluoride formed a colourless solution. A conductometric titration, in which it was used as an acid, against the strong solvobase tetramethylammonium chloride showed no breaks, although the conductivity decreased slightly as it was added. The product isolated was tetramethylammonium hydrogen dichloride (Found: Cl, 48·0. Calc. for $C_4H_{13}Cl_2N$: Cl, 48·5%). Silicon tetrafluoride will not act as a solvoacid, and will, therefore, not interfere when it is present as an impurity in other volatile fluorides.

Germanium tetrafluoride was sparingly soluble, forming a white precipitate and colourless solution. In a titration, as an acid, against tetramethylammonium chloride no break was

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[7] Waddington and Klanberg, *J.*, 1960, 2329.

[8] Allen, *Biochem. J.*, 1940, **34**, 858.

[9] Hoffman and Gutowsky, *Inorg. Synth.*, 1953, **4**, 145, 147.

[10] Williams, *Inorg. Synth.*, 1957, **5**, 95.

[11] Lange and Müller, *Ber.*, 1930, **63**, 1067.

[12] Brauer, " Handbuch der Präparativen Anorganischen Chemie," Ferdinand Enke Verlag, Stuttgart, 1960, Vol. I, p. 183.

[13] Hoffman, *Inorg. Synth.*, 1953, **4**, 150.

[14] Ref. 12, p. 190.

[15] Woolf and Greenwood, *J.*, 1950, 2200.

observed when the molar ratio was 0·5 : 1·0 or 1·0 : 1·0 ($GeF_4 : Me_4NCl$); the conductivity decreased smoothly as the acid was added. The product isolated at room temperature in a well-etched cell was of variable composition, as is shown by the following analyses (%) of three different experimental products:

| | Found (%) | | | | |
|---|---|---|---|---|---|
| | C | H | Cl | F | N |
| 1st product ................ | 24·3 | 7·0 | 5·4 | 32·3 | 6·6 |
| 2nd product ................ | 31·8 | 9·1 | 21·2 | 19·6 | 7·9 |
| 3rd product ................ | 23·9 | 6·7 | 0·0 | 35·0 | 7·4 |
| $(Me_4N)_2GeF_4Cl_2$ ........... | 26·1 | 6·6 | 19·3 | 20·6 | 7·6 |
| $(Me_4N)_2GeF_6$ .............. | 28·7 | 7·2 | 0·0 | 34·0 | 8·4 |

The infrared spectra of the products showed peaks characteristic of the tetramethylammonium ion and several others. The position, and intensity, of these peaks varied: however, there were Ge–F peaks at 630 and 585—580 cm.$^{-1}$ (cf. $GeF_6^{2-}$ at 600 cm.$^{-1}$ [16]) and probable Ge–Cl peaks at 475 and 460 cm.$^{-1}$ (cf. Ge–Cl in $GeCl_4$ at 461 cm.$^{-1}$ [17]).

*Group V Trifluorides.*—Phosphorus trifluoride formed a colourless solution at −111·6°; after removal of the solvent at −111·6° nothing remained, so no solvolysis to phosphorus trichloride can have occurred. In a conductometric titration against tetramethylammonium chloride the conductivity remained constant and the product isolated was tetramethylammonium hydrogen dichloride (Found: Cl, 45·7%): this was confirmed by its infrared spectrum.

Arsenic trifluoride was sparingly soluble, forming a white precipitate and colourless solution. The white solid product isolated after removal of the solvent was pumped under a high vacuum at −85° for 4 hr. to remove any hydrogen fluoride: a colourless liquid product with a vapour pressure of 15 mm. remained at room temperature. The vapour pressures of hydrogen fluoride, arsenic trifluoride, and arsenic trichloride are 700, 140, and 11 mm., respectively, at room temperature. The presence of chloride in the product was confirmed qualitatively. Total solvolysis to arsenic trichloride has occurred: $AsF_3 + 3HCl = AsCl_3 + 3HF$.

Antimony trifluoride, purified by vacuum-sublimation, formed a white precipitate and colourless solution. Solvolysis to antimony trichloride occurred and the product isolated was a mixture of antimony trichloride and hydrogen fluoride.

*Group V Pentafluorides.*—Phosphorus pentafluoride formed a colourless solution, and when treated with strong bases acted as a source of fluorophosphoric acid; the stoicheiometry of this reaction is shown by the equation: $2Me_4NCl + 3PF_5 = 2Me_4NPF_6 + PF_3Cl_2$. In titrations with tetramethylammonium chloride and pyridine, precipitation occurred and both curves showed breaks when the molar ratio was 1·5 : 1·0 ($PF_5$ : Base) (see Figs. 1 and 2). The products isolated were tetramethylammonium hexafluorophosphate (Found: C, 22·1; H, 5·8; Cl, 0; F, 52·3; N, 6·8; P, 14·3; increase in wt., 99. Calc. for $C_4H_{12}F_6NP$: C, 21·9; H, 5·5; F, 52·0; N, 6·4; P, 14·1; increase in wt., 100%) and pyridinium hexafluorophosphate (Found: C, 26·7; H, 3·1; Cl, 0; F, 51·0; N, 5·9; P, 13·8. Calc. for $C_5H_5F_6NP$: C, 26·7; H, 2·7; F, 50·6; N, 6·2; P, 13·8%). The chemical reactions of these compounds, forming insoluble salts with nitron and tetraphenylarsonium chloride,[18] and infrared spectra are consistent with their formulation as an ionic species, containing cations and hexafluorophosphate ions. A mixture of 1·0 mole of tetramethylammonium chloride and 0·96 mole of phosphorus pentafluoride reacted to form tetramethylammonium hexafluorophosphate and hydrogen dichloride (1·0 mole, 0·55 mole), and not tetramethylammonium chloropentafluorophosphate (Found: Cl, 12·7. Calc. for $1·0Me_4NPF_6 + 0·55Me_4NHCl_2$: Cl, 13·1. Calc. for $C_4H_{12}ClF_5NP$: Cl, 15·0%). Tetramethylammonium hydrogen dichloride is known to lose hydrogen chloride fairly readily at room temperature, having a vapour pressure of *ca.* 2 mm., thus accounting for the slightly low results. The infrared spectrum of the product confirmed the presence of $Me_4N^+$, $HCl_2^-$, and $PF_6^-$ ions.

It was not possible to detect any phosphorus dichlorotrifluoride (covalent form, m. p. −125°, b. p. 7·1° [19]) by its infrared spectrum in the solvent removed from this experiment after fractionation from a freezing pentane bath: as it would have constituted only 0·5% of the

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[16] Peacock and Sharp, *J.*, 1959, 2762.

[17] Lindeman and Kent Wilson, *Spectrochim. Acta*, 1957, **9**, 48.

[18] Van Wazer, " Phosphorus and its Compounds," Interscience Publ. Inc., New York, Vol. I, 1958, p. 808.

[19] Kennedy and Payne, *J.*, 1959, 1228.

excess solvent this is not surprising. The ionic form of phosphorus dichlorotrifluoride, tetrachlorophosphonium hexafluorophosphate, $PCl_4^+PF_6^-$, was formed only from phosphorus pentachloride and phosphorus pentafluoride in the solvent, as is shown by the equation, $2PCl_5 + 3PF_5 = 2PCl_4^+PF_6^- + PF_3Cl_2$ (Found: Cl, 45·9; increase in wt., 49. Calc. for $Cl_2F_3P$: Cl, 44·6; increase in wt., 52%). The infrared spectrum showed peaks characteristic of the tetrachlorophosphonium [20] and hexafluorophosphate ions.[16]

Reaction of nitrosyl chloride, a very weak base, with phosphorus pentafluoride gave a very small amount of yellow solid, which dissociated in a " dry box." Nitrosyl hexafluorophosphate cannot have been formed as this is a well-characterised solid; [21] the product may have been unstable nitrosyl chloropentafluorophosphate. It appears that the formation of hexafluorophosphates from phosphorus pentafluoride can only be initiated by strong bases.

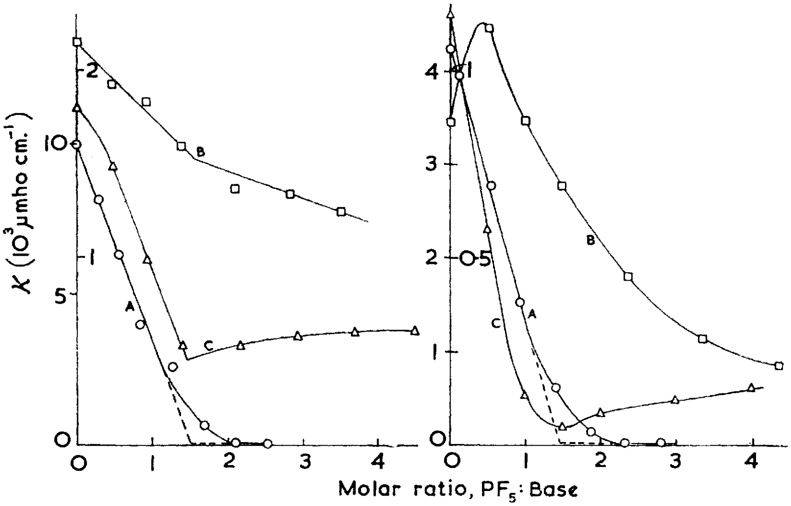

FIG. 1. FIG. 2.

Conductometric titrations of $PF_5$: (FIG. 1) (A), 0·29M-$Me_4NCl$, (B) 0·33M-$Ph_3As$, and (C) (inner figures) 0·2M-$Ph_3PO$; (FIG. 2) (A) 0·29M-pyridine, (B) 0·21M-$Ph_2POCl$, and (C) (inner figures) 0·23M-$Me_2SO$.

Triphenylarsine [22] and acetone [23] react with boron trichloride in liquid hydrogen chloride to form a tetrachloroborate in solution, but on removal of the solvent it is possible to isolate only the boron trichloride adduct. In a titration of triphenylarsine and phosphorus pentafluoride there was a sharp break when the molar ratio was 1·6 : 1·0 ($PF_5$ : $Ph_3As$) (see Fig. 1). The product isolated was unstable and slowly lost hydrogen fluoride and phosphorus pentafluoride, reverting to the original arsine: the infrared spectrum of the product immediately after preparation showed a $PF_6^-$ ion peak at 840 cm.$^{-1}$.[16] A titration of acetone and phosphorus pentafluoride was less satisfactory, as there was no sharp end-point and precipitation occurred: the relatively high equivalent conductivity at the end-point ($\Lambda = 0{\cdot}62$ mho cm.$^2$ mole$^{-1}$) suggests that a salt and not an adduct was being formed.[22] The white solid product was very unstable and readily decomposed to a tar, but an infrared spectrum, recorded immediately after isolation, showed hexafluorophosphate ion peaks.

Dimethyl sulphide,[22] acetonitrile,[23] and dimethyl sulphoxide [6] all react with boron trichloride in liquid hydrogen chloride, to form boron trichloride adducts in solution. Titrations of dimethyl sulphide and dimethyl sulphoxide against phosphorus pentafluoride both showed breaks when the molar ratio was 1·5 : 1·0 ($PF_5$ : Base), although precipitation occurred in the latter case (Fig. 2).

The high conductivity at the end-point in the dimethyl sulphide titration indicates that a

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[20] Waddington and Klanberg, *J.*, 1960, 2339.
[21] Sharp, personal communication.
[22] Peach and Waddington, *J.*, 1961, 1238.
[23] Peach and Waddington, *J.*, 1962, 600.

salt was formed in solution.[22] The white solid product, dimethylsulphonium hexafluorophosphate, was somewhat unstable (Found: F, 52·7; P, 13·8. Calc. for $C_2H_7F_6PS$: F, 54·8; P, 14·9%), but its infrared spectrum immediately after it had been isolated contained a hexafluorophosphate ion peak at 840 cm.$^{-1}$.[16] The dimethyl sulphoxide product was rather more stable and was *dimethylsulphoxidium hexafluorophosphate*, $Me_2SOH^+PF_6^-$ (Found: C, 11·2; H, 2·7; F, 51·4; P, 14·0. $C_2H_7F_6OPS$ requires C, 10·7; H, 3·1; F, 50·9; P, 13·8%). The infrared spectrum showed $PF_6^-$ peaks at 835 and 559 cm.$^{-1}$, OH peaks at 3320 and 1650 cm.$^{-1}$ and an S=O peak at 1020 cm.$^{-1}$.

A very unstable white solid product was isolated at $-95°$ after reaction of acetonitrile and phosphorus pentafluoride; it became yellow at room temperature but the infrared spectrum showed a $PF_6^-$ ion peak at 840 cm.$^{-1}$. The acetonitrile–phosphorus pentafluoride adduct is not well characterised.[24]

Triphenylphosphine oxide with boron trichloride in liquid hydrogen chloride forms a mixture of tetrachloroborate and boron trichloride adduct.[6] In a titration against phosphorus pentafluorides (see Fig. 1) it was only possible to detect salt formation and the product isolated was (*triphenylphosphine oxide*) *hexafluorophosphate* (Found: C, 52·4; H, 5·1; F, 27·4. $C_{18}H_{16}F_6OP_2$ requires C, 51·0; H, 3·8; F, 26·9%). The infrared spectrum was identical with that of the hydrochloride, $Ph_3PO,HCl$, and included two hexafluorophosphate ion peaks at 835 and 599 cm.$^{-1}$:[16] its structure is, therefore, $Ph_3POH^+PF_6^-$.

Diphenylphosphinyl chloride and phosphoryl chloride both react with boron trichloride in liquid hydrogen chloride, to form oxygen-co-ordinated adducts.[25]

Diphenylphosphinyl chloride formed an unstable salt with phosphorus pentafluoride; the titration curve (Fig. 2) suggests ionisation and salt formation. The infrared spectrum showed a P–Cl frequency at 521 cm.$^{-1}$, $PF_6^-$ frequencies at 840 and 555 cm.$^{-1}$, and O–H peaks at 3300 and 1680 cm.$^{-1}$. Titration of phosphoryl chloride and phosphorus pentafluoride yielded a smooth curve, with steadily increasing conductivity. A white solid was isolated at $-85°$ which melted to a colourless liquid with a vapour pressure of *ca.* 35 mm. at room temperature. Analysis of this vapour by its infrared spectrum showed it to contain phosphoryl fluoride and chloride and a small amount of $POClF_2$.

Trimeric phosphonitrilic chloride, although a relatively strong base in liquid hydrogen chloride, does not react with boron trichloride (to form a stable tetrachloroborate), and the base is recovered unchanged.[26] In a reaction with phosphorus pentafluoride a white solid was isolated at $-85°$: this evolved 0·6 mol. of gas on warming to room temperature, leaving the original trimeric phosphonitrilic chloride. No fluorination of this compound had occurred.

Arsenic pentafluoride was relatively insoluble, forming a white precipitate and a colourless moderately conducting solution. A white solid was isolated at room temperature (cf. $AsF_5$, b. p. $-53·2°$): this was tetrachloroarsonium hexafluoroarsenate, a known solid,[27] contaminated with hydrogen fluoride (Found: As,* 21·5; Cl, 32·8; F, 32·0. Calc. for $AsCl_2F_3$: As,* 18·4; Cl, 34·9; F, 28·1%), although some of the volatile form, $AsF_3Cl_2$, was also formed (Loss of wt. on $AsF_5$ taken: 18·6, 22·9%). The infrared spectrum had peaks at 781sh, 697s, 667sh, 518w, 498w, and 403w cm.$^{-1}$: the hexafluoroarsenate ion has peaks at 700 and 400 cm.$^{-1}$.[16] The infrared frequencies of the tetrachloroarsonium ion, $AsCl_4^+$, ought to be similar to those of the isoelectronic germanium tetrachloride. The frequencies $\nu_3$ and $\nu_1 + \nu_4$ of silicon tetrachloride and germanium tetrachloride are shown in Table 2 together with the observed frequencies of the tetrachlorophosphonium ion, isoelectronic with silicon tetrachloride, and the tetrachloroarsonium ion. The presence of tetrachloroarsonium and hexafluoroarsonate ions in the solution would explain its relatively high conductivity.

TABLE 2.

Infrared frequencies of $MCl_4$ and $MCl_4^+$ (cm.$^{-1}$)

| | | | |
|---|---|---|---|
| $SiCl_4$ [20] | 621($\nu_3$), 647($\nu_1 + \nu_4$) | $GeCl_4$ [17] | 461($\nu_3$), 568($\nu_1 + \nu_4$) |
| $PCl_4^+$ (observed [20]) | 584, 650 | $AsCl_4^+$ (observed) | 498, 518 |

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* Readily hydrolysed arsenic, from the tetrachloroarsonium ion.

[24] Woolf, *J. Inorg. Nuclear Chem.*, 1956, **3**, 285; Muetterties, Bither, Farlow, and Coffman, *ibid.*, 1960, **16**, 52.

[25] Peach and Waddington, *J.*, 1962, 3450.

[26] Peach and Waddington, unpublished work.

[27] Dess, Parry, and Vidale, *J. Amer. Chem. Soc.*, 1956, **78**, 5730.

Antimony pentafluoride dissolved to a colourless solution, from which a mixture of liquid and solid products was isolated. This became totally liquid on storage in a closed Polythene vessel in a " dry box " for 3 days and was considerably less viscous than antimony pentafluoride. It was analysed (Found: Cl, 10·7; F, 29·1; F : Cl, 5 : 1. Calc. for $HSbF_5Cl$: Cl, 14·0; F, 37·5%), but the analysis was unsatisfactory as the liquid readily fumed in a " dry box." In reactions with trimethylamine inhomogeneous products of varying composition were isolated, illustrated by the following figures (%):

| | Found (%) | | | | |
|---|---|---|---|---|---|
| | C | H | Cl | F | N |
| 1st product | 19·3 | 5·7 | 10·9<br>17·3 | 21·4<br>27·1 | 4·0 |
| 2nd product | 12·8 | 4·4 | 12·1 | 24·0 | 4·9 |
| 3rd product | — | — | 25·4 | — | — |
| $Me_3NHSbF_5Cl$ | 11·5 | 3·2 | 11·4 | 30·4 | 4·5 |

The third experimental product had been equilibrated at −95° for 22 hr., and these results show that slow exchange of chlorine occurred. The infrared spectra showed Sb–F frequencies at *ca.* 670 cm.$^{-1}$, the Sb–F frequencies occurring in $SbF_6^-$ at 660 cm.$^{-1}$.[16]

## DISCUSSION

The reactions of non-metallic fluorides can be divided into four categories: (1) No reaction: $SiF_4$, $PF_3$. (2) Total solvolysis: $AsF_3$, $SbF_3$, ($GeF_4$), ($SbF_5$). (3) " Disproportionation: " $PF_5$, $AsF_5$. (4) Chlorofluoro-anion formation: $BF_3$, ($GeF_4$), ($SbF_5$).

The aim of the present experiments was to prepare ions of the type $MF_xCl_y^{n-}$: this type of ion is only formed when boron trifluoride acts as a solvoacid in liquid hydrogen chloride. The similar ion, $BF_3Br^-$, could not be prepared by using boron trifluoride as a solvoacid in liquid hydrogen bromide: boron trifluoride has no acidic properties in liquid hydrogen bromide.[28] Germanium tetrafluoride and antimony pentafluoride form ions of the type $GeF_xCl_{(6-x)}^{2-}$ and $SbF_xCl_{(6-x)}$.

Silicon tetrafluoride and phosphorus trifluoride are both non-acidic in hydrogen fluoride;[29] hexafluorosilicate ions even react with liquid hydrogen fluoride to liberate silicon tetrafluoride. There is no compound known containing the tetrafluorophosphate ion, $PF_4^-$.[30] It is not, therefore, surprising that these two compounds have no acidic properties in liquid hydrogen chloride.

All the other Group IV and V fluorides studied showed varying amounts of chlorine–fluorine exchange. Total solvolysis occurred with arsenic and antimony trifluoride, both of which are powerful fluorinating agents.

Phosphorus, arsenic, and antimony pentafluoride are all strong acids in liquid hydrogen fluoride, the acidity increasing in that order.[29] Both phosphorus and arsenic pentafluoride disproportionate in liquid hydrogen chloride, as is shown by the equations:

$$2MCl + 3PF_5 = 2MPF_6 + PF_3Cl_2$$

$$4HCl + 2AsF_5 = AsCl_4^+AsF_6^- + 4HF$$

The mechanism of these reactions is uncertain. They differ in that, for phosphorus pentafluoride, disproportionation occurs only in the presence of strong bases and no free hydrofluoric acid is produced. Neither reaction proceeds through the formation of a stable ion $MF_5Cl^-$, although this may be an intermediate unstable product, as in the reaction scheme:

$$PF_5 + HCl_2^- = PF_5Cl^- + HCl$$

$$PF_5Cl^- + PF_5 = PF_6^- + PF_4Cl$$

$$PF_4Cl + HCl_2^- = PF_4Cl_2^- + HCl$$

$$PF_4Cl_2^- + PF_5 = PF_6^- + PF_3Cl_2$$

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[28] Waddington and White, *Proc. Chem. Soc.*, 1960, 85.
[29] Audrieth and Kleinberg, " Non-aqueous Solvents," Wiley, New York, 1953, p. 200.
[30] Payne, *Quart. Rev.*, 1961, **15**, 173,

A similar reaction scheme involving free fluoride ions, which would immediately react with the solvent to form hydrofluoric acid, will explain the reaction of arsenic pentafluoride:

$$\begin{aligned} \mathrm{AsF_5 + HCl_2^-} &= \mathrm{AsF_5Cl^- + HCl} \\ \mathrm{AsF_5Cl^- + 2HCl} &= \mathrm{AsF_4Cl + HF + HCl_2^-} \\ \mathrm{AsF_4Cl + HCl_2^-} &= \mathrm{AsF_4Cl_2^- + HCl} \\ \mathrm{AsF_4Cl_2^- + 2HCl} &= \mathrm{AsF_3Cl_2 + HF + HCl_2^-} \\ & \downarrow \\ & \mathrm{AsCl_4^+\,AsF_6^-} \end{aligned}$$

The compounds $PF_4Cl$, $AsF_4Cl$, and $AsF_3Cl_2$ are unknown, but $PF_3Cl_2$, $PCl_4^+PF_6^-$, and $AsCl_4^+AsF_6^-$ are relatively stable.[30] The difference in the reactions of phosphorus and arsenic pentafluoride may be that the unknown $AsF_3Cl_2$ immediately rearranges to $AsCl_4^+AsF_6^-$, whereas $PF_3Cl_2$ does not form $PCl_4^+PF_6^-$ so readily.

This trend would be expected to continue in antimony pentafluoride, with the formation of tetrachlorostibonium hexafluoroantimonate, $SbCl_4^+SbF_6^-$, which can be prepared by the chlorination of antimony trifluoride.[31] There is no indication of this. The increased stability of the known [3] ion $SbF_5Cl^-$ may prevent this reaction. Nitrosyl chloride, in liquid hydrogen chloride, reacted with antimony pentafluoride to form nitrosyl pentafluorochloroantimonate;[3] the reaction without the solvent produces nitrosyl hexafluoro- and hexachloro-antimonate.[32]

The disproportionation of phosphorus pentafluoride to fluorophosphoric acid has been used to afford stable hexafluorophosphates of protonated bases which react with boron trichloride to form adducts. All the strong bases studied were shown to form hexafluorophosphate in solution, and not phosphorus pentafluoride adducts. The protonated bases were not very stable in the solid state; the only stable solids isolated were $Ph_3POH^+PF_6^-$ and $Me_2SOH^+PF_6^-$. Evidence was found, in titrations, for the existence of the ions $MeCNH^+$, $Ph_3AsH^+$, $Me_2SH^+$, and $Ph_2POClH^+$ in solution. The fluorination of phosphoryl chloride, a weak base, may be due to the formation of the adduct, $POCl_3,PF_5$, and its subsequent decomposition: no fluorination of the other compounds containing phosphorus–chlorine bonds (trimeric phosphonitrilic chloride and diphenylphosphinyl chloride) occurred and it must be concluded that these two compounds are sufficiently strong bases to make the phosphorus pentafluoride disproportionate, forming the salts $(PNCl_2)_3H^+PF_6^-$ and $Ph_2POClH^+PF_6^-$ in solution, which decomposed without fluorination of the P–Cl bonds.

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[31] Kolditz and von der Leith, *Z. anorg. Chem.*, 1961, **310**, 236.

[32] Ruff, Zender, Knock, and Graf, *Ber.*, 1909, **42**, 4021.