HALIDES OF PHOSPHORUS, ARSENIC, ANTIMONY, AND BISMUTH

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I. Introduction

The growth of inorganic chemistry in recent years has led to a substantial increase in our knowledge of the halogen compounds of the elements of the fifth main group of the periodic table. These compounds are usually sensitive to hydrolysis and have to be handled under conditions such that water is excluded. It is understandable, therefore, that special techniques associated with the study of nonaqueous solvents have made a major contribution to progress in this field.

This article is concerned mainly with the simple halides of phosphorus, arsenic, antimony, and bismuth; compounds that also contain other elements or groups will be considered only to a limited extent. Nitrogen compounds show special features associated with the absence in nitrogen of *d* electrons for bonding, and are not easily discussed together with compounds of the heavier elements; they will therefore be omitted. Bismuth has metallic properties that differentiate its compounds from those of elements in the middle of the group; the break in properties between the compounds of antimony and bismuth is not, however, so marked as that between compounds of nitrogen and phosphorus.

The compounds that will be described fall into two large groups, according to whether the central atom has an oxidation state of +5 or +3. Both simple and complex halides are known in each of these groups. There are also halides of minor importance in which the elements have oxidation states below +3.

II. Halides with Oxidation State +5

A. SIMPLE HALIDES

1. Preparation and Chemical Properties

Halides of the type AX_5, where A is P, As, Sb, or Bi, and X is F, Cl, Br, or I, may generally be obtained by interaction of the elements. It is also possible to react AX_3-type compounds with the corresponding halogen, and this is particularly useful when X = F. The halides SbF_5 and BiF_5 are made in this way. The compounds $SbBr_5$ (cf. Section II,A,2), SbI_5, and arsenic(V) and bismuth(V) halides other than the fluorides are unknown.

Exchange reactions may be used in preparing PF_5 (*178*), AsF_5 (*115*), and SbF_5 (*95, 165*):

$$[PCl_4][PCl_6] + 2AsF_3 \rightarrow 2PF_5 + 2AsCl_3 \tag{1}$$

$$[AsCl_4][AsF_6] + 4AgF \rightarrow 2AsF_5 + 4AgCl \tag{2}$$

$$[SbCl_5] + 5HF \rightarrow SbF_5 + 5HCl \tag{3}$$

Arsenic pentafluoride is also produced in the reaction (*166*).

$$NO[AsF_6] + SbF_5 \rightarrow NO[SbF_6] + AsF_5 \tag{4}$$

and by the interaction of SbF_5 and AsF_3 in the presence of bromine (*163*).

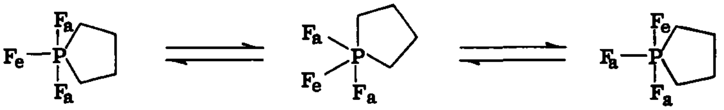
All halides of the type AX_5 are very hygroscopic and are hydrolyzed by water. Bismuth pentafluoride, a white solid, becomes yellow with the least trace of water and readily fluorinates other substances, with reversion to BiF_3.

2. Structures

Halides with the general formula AX_5 have been found by spectroscopic, X-ray, and electron diffraction methods to have a trigonal bipyramidal configuration, corresponding to sp^3d hybridization. On general grounds a square pyramid is almost equally probable (*121*), but there is so far no evidence to justify the assignment of this structure to the AX_5 halides. Bonding in the bipyramidal form may be thought of as arising from two sets of hybrids (*138*): sp^2 bonds in the planar, and pd bonds in the apical, positions. The difference in energy between these two sets of bonds should become smaller as the halogen X becomes more negative. The difference would thus be smallest in PF_5, and it is interesting to note that the F^{19}

nuclear magnetic resonance spectrum of PF_5 does not show the presence of fluorine in different environments (*62, 124, 139*). A rapid exchange between the fluorine atoms in PF_5 is therefore assumed (*8*); a square pyramid may be an intermediate configuration. The infrared spectrum of PF_5 is consistent with the trigonal bipyramidal configuration (*61, 146*). Clearly, therefore, the exchange process occurs at a rate smaller than that of changes between vibrational levels. Electron diffraction studies lead to the same structure (*18, 19*).

In connection with the F^{19} nuclear magnetic resonance spectrum, it may be noted that replacement of two F atoms by simple alkyl or aryl groups produces different chemical shifts for the remaining F ligands in the equatorial and apical positions. More rapid exchange of the F atoms takes place in compounds of the type RPF_4. In $(CH_2)_4PF_3$, with a cyclic organic group, an intramolecular exchange of the type shown below is believed to occur:



(5)

In this compound, the C—P—C angle is probably intermediate between 90°, the value for the equatorial-axial position angle, and 120°, the ideal value for the equatorial-equatorial position angle, and this makes the exchange possible. In accordance with this hypothesis, the cyclic compound $(CH_2)_5PF_3$ shows no exchange: in this case the C—P—C angle must be almost 120°.

From electron diffraction measurements, the PCl_5 molecule in the vapor state is present in the form of a triangular bipyramid (*19, 160, 161*). The P—Cl bond distance in the basal plane is 2.04 Å, which is shorter than for the P—Cl bonds involving the apical chlorine atoms (2.19 Å). Infrared studies of PCl_5 solutions in CCl_4 show that the axial bonds are more polar than the equatorial (*170*). Molten PCl_5, which may be obtained under pressure, resembles the vapor in containing PCl_5 molecules. This is established by Raman spectroscopy (*134*) and is in agreement with conductivity measurements (*182*). The pentachloride in the molecular form does not give rise to an appreciable conductivity.

The structure is different in the solid state, and X-ray investigations show that the lattice of the solid P(V) chloride is built up of $[PCl_4]^+$ and $[PCl_6]^-$ ions (*27*). This is confirmed by the Raman spectrum (*52*). Many AX_5-type compounds are found to be capable of existing in two different forms, one of which is molecular and the other saltlike. Thus, solid PBr_5 contains the ions $[PBr_4]^+$ and $[Br]^-$ (*152*). In nonpolar solvents such as

CCl_4 and CS_2 it dissolves as PBr_5 molecules, which dissociate in part to PBr_3 and Br_2 (*81, 150*):

$$PBr_5 \rightleftharpoons PBr_3 + Br_2 \qquad (6)$$

The ready dissociation of PBr_5 indicates that PI_5 would be even less stable; in fact it has not so far been prepared.

Arsenic pentafluoride has a structure analogous to that of PF_5. Nuclear magnetic resonance studies again show that the F atoms are all equivalent (*139*). Presumably the lattice of the solid is also built up from molecules. Certain solvents appear, however, to be capable of changing the structure of the halide (Section II,A,3).

Nuclear magnetic resonance investigations with liquid SbF_5 show that there is association through fluorine *cis*-bridges (*73*). This property illustrates the fact that antimony has more orbitals available than are used in the isolated molecule. This electron deficiency is made good by accepting electron pairs from fluorine atoms in a neighboring molecule. Antimony pentafluoride is probably transformed into a polar form under the influence of solvents (Section II,A,3).

Antimony pentachloride has been studied in the solid, liquid, and vapor states: a triangular bipyramid is present in each case. X-ray studies at $-30°$ gave the axial and equatorial Sb—Cl distances as 2.34 Å and 2.29 Å, respectively (*142*). Corresponding values obtained for $SbCl_5$ vapor at 100°C by electron diffraction are 2.43 Å and 2.31 Å (*161*). The effect of temperature in increasing the bond length is apparent. Raman spectroscopy shows that the Sb atom in $SbCl_5$ is not located exactly in the equatorial plane of the bipyramid but is somewhat displaced (*134, 135*). This indicates that to some extent there is a transition to the $[SbCl_4]^+$ ion and helps to explain the electrolytic conductivity that is observed in acetonitrile solution.

Antimony pentabromide has been isolated only as the ether adduct, $SbBr_5 \cdot (C_2H_5)_2O$ (*154*). The bromine content corresponding to this formula is not usually found, as the compound is appreciably dissociated at room temperature to give free bromine. Antimony pentaiodide is unknown, even in the form of addition compounds.

Bismuth pentafluoride under normal conditions is a white solid, which is probably polymerized by fluorine bridges. X-ray powder photography shows it to have the same structure as the body-centered tetragonal α-UF_5 (*49*). Other halides of bismuth(V) are unknown.

3. Action of Solvents and Formation of Addition Compounds and Complexes

Phosphorus pentachloride is soluble in both polar and nonpolar solvents. In the first case the presence of ions is shown by conductivity measurements, whereas solutions in nonpolar solvents exhibit no appreciable conductivity. Transport measurements on solutions of PCl_5 in CH_3CN, a polar solvent, have shown the presence of $[PCl_4]^+$ and $[PCl_6]^-$ ions (*144*). These are also present in the solid pentachloride and one may assume that the concentration- and temperature-dependent equilibrium

$$2PCl_5 \rightleftharpoons [PCl_4]^+ + [PCl_6]^- \quad (7)$$

is set up in these solutions. It is uncertain whether undissociated ion pairs, $[PCl_4^+PCl_6^-]$, are stable under these conditions or whether they form aggregates of PCl_5 molecules with chlorine bridges as soon as they are produced.

The ions present in the solid are not necessarily present in polar solvents. Thus conductometric titrations and transport measurements with PBr_5 in CH_3CN show $[PBr_6]^-$ ions to be present (*64*), although the solid pentabromide must be formulated as $[PBr_4]Br$ (Section II,A,2). In general it seems that the solvent may participate in the dissociation equilibrium of the six-coordinated anions, depending on the values of the corresponding dissociation constants, in the following way.

$$[AX_6]^- \rightleftharpoons AX_5 + X^- \quad (8)$$

$$AX_5 + L \rightleftharpoons AX_5L \quad (9)$$

The addition compound $AX_5 \cdot L$ is able to dissociate further:

$$AX_5 \cdot L \rightleftharpoons [AX_4]^+ + X^- + L \quad (10)$$

Thus, when equilibrium is displaced to the right, $[AX_6]^-$ ions do not play a major part and vice versa. Whether $[AX_6]^-$ or simple X^- ion is present will then depend on the solvent.

It should also be noted that the effect of a solvent on the formation of ions cannot be accounted for simply in terms of the dielectric constant or dipole moment. For example, solutions of PCl_5 of the same concentration in acetonitrile and nitrobenzene differ in conductivity by roughly an order of magnitude (*144*), in spite of the fact that the two liquids have comparable dielectric constants (cf. Table I). Solvation effects, which depend on the nature, size, and configuration of the solvent molecule, play a large part.

The pentafluorides of arsenic and antimony are probably molecular in all the states of aggregation. There are, however, indications that polar forms are produced in CH_3CN, since the compounds $AsF_5 \cdot CH_3CN$ and $SbF_5 \cdot CH_3CN$ crystallize from this solvent and the solutions exhibit conductivities comparable with values for phosphorus(V) chloride (Table II).

The situation is similar for $SbCl_5$. The pure halide has a molecular structure (Section II,A,2). The compound $SbCl_5 \cdot CH_3CN$, which has long

TABLE I

SPECIFIC CONDUCTIVITIES OF PHOSPHORUS(V) CHLORIDE IN CH_3CN AND $C_6H_5NO_2$ AT 25°C

Solvent	Concentration (moles/liter)	Conductivity (Ω^{-1} cm^{-1})	Dielectric constant	Dipole moment	Reference
CH_3CN	0.0339	$9.69 \cdot 10^{-4}$			
CH_3CN	0.0495	$1.41 \cdot 10^{-3}$	37.5(20°C)	3.84	(*144*) (*90*)
$C_6H_5NO_2$	0.0470	$1.57 \cdot 10^{-4}$	34.7	4.27	(*144*)
$C_6H_5NO_2$	0.0517	$1.77 \cdot 10^{-4}$			(*144*)

been known (*67*), is formed with CH_3CN. Acetonitrile solutions are conducting, showing that ions are present (Table II). Because of the relatively high melting point of $SbCl_5 \cdot CH_3CN$ (175°C), it has been assumed to have the polar structure $[SbCl_4(CH_3CN)_2][SbCl_6]$ in the solid state. Infrared measurements are not inconsistent with this (*6*); X-ray studies, which would be decisive, have not yet been made.

TABLE II

SPECIFIC CONDUCTIVITIES OF AsF_5 AND SbF_5 IN CH_3CN AT 25°C[a]

Compound	Concentration (moles/liter)	Conductivity (Ω^{-1} cm^{-1})	Reference
$AsF_5 \cdot CH_3CN$	0.011	$2.0 \cdot 10^{-3}$	(*107*)
$SbF_5 \cdot CH_3CN$	0.0112	$1.63 \cdot 10^{-4}$	(*107*)
$SbCl_5 \cdot CH_3CN$	0.0114	$1.49 \cdot 10^{-3}$	(*104*)

[a] The conductivity of the pure solvent was $1.2 \cdot 10^{-7}$ Ω^{-1} cm^{-1}.

A whole series of addition compounds of the AX_5 halides is known. Phosphorus(V) chloride forms solvates of the composition $P_2Cl_{10} \cdot 5AsCl_3$ and $P_2Cl_{10} \cdot 4SbCl_3$ (*90*). In preparative work the solubility of SbF_5 in SO_2 is important. From such a solution the compound $SbF_5 \cdot SO_2$ (m.p. 57°C) may be crystallized (*3*). The first product of the interaction of SbF_5 and SO_3 is SbF_5SO_3. This has been shown by nuclear magnetic resonance and infrared and Raman spectroscopy to be $SbF_4^+SO_3F^-$, SbF_4^+ groups being linked in a polymeric structure by means of the SO_3F^- groups (*54*).

Antimony tri- and pentafluoride form very stable compounds, e.g., $SbF_5 \cdot 2SbF_3$, which distills unchanged at 390°C (*165*). No exact study of their structures has so far been made. It is possible that they are saltlike in the solid state (e.g., $[SbF_2][SbF_6] \cdot SbF_3$) and go over to a molecular form on vaporization. Antimony pentafluoride dissolves in AsF_3 and the conductivity is thereby greatly increased (*191*), so that the compound $AsF_3{\cdot}SbF_5$ could be formulated as $[AsF_2][SbF_6]$. Analogous compounds such as $[ClF_2][AsF_6]$, $[ClF_2][SbF_6]$ (*169*), $[BrF_2][SbF_6]$, and $[BrF_2][BiF_6]$ (*48, 60, 190*) are formed with ClF_3 and BrF_3. Both O_2F salts of the type $O_2^+[AF_6]^-$ are formed by PF_5, AsF_5, and SbF_5 (*192*). The structures of the compounds SbF_5Br, SbF_5I, $(SbF_5)_2I$, and SbF_5S, which are formed from SbF_5 and the corresponding elements (*164*), are at present unknown.

4. The $[AsCl_4]^+$ *Ion and the Instability of* $AsCl_5$

Consideration of the pentachlorides of phosphorus, arsenic, and antimony shows that of arsenic to be missing. Liebig and Wöhler tried unsuccessfully to prepare $AsCl_5$ (*120*) and various workers since then have also obtained negative results (*9, 78, 126, 159, 172*). Supposedly successful preparative methods (*4*) have been disproved (*173*). This is in keeping with the fact that the system $AsCl_3$–Cl_2 gives a simple eutectic: no compound formation can be detected (*12*). The instability of $AsCl_5$ is explained on the basis that arsenic is not sufficiently positive to behave like antimony in its pentachloride, where sufficiently strong bonds are obtained by double bond formation. Single bonds such as are approximately present in phosphorus(V) chloride are already too weak in arsenic(V) chloride since, under otherwise similar conditions, the bond strength decreases from phosphorus to antimony (*170*).

A number of compounds are known which contain the cation $[AsCl_4]^+$, with arsenic in the +5 state. These are $[AsCl_4][PCl_6]$ (*31, 58*), $[AsCl_4][SbCl_6]$ (*59*), $[AsCl_4][AsF_6]$ (*40, 87*), and $[AsCl_4][SbF_6]$ (*115*). It is notable that $[AsCl_4][AsCl_6]$, which is an isomer of $AsCl_5$, is missing from this sequence. One may assume that when arsenic is unable to form a stable compound with five chlorine atoms $[AsCl_5]$, the $[AsCl_6]^-$ ion will also be unstable. This does not, however, exclude the possible existence of the saltlike compound $[AsCl_4]Cl$.

When $[AsCl_4]^+$ compounds are brought together with Cl^- ions in $AsCl_3$ solution, immediate oxidation of the chloride to chlorine takes place (*114*):

$$[AsCl_4]^+ + Cl^- \rightarrow AsCl_3 + Cl_2 \qquad (11)$$

This indicates the instability of $[AsCl_4]Cl$. The $[AsCl_4]^+$ ion is stable only in association with large anions, as is apparent from the examples given above. It is, however, possible to isolate the compounds $[AsCl_4][AlCl_4]$ and $[AsCl_4][GaCl_4]$ as solids, and it is probable that $[AsCl_4][TaCl_6]$, $[AsCl_4][FeCl_4]$, and $[AsCl_4][AuCl_4]$ exist in $AsCl_3$ solution (*114*). Tantalum pentachloride and $FeCl_3$ have a low solubility in $AsCl_3$, so that the decomposition of the corresponding $[AsCl_4]^+$ compounds when the solution is concentrated is understandable. Gold(III) chloride, which is freely soluble in $AsCl_3$, forms square-planar $[AuCl_4]^-$ complexes; this ion clearly polarizes the $[AsCl_4]^+$ ion, and attempts to separate solid $AsCl_4^+AuCl_4^-$ lead to decomposition.

B. MIXED HALIDES

1. PX_2F_3

a. PCl_2F_3-$[PCl_4][PF_6]$. The compound PCl_2F_3 (*151*) is formed in the reaction

$$PF_3 + Cl_2 \rightarrow PCl_2F_3 \qquad (12)$$

It is a gas at room temperature under normal pressures and condenses at +7.1°C (*82*). The melting point is −124°C (*74*). The isomeric saltlike compound has the structure $[PCl_4][PF_6]$, and may be obtained by careful chlorine-fluorine exchange between $[PCl_4][PCl_6]$ and AsF_3 in $AsCl_3$ solution (*88*):

$$[PCl_4][PCl_6] + 2AsF_3 \rightarrow [PCl_4][PF_6] + 2AsCl_3 \qquad (13)$$

Unlike the gaseous molecular compound PCl_2F_3, this isomer is a white solid which sublimes with decomposition at +135°C. The conductivity of PCl_2F_3 in acetonitrile is small (*82*), whereas that of $[PCl_4][PF_6]$ is relatively high (*88*). Transformation of $[PCl_4][PF_6]$ into PCl_2F_3 on sublimation is only partial. The change of PCl_2F_3 into $[PCl_4][PF_6]$ occurs, in all probability, only in the presence of traces of moisture and then only to a small extent (*82*). Presumably reaction takes place according to the following equations

$$2PCl_2F_3 \rightarrow PCl_3F_2 + PClF_4 \rightarrow PCl_4F + PF_5 \rightarrow [PCl_4][PF_6] \qquad (14)$$

The reverse reactions occur when $[PCl_4][PF_6]$ is sublimed, although the greater part of starting material is reformed by reaction of PCl_4F with PF_5. This is a case of indirect sublimation.

The compound PCl_3F_2 has been made recently by the interaction of $PClF_2$ and chlorine. It has a melting point of −63.0°C (*74*). Both this reaction and the analogous reaction leading to PBr_3F_2 were, however, mentioned earlier (*14*, *15*).

b. PBr_2F_3-$[PBr_4][PF_6]$. Similar relationships exist for the compounds PBr_2F_3 and $[PBr_4][PF_6]$. The molecular compound PBr_2F_3 is formed from PF_3 and bromine (*131*). It is obtained as a liquid which boils with decomposition at +15°C. The isomer $[PBr_4][PF_6]$ results from Br-F exchange in the reaction of phosphorus(V) bromide with AsF_3 (*97*). It sublimes with decomposition at +135°C (Section II,B,2,b).

It is remarkable that the $[PBr_4]^+$ ion in the presence of AsF_3 reacts only slowly with exchange of Br for F. Indeed, at 0°C, AsF_3 solutions of

$[PBr_4][PF_6]$ may be kept for some time without perceptible reaction, and conductivity studies have been made in this solvent (*97*). On the other hand, $[PCl_4][PF_6]$ reacts vigorously with pure AsF_3 to give PF_5 (*88*). Conductivity measurements on $[PCl_4][PF_6]$ were therefore made in CH_3CN. In both cases the results support the idea of an ionic structure. Since $[PF_6]^-$ ions are very resistant to hydrolysis and $[PCl_4]^+$ or $[PBr_4]^+$ is readily destroyed by water, it was possible to establish the structures of the compounds by noting the action of moisture.

2. PX_4F

a. PCl_4F-$[PCl_4]F$. When sublimed (135°C), the compound $[PCl_4][PF_6]$ reacts according to the equation

$$[PCl_4][PF_6] \rightarrow PCl_4F + PF_5 \tag{15}$$

The decomposition temperature is lowered considerably by the presence of $AsCl_3$. Under these conditions, some gas evolution is observed at 70°C and is vigorous at 80°C. The resulting mixture of gases may be separated very readily by a simple reflux condenser since PCl_4F condenses at +67°C, whereas the condensation temperature of PF_5 is −75°C and therefore passes the condenser. Fractional distillation of the residual mixture of PCl_4F and $AsCl_3$ enables the former to be collected as a liquid (melting point −59.0°C) (*74*) with a specific conductivity of 2×10^{-7} ohm^{-1} cm^{-1} at 20°C. This value shows the liquid to have a molecular structure. It is not stable over long periods, however, and is transformed quantitatively into a white solid of the same composition. This sublimes at +175°C and melts under pressure at +177°C. These properties indicate an ionic structure, which is in agreement with the observation that its solution in acetonitrile shows electrolytic conductivity (e.g., 1.03×10^{-3} ohm^{-1} cm^{-1} at a concentration of 0.0621 mole/liter) (*89*). The half-life time for the transformation of the liquid to solid at room temperature is about 35 hours, with an activation energy of 10.6 kcal/mole and the very low value of 4.37 for the frequency factor (*92*).

The molecular form of PCl_4F is always obtained initially when the compound separates from the vapor phase, but the saltlike compound crystallizes directly from polar solvents, such as $AsCl_3$. When the solid is melted, however, conductivity measurements show that the molecular form is present. A transformation must therefore occur on melting (*89*).

The saltlike compound may be formulated either as $[PCl_4]F$ or as $[PCl_4][PCl_4F_2]$, with a six-coordinated anion. Which of these structures exists in the solid state is at present unknown. The question of the size of the ion in solution has been discussed (Section II,A,3). From recent measurements in acetonitrile it seems that $[PCl_4F_2]^-$ ions are present (*101*). The original cryoscopic measurements in acetic acid, which pointed to F^- (*89*), should be treated with reserve since reaction takes place with the solvent and the degree of dissociation is also too small.

b. PBr_4F-$[PBr_4]F$. Analogous considerations apply to the compounds PBr_4F and $[PBr_4]F$. In this case, however, another preparative method has to be used as the molecular compound is no longer stable under the conditions for the sublimation of $[PBr_4][PF_6]$. Lowering of the decomposition temperature by solvents is also not effective. The reaction

$$PBr_2F + Br_2 \rightarrow PBr_4F \tag{16}$$

at −75°C is suitable (*94*, see also *15*). The molecular compound PBr_4F changes slowly below −30°C into $[PBr_4]F$ or $[PBr_4][PBr_4F_2]$, which melts with decomposition at +87°C and gives a conducting solution in acetonitrile. The solvate $[PBr_4]F \cdot 2CCl_4$ is also known. This formula shows only the composition; the structure of the solid is still unknown. A reaction analogous to that shown in Eq. (16) leads to PCl_4F (*14*, *74*):

$$PCl_2F + Cl_2 \rightarrow PCl_4F \tag{17}$$

3. $[AsCl_4][AsF_6]$

Arsenic trifluoride and chlorine react as follows (*40*, *87*):

$$2AsF_3 + 2Cl_2 \rightarrow [AsCl_4][AsF_6] \tag{18}$$

Traces of water have a catalytic action (*40*). Formation of $[AsCl_4][AsF_6]$ is also very greatly accelerated if $AsCl_3$ is present as a solvent or a suspension medium (*91*). This is associated with the chlorinating action of an $AsCl_3/Cl_2$ mixture. The ionic character of $[AsCl_4][AsF_6]$ in AsF_3 solution has been demonstrated by conductivity measurements (*87*). Water causes hydrolysis of the $[AsCl_4]^+$ ion while $[AsF_6]^-$ remains completely unattacked. Sublimation of $[AsCl_4][AsF_6]$ in vacuum may give the molecular form $AsCl_2F_3$, but extensive decomposition occurs.

The compound $[AsCl_4][AsF_6]$ can be used for the preparation of other hexafluoroarsenates, particularly those involving nonmetallic cations. The following preparations may be mentioned (*113*):

$$[AsCl_4][AsF_6] + SCl_4 \rightarrow [SCl_3][AsF_6] + AsCl_3 + Cl_2 \tag{19}$$

$$[AsCl_4][AsF_6] + SeCl_4 \rightarrow [SeCl_3][AsF_6] + AsCl_3 + Cl_2 \tag{20}$$

$$[AsCl_4][AsF_6] + TeCl_4 \rightarrow [TeCl_3][AsF_6] + AsCl_3 + Cl_2 \tag{21}$$

In these reactions, the $[AsCl_4]^+$ cation abstracts Cl^- ions from the other reactant. These may be present initially or be produced during the reaction. The compound $[SCl_3][AsF_6]$ produced in reaction (19) was described previously but wrongly formulated as $2AsF_3 \cdot SCl_4$ (*162*).

4. $SbCl_2F_3$

The compound $SbCl_2F_3$ is of technical interest because of its catalytic action in the Swarts reaction, which involves exchange of chlorine for fluorine in organic chlorides. This exchange reaction was first studied with $SbCl_3F_2$ (*175*). There are various publications and patents on the use of $SbCl_2F_3$ (*68–70, 71, 123*). The compound is prepared very simply by the interaction of antimony trifluoride with chlorine under pressure (*102*) or with chlorine trifluoride (*36*). It is produced initially as an oil which crystallizes with difficulty. The compound yields a conducting solution in arsenic trifluoride but a slow reaction occurs. Oxidation of the arsenic and partial reduction of the antimony occur to form $[AsCl_4][SbF_6]$ (*115*). Ions are also formed when $SbCl_2F_3$ dissolves in liquid SO_2 (*115*). The assumption that the crystalline compound has the saltlike structure $[SbCl_4][SbF_6]$ is not supported by spectroscopic measurements (*36*). The solid compound when free from solvate consists of $SbCl_2F_3$ molecules.

5. $[SbCl_4]F$ *and Other Antimony(V) Halogenofluorides*

The following compounds have been identified in a study of the system $SbF_5/SbCl_5$ (*167*):

(1) $(SbF_5)_3{\cdot}SbCl_5$
(2) $(SbF_5)_2{\cdot}SbCl_5$
(3) $SbF_5{\cdot}SbCl_5$
(4) $(SbF_5)_2{\cdot}(SbCl_5)_3$
(5) $SbF_5{\cdot}(SbCl_5)_2$
(6) $SbF_5{\cdot}(SbCl_5)_3$

The formulas merely indicate compositions and the structures are still unknown. The work described under reference (*167*) also gave indications of $(SbF_5)_3{\cdot}(SbCl_5)_2$ (described in Section II,B,4).

Interaction of $SbCl_5$ and AsF_3 gives the crystalline compound $SbCl_4F$ (*91*), which did not come to light in the systematic investigations referred to above.

$$3SbCl_5 + AsF_3 \rightarrow 3SbCl_4F + AsCl_3 \qquad (22)$$

It forms very readily and it seems reasonable to suppose that compound 6 was in reality $SbCl_4F$ in an impure form. It dissolves in AsF_3 to form ions and has been formulated as $[SbCl_4]F$. Addition of AsF_3 then leads to the formation of $[AsF_4]^-$ ions in solutions, although $[SbCl_4][AsF_4]$ cannot be obtained in the solid form. Sulfuryl chloride, which has a dielectric constant of only 10 and therefore little tendency to cause dissociation, dissolves $SbCl_4F$ in the molecular form. The same is true for CCl_4.

Spectroscopic measurements serve to verify that the crystalline compound is saltlike in character and contains $[SbCl_4]^+$ ions. In the molten state an Sb-F vibrational frequency is observed, in addition to other vibrational frequencies, which indicates the presence of the molecular form. One fluorine atom is probably situated in the trigonal basal plane (*35*). The vapor also consists of molecules. Fluorine exchange reactions may be brought about by $SbCl_4F$ as well as with $SbCl_2F_3$. The substances $SbBr_2F_3$ and SbI_2F_3 are mentioned in a patent specification (*68*), although it is not clear if they are definite compounds.

6. *Phosphorus(V) Bromochlorides*

Literature reports on phosphorus(V) bromochlorides are somewhat confused. According to relatively early work (*127*, *186*), bromine reacts with phosphorus trichloride to give PCl_3Br_2. This reaction proved, however, to be rather problematical (*128*). When bromine and phosphorus trichloride react, compounds are readily formed in which there are more than five halogen atoms per atom of phosphorus, e.g., PCl_2Br_7 (*153*), PCl_3Br_n ($n = 4$ to 10) (*129*). Recently PCl_3Br_4, PCl_3Br_8, and PCl_3Br_{10} have been described (*77*) and these are considered to be polybromides with the general structure $[PCl_3Br]^+[Br(Br_2)_n]^-$. Compounds with nonstoichiometric compositions have also been reported. Among these is $PCl_3Br_{5.1-5.7}$, which loses bromine continuously in vacuum and is transformed to $PCl_{4.8}Br_{0.4}$. When the latter is sublimed in vacuum at 50°, $PCl_{4.67}Br_{0.33}$ is produced (*149*). This is a substance whose cubic elementary cell should contain $8[PCl_4]^+$, $4[PCl_6]^-$, and $4Br^-$ ions. There are five halogen atoms per atom of phosphorus. The compounds PCl_3Br_2 and PCl_4Br are also mentioned in the earlier literature (*153*, *156*). A good deal of further work is needed to clarify the position.

If PCl_3 and Br_2 are allowed to react in $AsCl_3$ solution instead of directly, the product no longer contains excess of halogen. The structure of the product, at least in $AsCl_3$ solution, has been shown to be $[PCl_4][PCl_5Br]$ (*98*). It crystallizes from solution as an $AsCl_3$ solvate which goes over at once in vacuum into the bright yellow P_2Cl_9Br. This may be assigned the structure which is found in solution. Decomposition occurs upon heating above 120°C and the residue consists of phosphorus(V) chloride. It seems likely that $PCl_{4.67}Br_{0.33}$ is a product of the partial decomposition of $[PCl_4][PCl_5Br]$.

7. *Hexahalogeno Anions with Various Ligands*

There are various examples of this type of compound so that comparisons are possible, in spite of the fact that some of the investigations are inconclusive. Most progress has been made with the antimony compounds, where the salt $Na[SbCl_2F_4]$ has been isolated (*115*). Reaction between SbF_5 and NaCl in liquid SO_2 gives a mixture of $Na[SbCl_2F_4]$ and $Na[SbF_6]$. The hexafluoroantimonate is easily separated because of its low solubility in SO_2. This result is rather surprising, since $Na[SbClF_5]$ would be expected as the only reaction product. Interaction of $SbCl_5$ and HF, which gives SbF_5 as the end product (*165*), proceeds through complex acids containing the anions $[SbCl_nF_{6-n}]^-$, where $n = 5, 4, 3, 2, 1, 0$. When $SbCl_5$ is dissolved in HF at $-75°C$, the anion $[SbCl_5F]^-$ is formed: the exchange reaction entailing replacement of Cl by F sets in above $-40°C$, the first three Cl atoms being relatively easily replaced. Above 0°C, $[SbCl_2F_4]^-$ is attacked and exchange of the last Cl atom occurs slowly at room temperature (*95*). This is the reason for the retardation observed earlier toward the end of the reaction between $SbCl_5$ and HF (*165*). Clearly the ion $[SbClF_5]^-$ is comparatively stable, and some of its salts are known, particularly those with organic cations (pyridinium, picolinium, quinolinium, etc.) (*155*).

From these results it is reasonable to suppose that the reaction between SbF_5 and NaCl in SO_2 involves a dissociation equilibrium for the pentafluoride:

$$2SbF_5 \rightleftharpoons [SbF_4]^+ + [SbF_6]^- \tag{23}$$

The cations will then react with Cl^- (Section II,A,3). Reaction also takes place between $SbCl_2F_3$ and NaF in SO_2 to give $Na[SbCl_2F_4]$ (*115*). In this case it is still uncertain if the molecular form of the halide is invoked or if there is again an equilibrium giving the ions $[SbCl_2F_2]^+$ and $[SbCl_2F_4]^-$. Halogenoantimonates containing CF_3 groups are formed according to the equation

$$[Sb(CF_3)_3(OH)_3]^- + 3HX \rightarrow [Sb(CF_3)_3X_3]^- + 3H_2O \tag{24}$$

where X = Cl, Br. The reaction

$$Sb(CF_3)_3Cl_2 + NOCl \rightarrow NO[Sb(CF_3)_3Cl_3] \tag{25}$$

has also been described (*44*).

In contrast to the above, chlorobromoantimonates seem not to exist. Under conditions when these complexes should be produced, as for example in the reaction between $[SbCl_4]^+$ and Br^- ions, a mixture of hexachloro- and hexabromoantimonates results. This has been established by a study of the X-ray diagram of the tetraethylammonium salts, and from the absorption spectra in the visible region of the tetraethylammonium salts in acetonitrile (*101*). Chlorofluoroantimonates have characteristic X-ray powder diagrams quite distinct from those of hexachloro- and hexafluoroantimonates.

Phosphorus yields the compounds $[PCl_4][PCl_5Br]$ (Section II,B,6) and $[PCl_4][PCl_5F]$. The latter is a by-product of the decomposition of $[PCl_4][PF_6]$ (*83*). The existence of $[PCl_4][PCl_4F_2]$ also seems likely (Section II,B,2). Alkali and tetraethylammonium salts with mixed hexahalogeno anions have not yet been described for these elements. Further research is clearly called for, particularly to explain the nonexistence of bromochloroantimonates(V) and why, in the case of phosphorus, the $[PCl_5Br]^-$ ion has been found.

Arsenic(V) and bismuth(V) are found as anionic complexes only with fluorine as the ligand. The $[AsF_6]^-$ ion is very resistant to hydrolysis and is comparable in this respect with $[PF_6]^-$. Other reports in the earlier literature arise from confusion with $[AsF_5OH]^-$ (*109*). The $[SbF_6]^-$ ion, on the other hand, is more readily hydrolyzed and various fluorohydroxy antimonates result (*108, 112, 116, 118*). The hydrolysis of $[N(C_2H_5)_4][SbF_6]$ to the mono- and dihydroxy compounds is very readily carried out on a preparative scale (*103*). The hexafluorobismuthate ion, $[BiF_6]^-$, may also be hydrolyzed, but oxygen is liberated and reduction to bismuth(III) takes place (*107*).

III. Halides with Oxidation State +3

A. SIMPLE HALIDES

1. Preparation

The group of halides of the type AX_3 includes some which have been known for 300 years. Antimony trichloride was described by Glauber in 1648 and bismuth trichloride by Boyle in 1664 (*145*). The other halides were also discovered many years ago. Although they have since been widely studied, their properties are not known in every detail. The physical properties recorded in the literature show some discrepancies.

These compounds may be prepared directly from the elements, although this route is not always the most suitable. The reactivity of fluorine is such that the pentafluoride is formed as a secondary product with phosphorus and arsenic and also to a smaller extent with antimony. Bismuth becomes coated during fluorination with a solid layer of fluoride which hinders further reaction.

Halogen exchange reactions are best for the preparation of PF_3, e.g., (*130, 132*):

$$PCl_3 + AsF_3 \rightarrow PF_3 + AsCl_3 \tag{26}$$

Phosphorus tribromide is also suitable as a starting material and zinc fluoride has been used as an alternative source of fluorine (*133*). Arsenic trifluoride is prepared from As_4O_6 and HF, produced from CaF_2 and concentrated sulfuric acid (*191*).

$$As_4O_6 + 12HF \rightarrow 4AsF_3 + 6H_2O \tag{27}$$

The water is taken up by the sulfuric acid. Antimony and bismuth trifluorides are formed from the corresponding oxide and concentrated aqueous hydrofluoric acid. The antimony compound may be purified after evaporation by sublimation.

The trichloride and triiodide of arsenic are made by analogous methods. In the case of $BiCl_3$, reaction between the elements may be used or, alternatively, that between $SOCl_2$ and either Bi or Bi_2O_3 (*141*). All of these trihalides are hydrolyzed by water, although not so vigorously as the pentahalides.

2. Structure

The molecules of the trihalides, AX_3, form triangular pyramids with the atom A at the apex. Bonding is primarily between the three *p* electrons of A and *p* electrons of the halogens. The remaining pairs of free electrons are also involved, however, as may be seen from the increase of valency angle to a value greater than 90° (Table III).

TABLE III
VALENCY ANGLE FOR HALIDES OF THE TYPE AX_3

Halide	XAX°	Reference
PF_3	104 ± 4	(*19*)
PCl_3	100°6′ ± 20′	(*86*)
PBr_3	101.5 ± 1.5	(*176*)
PI_3	102 ± 2	(*176*)
AsF_3	102 ± 2	(*85*)
$AsCl_3$	98.4 ± 0.5	(*86*)
AsI_3	100 ± 2	(*55*)
$SbCl_3$	99.5 ± 1.5	(*84*)
$SbBr_3$	96 ± 2	(*55*)
	98	(*66*)
SbI_3	98 ± 2	(*55*)
	99	(*66*)
$BiCl_3$	100 ± 6	(*171*)
$BiBr_3$	100 ± 4	(*171*)

Solid SbF_3 forms a molecular lattice whereas that of BiF_3 is ionic, based on a CaF_2-type lattice into which additional F^- ions are introduced. Bismuth triiodide forms a layer lattice.

3. Uses

The halides PCl_3, PBr_3, AsF_3, $AsCl_3$, $AsBr_3$, and $SbCl_3$ have frequently been used as nonaqueous solvents. They exhibit relatively low conductivities (Table IV) which arise from weak dissociation of the type:

$$2AsF_3 \rightleftharpoons [AsF_2]^+ + [AsF_4]^- \qquad (28)$$

Their high cryoscopic constants (Table IV) also make them suitable for determining molecular and ionic weights.

These trihalides possess to a very marked degree the property of exchanging their halogen atoms with those of other compounds. The fluorides, AF_3, are especially useful in this connection, the trifluorides of arsenic (see Eq. 26) and antimony providing good examples of this. Fluorine exchange between Si—Cl compounds and SbF_3 is strongly retarded by $AlCl_3$ or BF_3 (*136, 137*). This observation supports the theory that the free electron pair on antimony initiates the exchange on silicon (*137*).

TABLE IV
SELF-CONDUCTIVITIES OF HALIDES OF THE TYPE AX_3

Halide	Conductivity (Ω^{-1} cm^{-1})	Cryoscopic constants[a] (degrees/mole)	References
PF_3	10^{-9} (−113°C)	—	(*189*)
AsF_3	5×10^{-6} (20°C)	7.38	(*87, 91*)
$AsCl_3$	$1.4\text{–}1.6 \times 10^{-7}$	9.74	(*90, 180*)
$SbCl_3$	1.6×10^{-6} (18°C)	17.95	(*179, 181*)
SbF_3	10^{-6} (solid)	—	(*189*)

[a] Referred to 1000 gm of solvent.

4. Complexes and Addition Compounds

Phosphorus trifluoride is encountered as a ligand in complexes. Thus the compound $[(PF_3)_2PtCl_2]$ is known and, from the magnitude of the dipole moment (4.4 ± 0.5 Debye units), this must occur in the *cis* form. The Pt—P bond may be explained by the use of the *d* electrons of the metal for $d\pi$—$d\pi$ bonding to phosphorus. The *cis* complex $[(CO)_2PtCl_2]$ has a similar dipole moment (4.65 ± 0.5 Debye units), and PF_3 and CO are comparable as ligands: neither reacts with BF_3, $AlBr_3$, or $AlCl_3$. Phosphorus trifluoride is able to replace the CO in $[Ni(CO)_4]$ (*23*), the product, $[Ni(PF_3)_4]$, being very resistant to hydrolysis. Thus, when distilled with steam it is hydrolyzed only to a small extent and no reaction occurs with cold water (*187*). The compounds $[Ni(PCl_3)_4]$ (*75*), $[Ni(PBr_3)_4]$ (*187*), $[Ni(CO)_3SbCl_3]$, and $[Fe(CO)_3(SbCl_3)_2]$ (*188*) are also known, although the normal properties of the halide are changed less in them than in $[Ni(PF_3)_4]$. They are more readily hydrolyzed owing to a smaller tendency to π-bond formation. Dialkylaminophosphorus fluorides, $(R_2N)_nPF_{3-n}$ (*168a*), and alkyl phosphorus fluorides, R_nPF_{3-n}, form similar complexes. The latter compounds are obtained by halogen exchange on R_nPCl_{3-n}

complexes of nickel(0). Free alkyl phosphorus chlorides with unsubstituted alkyl groups cannot be transformed into the fluorides R_nPF_{3-n} by means of KSO_2F, AsF_3, or SbF_3 (*168*).

Although halide ions cannot be added to PF_3 (*189*), the trifluorides of the heavier atoms of this group all form anionic complexes. Potassium fluoride, for example, is sufficiently soluble in AsF_3 to form $K[AsF_4]$ (*191*). The analogous chloroarsenate(III), $K[AsCl_4]$, has also been isolated (*59*). Tetrachloroarsenates(III) of organic cations are also known. The anion $[AsCl_5]^{2-}$ is stable in association with the ethylammonium cation, while antimony(III) gives complexes formulated as $[SbCl_4]^-$, $[SbCl_5]^{2-}$, and $[SbCl_6]^{3-}$ (*2, 46, 76, 77*). Compounds of the composition $M_2[SbX_6]$, with $M = NH_4^+$, Rb^+, and $X = Cl^-$, Br^-, are diamagnetic and therefore do not contain antimony in the +4 state. They may be formulated as $M_4^+[Sb^{III}X_6]^{3-}[Sb^{V}X_6]^-$ (*79*). Salts formed by organic cations with the anions $[As_2Cl_9]^{3-}$ and $[As_3Cl_{11}]^{2-}$ may also be noted (*59, 147, 184*).

Corresponding antimony compounds such, for example, as $3RbCl{\cdot}2SbCl_3$ (*185*) are also known. Structural studies with $3CsCl{\cdot}2AsCl_3$ showed that $AsCl_3$ groups were embedded between Cs^+ and Cl^- ions in such a way that all atoms are in approximately cubic close-packing (*72*). In this case, therefore, there is no question of complexes with halogen bridges, although it is not known if this is also true for the antimony compounds.

Halogen bridges have, however, been found in fluoroantimony(III) compounds. In $Cs[Sb_2F_7]$ two Sb atoms are linked by a fluorine bridge, giving antimony a coordination number of 4 (*21*). Fluorine bridges also occur in $KSbF_4$. Here antimony has a coordination number of 5, the structural unit being $[Sb_4F_{16}]^{4-}$ with double fluorine bridges (*20*). In $K_2[SbF_5]$ the coordination number 5 is again found, the anion having an octahedral structure, with one octahedral position occupied by the free pair of electrons (*22*). The compound $NOCl{\cdot}BiCl_3$ (*158, 174*) may be $NO[BiCl_4]$.

Numerous adducts of the halides AX_3 with, for example, tertiary amines or arsines are reported in the literature, but these will not be considered here. Decomposition reactions occur with primary or secondary amines (*65, 140*). The compound $2AsF_3{\cdot}3SO_3$ (*45*), which is formed from AsF_3 and SO_3, has a complicated structure that has been elucidated by nuclear magnetic resonance spectroscopy (*53*).

B. MIXED HALIDES

Partial exchange of the halogen atoms in PCl_3 and PBr_3 for fluorine gives PCl_2F, $PClF_2$, PBr_2F, and $PBrF_2$. Fluorine may be introduced with, for example, SbF_3 and $SbCl_5$, PBr_5, or Br_2 as catalyst, while CaF_2 may be used as the fluorinating agent at higher temperatures (*14, 15, 74, 94*). Phosphorus trifluoride is unsuitable for the exchange reaction with PCl_3.

The compound $PClF_2$ is also formed by cleavage of the P—N bond in dialkylaminophosphorus difluoride by means of HCl (*143*):

$$R_2NPF_2 + 2HCl \rightarrow PClF_2 + [R_2NH_2]Cl \qquad (29)$$

Raman spectroscopy shows that when PCl_2F and PBr_2F are mixed, the compound PBrClF is present in the equilibrium (*37*, *38*, *39*, *51*). An equilibrium mixture containing PCl_2Br and PBr_2Cl is also formed when PCl_3 and PBr_3 are mixed at room temperature (*50*). Both of these compounds may be isolated (*128*, *157*).

The mixed halides can serve as starting materials for the preparation of mixed P(V) halides (Section II,B,2). Fluorophosphites can also be made from PCl_2F (*24*, *25*, *28*, *122*):

$$PCl_2F + 2ROH \rightarrow (RO)_2PF + 2HCl \qquad (30)$$

No mixed halides of arsenic are known apart from those with pseudohalide groups. The CF_3 group also occurs in As(III) compounds in association with halogens or pseudohalogens, and compounds of the types CF_3AsX_2 and $(CF_3)_2AsX$ are known, with X = F, Cl, Br, I, CN, SCN (*17*, *43*, *183*). Analogous compounds are known for phosphorus and antimony (*7*, *34*). It is interesting in this connection that AsF_3 and $AsCl_3$ are immiscible; their mutual solubility is small. The mixed halide $SbBrI_2$ is said to result in the interaction of $SbC_2H_5I_2$ and bromine in chloroform (*26*). Hydrolysis of the mixed A(III) halides has not yet been studied in detail. In general the ease of hydrolysis is intermediate between those for the appropriate simple halides.

IV. Halides with Oxidation States $< +3$

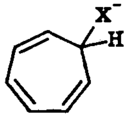
Little is known so far about this class of compound and it is not clear if the various substances reported in the literature are true compounds. This is the case, for example, with $As_{11}Cl$ (*10*). The compound P_2I_4, which is produced from white phosphorus and iodine in benzene or carbon disulfide, has been more closely studied. It contains a P—P bond and the free electron pairs are *trans* to one another in the solid compound (*119*). In solution the two PI_2-groups are distorted by a mean angle of about 85° (*4a*). Boron tribromide gives the adduct $P_2I_4 \cdot 2BBr_3$ (*177*). The chloro compound, P_2Cl_4, is obtained in the reaction between PCl_3 and hydrogen in an electric discharge (*11*, *167a*), or by the action of a high tension discharge between mercury electrodes on PCl_3 (*47*). The discharge reaction may also be carried out in PCl_3 vapor above solutions of PCl_3 and white phosphorus (*167a*) or in PCl_3 vapor in the presence of bronze wool (*79a*). The P—P bond energy in P_2Cl_4 is 58 kcal/mole (*167b*). When the calculated quantities of arsenic and iodine are heated in an atmosphere of hydrogen,

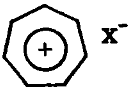
As_2I_4 is formed (*80*). No antimony compound of this type is known, although there are derivatives of this sort for bismuth. The existence of a tetrameric monochloride, Bi_4Cl_4, seems certain, and it has also been established by phase studies (*29*, *30*). The monobromide, BiBr, and monoiodide, BiI, are present in the equilibrium mixture formed in the reaction of gaseous $BiBr_3$ or BiI_3 with molten bismuth (*32*, *33*). Mention must also be made of the hydrogen compound PH_2F_3, which results when hypophosphorous acid and HF are mixed at −78°C and allowed to warm to room temperature (*13*). Transformation into the hypothetical phosphonium salt $[PH_4][PF_6]$ has not been observed.

V. Isomerism and Bonding

A. DIRECT BOND ISOMERISM

Reference has already been made in several places to the remarkable observation that halides of the same composition may occur in both a molecular and a saltlike form (*93*). In some cases the two forms exist side by side (e.g., PCl_2F_3-$[PCl_4][PF_6]$) or can be observed together (PCl_4F-$[PCl_4]F$). A similar phenomenon has been observed in the organic field, e.g.,





(X = Cl, Br)

Tropylidene halides (chloride and bromide liquid at room temperature)

Tropylium halides (*182a*) (chloride, colorless crystals, m.p. 103°C; bromide, yellow tabular crystals, m.p. 203°C)

It has been suggested that this be referred to as direct bond isomerism.

B. THE INFLUENCE OF THE STATE OF AGGREGATION

In contrast to what has been said above (Section V,A), there are compounds whose molecular and saltlike forms exist in different temperature ranges. Transition then occurs on melting or vaporization. An example of this is afforded by phosphorus(V) chloride, the lattice of which is made up of $[PCl_4]^+$ and $[PCl_6]^-$ ions, whereas the melt or vapor contains PCl_5 molecules. In such a case the isomerism is correctly referred to as dependent on the state of aggregation. Another example which has not been mentioned so far is the compound $[As(OC_2H_5)_4][AsF_6]$. It is formed when $FAs(OC_2H_5)_2$ or $F_2As(OC_2H_5)$ is oxidized with chlorine or bromine (*100*) and has a melting point of 63°C. It may be distilled at 140°–145°C/10^{-3}–

10^{-4} mm Hg, and presumably the vapor contains homopolar molecules of $As(OC_2H_5)_2F_3$ (*106*). Analogous behavior is exhibited by $[SbCl_4]F$.

The phenomenon of bond isomerism depending on the state of aggregation, like that of direct bond isomerism, is not restricted to halides of P, As, and Sb. Anhydrous nitric acid, for example, shows appreciable ionic conductivity in the liquid state, but the vapor consists of molecules (*1, 125*). Well-defined salts such as $Cu[NO_3]_2$ may also be mentioned in this connection. The vapor of copper(II) nitrate contains molecules (*5*). The concept of isomerism is used here in a broad sense, as the example of anhydrous nitric acid shows. Whereas classical isomerism is restricted to two molecules of the same composition, the phenomenon under discussion here relates to the system as a whole. Liquid HNO_3 may also be thought of as a solution containing an ionic form dissolved in the anhydrous acid, which functions as the solvent. This relation is involved in the next type of bond isomerism to be discussed, where the solvent plays a part.

C. THE INFLUENCE OF SOLVENTS

Polar and nonpolar solvents have the property of dissolving certain substances in either a saltlike or a polar form. Thus a solution of phosphorus(V) chloride in acetonitrile contains $[PCl_4]^+$ and $[PCl_6]^-$ ions, whereas in carbon tetrachloride PCl_5 molecules are present. In polar solvents it is necessary to assume an equilibrium that depends on temperature and concentration (see Eq. 7). A similar relationship exists for antimony(V) chloroethoxy compounds, e.g., $SbCl_4(OC_2H_5)$ and $[SbCl_4][SbCl_4(OC_2H_5)_2]$ (*96, 105, 110, 111*).

The case also arises where a compound is changed to another form under the influence of a solvent, as for example with $SbCl_5$ or SbF_5 in acetonitrile (Section II,A,3). The compound $(CF_3)_3PCl_2$ may also be mentioned in this connection since it exhibits conductivity in acetonitrile. The following equilibrium may be postulated (*42*):

$$2(CF_3)_3PCl_2 \rightleftharpoons [P(CF_3)_3Cl]^+ + [PCl_3(CF_3)_3]^- \qquad (31)$$

The CF_3 group may be regarded as a pseudohalogen and it is therefore not surprising that the CF_3 derivatives resemble the normal halides. For $(CF_3)_2PCl_3$ the transformation to an ionic form such as is observed for PCl_2F_3 seems to be prevented, for conductivity measurements in this case give no indication of an equilibrium involving bond isomerism. Organoantimony compounds of the type R_3SbCl_2, $R_3SbCl(OCH_3)$, and R_2SbCl_3 (where $R = CH_3$, C_6H_5, $C_6H_5CH_2$) also show no tendency to give heteropolar forms in polar solvents (*99*). For the change to occur it is necessary that at least the bonding of one ligand should be so deformed that an ion can be split off. The exact bonding relationships in the substances under consideration are, however, so little understood that no conclusive statement is possible.

A further example of bonding isomerism that depends on the solvent may be taken from purely organic compounds. The following equilibrium exists between anisolesyndiazo cyanide and the corresponding diazonium cyanide (*63*):

(32)

The diazonium cyanide in the solid state is able to exist only as the solvate with two molecules of HCN (*63*), which is analogous to the case of the solvate formed by $SbCl_5$ with CH_3CN.

D. INTERMEDIATE STATES

It is quite understandable that the molecular form of a substance showing bonding isomerism should react differently from the ionic form. It follows that the nature of the solvent will influence the mode of reaction of such substances very strongly. In cases where an equilibrium is involved, both temperature and concentration will also have a considerable influence for a given solvent.

The influence of the solvent will not, however, be restricted to that on the equilibrium: solvation may also lead to a partial displacement of bond polarity. This may be regarded as an intermediate state between the two extremes involved in bond isomerism. The effects of different solvents on the same reaction may be considered from this point of view. It is understandable that radical reactions take place more quickly in nonpolar than in polar solvents. The photochemical oxidation of iodoform, for example, occurs more than 50 times more rapidly in carbon tetrachloride than in the polar solvent acetone (*148*). On the other hand, reaction between $N(C_2H_5)_3$ and C_2H_5I to give $[N(C_2H_5)_4]I$ is more than 100 times faster in nitrobenzene than in the nonpolar hexane (*56*).

The effect of a solvent in a particular reaction cannot, however, be related simply to the dipole moment or the dielectric constant (Section II,A,3). Special properties, such as the ability to form strong or weak hydrogen bonds and steric considerations in the formation of solvates, also play a part. Displacement of the bond polarity is closely linked with solvation and this, coupled with the blocking of the potential sites for reaction by solvate molecules, is the basic cause of the effect on the reaction. In this connection, spectroscopic properties of the solvent are more revealing than the value of the dipole moment or dielectric constant. Thus the charge transfer bands of 1-ethyl-4-carbomethoxypyridinium iodide have been measured in various solvents and yield the so-called Z values from the transition energies. Pyridine-1-oxide is suitable as a reference substance for weakly polar solvents (*117*), but pyridinium-N-phenolbetaines have the advantage of giving a broader Z scale (*41*). Another way in which different solvents may be characterized is by comparing the half-widths of selected vibrational bands. The CO vibrational band in metal carbonyls has been used for this purpose (*16*). Polar solvents increase the half-width and this method is particularly suited to the study of weakly polar solvents. Finally, reference may be made to the Y values given in the literature for solvents. These are based on measurements of the rate of dissociation for a reference reaction in various solvents, and are related to their ionizing powers (*57*).

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