HALIDES OF THE PHOSPHORUS GROUP ELEMENTS (P, As, Sb, Bi)

By D. S. PAYNE

(THE UNIVERSITY, GLASGOW)

IT is a commonplace to observe that the past decade has seen a renaissance of inorganic chemistry. During this period certain topics, notably the chemistry of uranium and the transuranic elements, the hydrides of boron and their derivatives, and non-aqueous solvent systems have been investigated with great intensity to give results of considerable interest. However, during this period a steady stream of work has appeared dealing with the chemistry of many, if not all, of the superficially well-known elements. This new knowledge, whilst perhaps less spectacular, is important in that it leads to a more complete picture of the potentialities, and a better understanding of the general underlying principles, of the "well-known" elements. Amongst the groups of elements whose chemistry is accepted as being well known, one of the best examples is the phosphorus group. There is a particular interest in this group of elements both in its juxtaposition to the sulphur and the silicon group, and because of the occurrence of at least two distinct series of compounds (M^{III} and M^{V}). Recent work has added considerably to our knowledge of these elements, and it is the purpose of this Review to draw attention to this, consideration being limited to the halides only. Nitrogen, whilst having a certain similarity to the phosphorus group elements, arising from the ability to form a simple octet leading to tervalency, has substantial differences because of its inability to make use of orbitals beyond the 2*s* and 2*p* levels. The extent to which the phosphorus group utilises the orbitals available for bonding varies markedly, with both the element and the nature of the atom or group involved in bond formation; it is most marked in the case of the 3*d* orbitals of phosphorus and least obvious in the case of the 6*d* orbitals of bismuth.

Before discussing the detailed chemistry of the halides it is appropriate to mention certain relevant features of the elements concerned. The following electronegativity data, including values for the halogens, are taken from Pritchard and Skinner's review:[1] N = 3·0, P = 2·1, As = 2·0, Sb = 1·9, Bi = 1·8, F = 3·9, Cl = 3·0, Br = 2·8, I = 2·5. However, the values for the phosphorus group are probably of varying reliability. Although the values, P = 2·19, As = 1·97, and Sb = 2·28 have recently been put forward,[2] their validity has already been challenged.[3] The 1st and 2nd ionisation potentials decrease from phosphorus to bismuth.

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[1] Pritchard and Skinner, *Chem. Rev.*, 1955, **55**, 745.
[2] Fineman and Daignault, *J. Inorg. Nuclear Chem.*, 1959, **10**, 205.
[3] Drago, *J. Inorg. Nuclear Chem.*, 1960, **15**, 237.

This trend is, however, broken in the 3rd, 4th, and 5th ionisation potentials, where a very slight increase occurs at bismuth. This, coupled with the greater size of the Bi^{3+} ion than of the other ions in the series, is a factor in the diminished stability of the higher valency states of bismuth compared to the other members of the group. Values for bismuth (8, 16·6, and 25·4 ev) are comparable with those for gallium (8·1, 15·9, and 30·6 ev); thus it might be expected that, solvation effects being comparable, chemical similarities between bismuth and gallium would exist. For example, obvious cationic tendencies might be observed, particularly in aqueous solution.

Van Wazer[4] has drawn attention to the principles of bonding in phosphorus compounds and these may quite appropriately be extended to the whole group. Setting aside the very small number of less-common configurations, four main types of situation are found.

(*a*) *Three-connected atoms.* In these situations the atom is at the apex of a triangular pyramid. This is a common arrangement and many examples have been investigated in detail. Evidence based on bond-length shortening and on enthalpy data[4] suggests that in the case of phosphorus there are three pure σ-bonds, with little or no π-character and this might well apply to the remainder of the group. The bond angle drops from $104° \pm 4°$ in phosphorus trifluoride to $100° \pm 2°$ in the tribromide; for the corresponding arsenic trihalides the values are $102° \pm 2°$ and $100° \pm 2°$ respectively, with a value of 98·5° for the tri-iodide. However, the angles in antimony trichloride and tribromide and in bismuth trichloride and tribromide are very similar; $96° \pm 4°$ and $96° \pm 2°$, $100° \pm 6°$ and $100° \pm 4°$ respectively.[6] The values of these angles fall between those expected for bonds involving pure p orbitals (90°) and that for sp^3-hybrid orbitals (109° 28′). The shapes of these molecules can be interpreted satisfactorily in terms of a greater repulsion between non-bond pairs and bond pairs than between bond pairs and bond pairs.[7]

(*b*) *Five-connected atoms.* The atom is at the centre of five atoms, the bonds usually being directed in a trigonal bipyramidal fashion. Molecules containing this arrangement are not common. Evidence suggests that for phosphorus these bonds are almost wholly of σ-type.[4] The general disposition of the five bonded pairs is that to be expected in terms of the simple repulsive forces between bond and non-bond pairs. Alternatively, the five bonds can be represented as arising from sp^3d-hybridised orbitals. In a few cases five-connected atoms can be encountered in anions of the type MX_5^{2-}. The structure here is that of a distorted octahedron (tetragonal pyramid) in which one of the octahedral positions is taken by a

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[4] Van Wazer, "Phosphorus and its compounds," Interscience, New York, 1958, Vol. I.
[5] Van Wazer, *J. Amer. Chem. Soc.*, 1956, **78**, 5709.
[6] Chem. Soc. Special Publ., No. 11.
[7] Gillespie and Nyholm, *Quart. Rev.*, 1957, **11**, 369.

non-bonded pair, such as occurs in $(NH_4)_2SbCl_5$ [8] and K_2SbF_5.[9] Similar related structures are found in $KSbF_4$ [10] and $NaSbF_4$.[11]

(*c*) *Six-connected atoms.* For a co-ordination number of six the arrangement is octahedral, as follows directly from consideration of repulsions of six equivalent electron pairs or from the form of sp^3d^2-hybridisation. This form, as a complex anion, is encountered more often than the five-co-ordinated situation. For phosphorus the ligands in such a system are largely σ-bonded.[4]

(*d*) *Four-connected atoms.* A feature of the halide chemistry of this group is the frequent occurrence of four co-ordinated atoms, usually as the cation MX_4^+. Van Wazer[4] has shown that in the case of phosphorus this co-ordination involves four σ-type bonds with an average of one π-bond per phosphorus atom, the bond order being 1·25. The π-bond appears necessary to reduce the positive charge, which would otherwise accumulate on the phosphorus atom as a result of electronegativity differences. The need for π-bonding is eliminated in three co-ordinate compounds with strongly electronegative ligands, the lone pair being responsible for balancing charge differences. In five- and six-co-ordinate phosphorus the lowest-energy *d*-orbital(s) are already in use and are not available for π-bonding.

The general picture, based on electronegativity differences of the bonds formed in the halides, is one of appreciable ionic character, particularly for the chlorides and fluorides. However, this ionic character is somewhat offset by π-bonding. Since *d*-orbitals can only be used in bonding where the ligand possesses a high relative electronegativity,[12] five- and six-co-ordinate compounds might be restricted to chlorides and fluorides. The effect of ligand size might also be to favour the chlorides and fluorides rather than the bromides and iodides. An additional factor in determining stability is the increasing tendency of the halogens on passing from fluorine to iodine to form p_π–d_π bonds.

As in the neighbouring groups, the mixed halides of the phosphorus group are apparently less stable than the simple halides, although there are certain exceptions, *e.g.*, PF_3Cl_2. The presence of fluoride in the mixed trihalides appears to increase the stability to re-organisation processes.[13] The stereochemical consequences of the various co-ordination polyhedra in the mixed halides have still to be realised, for example the compound PF_3Cl_2 could occur in three stereochemical forms (1), (2), and (3) [(1) appears to be the form present in the gaseous phase at room temperature], and the anion $PF_4Cl_2^-$ in two forms (4) and (5). So far it has not been

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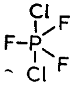
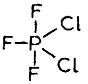
[8] Edstrand, Inge, and Ingri, *Acta Chem. Scand.*, 1955, **9**, 122.
[9] Byström and Wilhelmi, *Arkiv Kemi*, 1951, **3**, 461.
[10] Byström, Bäcklund, and Wilhelmi, *Arkiv Kemi*, 1952, **4**, 175.
[11] Byström, Bäcklund, and Wilhelmi, *Arkiv Kemi*, 1953, **6**, 77.
[12] Craig, Maccoll, Nyholm, Orgel, and Sutton, *J.*, 1954, 332.
[13] Delwaulle, Cras, Bridoux, and Migeon, XVIIth I.U.P.A.C. Conference, Munich, 1959.

possible to investigate these possibilities fully in the halides, although they have been recognised in the trifluoromethyl-derivatives where $(CF_3)_2PCl_3$ is in the *trans*-form, whereas $(CF_3)_3PCl_2$ is a mixture of various stereochemical forms.[14]


(1)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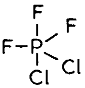
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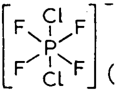
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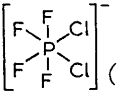
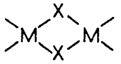

(5)

A common feature of halides generally is the existence of halogen bridges arising from donor bonds from halogen to acceptor orbitals on adjacent atoms; these bridges are often of the form shown at (*A*), incorporating a four-membered ring. Examples are more common amongst chlorides and bromides than amongst fluorides and iodides, possibly owing to steric and electronegativity factors. So far the possibility of such bridges in the halides of the phosphorus group elements appears limited to P_2Cl_{10}[15] and certain complex anions.


(*A*)

The importance of the tetrahedral configuration is shown in the existence of many halides, particularly the pentahalides, in ionic four-co-ordinate states in preference to molecular states with higher or lower co-ordination numbers. There are, however, a few pentahalides which occur as such, and give simple molecular lattices, *e.g.*, $SbCl_5$. Two forms of each of the halides might be expected, corresponding to molecular and ionic lattices, but in fact, evidence of this is limited to PCl_4F, $SbCl_4F$, and possibly to PCl_5. The ionic forms of the halides might be expected to be particularly stable in suitable solvent environments (high dielectric constant). The anionic form is often, but apparently not invariably six-co-ordinate.

The trihalides

Certain of the trihalides have a long and interesting history. Boyle[16] was the first to prepare bismuth trichloride (1664), whilst antimony trichloride was first correctly identified by Glauber in 1648. The simple trihalides are obtained by the direct interaction of the elements in stoicheiometric proportions. Only in the case of bismuth and fluorine is difficulty experienced owing to the formation of a protective halide film. The reactions are all exothermic to varying degrees. Various metathetical reactions are available for preparation, in some fashion depending for their success on the volatility or low solubility of the products. Metathesis is particularly

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[14] Harris, Ph.D. Dissertation, Cambridge, 1958.

[15] Kennedy and Payne, *J.*, 1960, 4126; Kennedy, Payne, Reed, and Snedden, *Proc. Chem. Soc.*, 1959, 133.

[16] Boyle, " Experiments and Consideration concerning Colour," London, 1664.

applicable to the preparation of the fluorides, *e.g.*, $PCl_3 + AsF_3 \rightarrow PF_3 + AsCl_3$. For the preparation of iodides it is convenient to utilise the reaction between the corresponding chloride and, for example, potassium iodide in a suitable solvent, such as acetone. Various halides, in particular the fluorides, can be prepared from the oxide or sulphide by the action of the hydrogen halide. In certain cases it is possible to achieve reaction between the oxide, or more favourably the sulphide, and elemental halogen. Phosphorus appears to be excluded from these reactions. The halides of bismuth and antimony can be obtained from aqueous solutions in the presence of excess of acid but this is impossible for arsenic or phosphorus halides (other than arsenic tri-iodide) owing to their ready hydrolysis.

The number of possible mixed trihalides is large, but so far only a few have been prepared. The methods used for their preparation have involved either the application of re-organisation reactions, in which mixtures of different trihalides are heated together until an equilibrium mixture has been obtained, or the partial exchange of halogens with another halide. Those mixed halides which have been isolated and whose individual properties have been recognised are PF_2Cl, $PFCl_2$,[17] PF_2Br, $PFBr_2$,[18] and $SbBrI_2$.[19] Others have so far only been identified in the course of ebullioscopic,[20] Raman spectra,[21,22] and nuclear magnetic resonance studies;[23] for example a mixture of phosphorus trichloride and tribromide produces, in a few minutes at room temperature, both PCl_2Br and $PClBr_2$ in equilibrium with the original halides,[23] whilst PCl_2F and PBr_2F give PFClBr in the equilibrium mixture. Mixtures of PCl_2F with PBr_3 and PBr_2F with PCl_3 yield mixtures containing a large number of molecular species; the isolation of the individual species has not been attempted. In no case is equilbrium established instantaneously, the reaction being considerably slower when fluoride is present in one of the molecules involved.[13,23] The reaction rates are appreciably faster than the re-organisation reactions of four-co-ordinated phosphorus. To date, attempts to prepare arsenic fluorochlorides by partial fluorination have not been successful.[24]

The trihalides exhibit many features of chemical interest. Reference has already been made to the re-organisation reactions of the phosphorus series and it appears likely that this type of reaction is general to the group. The composition of any equilibrium mixture will not, however, necessarily include appreciable amounts of mixed halides, unless there is some particular feature favouring stability.

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[17] Booth and Bozarth, *J. Amer. Chem. Soc.*, 1933, **55**, 3890.
[18] Booth and Frary, *J. Amer. Chem. Soc.*, 1939, **61**, 2934.
[19] Clark, *J.*, 1930, 2737.
[20] Raeder, *Z. anorg. Chem.*, 1933, **210**, 145.
[21] Delwaulle and Francois, *J. Chim. phys.*, 1949, **46**, 80.
[22] Delwaulle, *Compt. rend.*, 1947, **224**, 389.
[23] Fluck, Van Wazer, and Groenweghe, *J. Amer. Chem. Soc.*, 1959, **81**, 6363.
[24] Wilkins, *J.*, 1951, 2726.

The trihalides, in the liquid phase, are generally poor electrical conductors. Arsenic trifluoride has a specific conductance of 2·4 × 10^{-5} ohm^{-1} $cm.^{-1}$ at 25°, which is of the same order as values for bromine trifluoride, iodine pentafluoride, and hydrogen fluoride.[25] As with these other fluorides, the presence of potassium fluoride greatly increases the conductance, and the compound KF,AsF_3 ($K^+AsF_4^-$) can be isolated. Likewise, the addition of antimony pentafluoride results in an increase in conductance, and the compound SbF_5,AsF_3 is isolated. The self-ionisation of AsF_3 into AsF_2^+ and AsF_4^- is therefore postulated.[26] Phosphorus trifluoride, with a specific conductance of 10^{-9} ohm^{-1} $cm.^{-1}$ at —113°C, shows no tendency to form a complex with potassium fluoride.[27] Previous reports on the formation of PF_4^- by this reaction thus appear incorrect.[28] In contrast, fused antimony trifluoride has a relatively high conductance comparable with that of fused zinc fluoride.[27] Arsenic trichloride, with a dielectric constant of 12·8 at 20°C, is a poor conductor, but a good solvent for a wide range of halides, a feature made use of in the preparation of halide complexes.[29] Similar solvent properties are found for antimony trichloride[30] and antimony tribromide.[31] A common feature is the ability to promote ionisation of dissolved compounds by halide-ion transfer, leading to the formation of complex ions. The high transport number (0·88—0·97) for chloride ion in a solution of tetramethylammonium chloride in arsenic trichloride arises from the ease of the chloride exchange, $AsCl_3 + AsCl_4^- \rightarrow AsCl_4^- + AsCl_3$, by which electrolytic conductance occurs.[32]

Arsenic trichloride is a strongly polar molecule and numerous examples of its addition compounds are known. Most are best regarded as solvates, involving truly ionic species only in favourable situations. The system tetramethylammonium chloride–arsenic trichloride contains the compounds $(CH_3)_4NCl,AsCl_3$ and $(CH_3)_4NCl,3AsCl_3$, whereas, in the corresponding tetraethyl system, $(C_2H_5)_4NCl,2AsCl_3$ and $3(C_2H_5)_4NCl,5AsCl_3$ are recognised.[33] This tendency towards solvate formation is also shown by the existence of the compounds $2PCl_5,5AsCl_3$ and $2PCl_5,4SbCl_3$, which have been shown by cryoscopic and conductometric methods to contain the arsenic and antimony trihalide molecules as solvates only.[34] Although there is a considerable number of addition compounds of trichlorides and tribromides of arsenic and antimony, the simple MX_4^- unit has been recognised in only a few. One example, apparently well

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

[26] Gutmann, *Quart. Rev.*, 1956, **10**, 451; *Angew Chem.*, 1959, **71**, 57.

[27] Woolf, *J.*, 1955, 279.

[28] Lange and Stein, unpublished work reported by Simon, "Fluorine Chemistry," Vol. I., Academic Press Inc., New York, 1950, p. 139.

[29] Lindqvist, *Acta Chem. Scand.*, 1955, **9**, 73.

[30] Porter and Baughan, *J.*, 1958, 744.

[31] Jander and Weiss, *Z. Elektrochem.*, 1957, **61**, 1275; *ibid.*, 1958, **62**, 350.

[32] Gutmann, *Svensk Kem. Tidskr.*, 1956, **68**, 1.

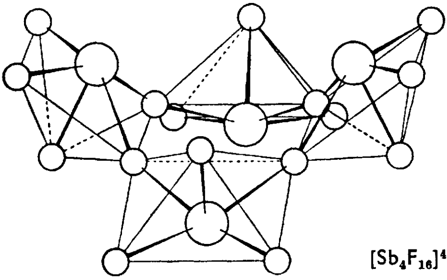
[33] Agerman, Andersson, Lindqvist, and Zackrisson, *Acta Chem. Scand.*, 1958, **12**, 477.

[34] Kolditz, *Z. anorg. Chem.*, 1957, **289**, 118.

substantiated, is $[Me_4N]^+[AsCl_4]^-$.[35] Potentiometric studies in arsenic trichloride should help to determine the true nature of the trihalide complexes.[36]

Although the existence of salts of the form $M^IM^{III}X_4$ (along with more complex forms) has long been recognised in the chemistry of arsenic, antimony, and bismuth, and the examples are very numerous, details of the structure are known in only a few instances. Despite the obvious interest in phosphorus analogues of these complexes, no convincing evidence has so far been presented for their existence.[27,33] Investigation of the tetrafluoroarsenites by nuclear magnetic resonance shows that these salts undergo rapid exchange with the arsenic trifluoride used as solvent.[37]

The numerous complexes of tervalent antimony with fluorine, formed from antimony trioxide, potassium carbonate and hydrofluoric acid, have been investigated in some detail. In K_2SbF_5 a co-ordination number of five is exhibited and the structure is in keeping with an octahedral arrangement with a non-bonding pair occupying the sixth corner,[9] leading to a square-pyramidal structure in which the antimony atom is in fact displaced outside the basal plane as a result of bond-pair–non-bond-pair repulsions.[38] KSb_2F_7, however, contains four-co-ordinate antimony and can be seen as two trigonal bipyramids linked through a bridging fluorine with non-bonding pairs at the pyramidal apices.[39] Four-co-ordination might be expected in the compounds $RSbF_4$ (R = K, Rb, Cs, NH_4, or Tl), however none has so far been shown to involve an $[SbF_4]^-$ ion. $KSbF_4$, for example, contains the $[Sb_4F_{16}]^{4-}$ complex ion, (6), in which a five-co-ordinate antimony is encountered, two of the fluorines in the SbF_5 polyhedron being shared.[10] A more complex structure is found for KSb_4F_{13} and for several isomorphous compounds. Here four independent antimony trifluoride groups are loosely joined to a fluorine ion (the thirteenth).[40] This structure could be described as involving a solvated fluoride ion and


$[Sb_4F_{16}]^{4-}$

(6)

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[35] Gutmann, *Z. anorg. Chem.*, 1951, **266**, 331.
[36] Andersson and Lindqvist, *Acta Chem. Scand.*, 1955, **12**, 79.
[37] Muetterties and Phillips, *J. Amer. Chem. Soc.*, 1957, **79**, 3686.
[38] Grdenić and Šćarnićar, *Proc. Chem. Soc.*, 1960, 147.
[39] Byström and Wilhelmi, *Arkiv Kemi*, 1951, **3**, 373.
[40] Byström and Wilhelmi, *Arkiv Kemi*, 1951, **3**, 17.

classified along with the arsenic and antimony trichloride solvates mentioned earlier.

Various bismuth compounds of the form $M^{I}BiX_4$ have been recognised, but none investigated structurally. It is tempting to assign a simple ionic form to compounds such as $BiCl_3,NOCl$ (*e.g.*, $NO^+BiCl_4^-$) but there is no supporting evidence.

The conductance of arsenic trifluoride and arsenic trichloride and the existence of AsF_3,SbF_5 and AsF_3,BiF_3 suggest an AsX_2^+ cation. However, no evidence, direct or indirect, is available in support.

One feature of the trihalides of particular interest is their ability to act as electron-pair donors and to a lesser extent as acceptors. In the role of donor the high electronegativities of the halogens would lower the bonding capacity, but this effect should diminish on passing from fluorine to iodine. Little is known, however, of the complexing tendencies of the tribromides and tri-iodides so that discussion must be confined to the trichlorides and trifluorides. The withdrawal of electrons by the halogens would favour acceptor π-bonding by the *d*-orbitals. Investigation has so far been confined to the examination of the stability of complexes with obvious acceptor molecules such as the boron halides.

Recent work[41] reports the failure of the trichlorides or tribromides of arsenic and antimony to form complexes with halides of boron, aluminium, or gallium; indications are that previous reports of addition compounds are incorrect. Weak complexes between phosphorus trichloride and these three halides are, however, found. The gallium trichloride–phosphorus trichloride system contains the complex $Cl_3P \rightarrow GaCl_3$ in the solid, but it is not stable otherwise.[42] A number of adducts between the trihalides and organic amines and oxides are known with varying molecular ratios.[43] Examples of 1:1 compounds are Me_3As,PCl_3, $Me_3N,AsCl_3$, $Me_3N,SbCl_3$, and Me_3N,PBr_3, of 1:2 compounds $Et_3N,2SbCl_3$, of 2:1 compounds $2Me_3P,PCl_3$ and $2Me_3P,AsCl_3$.[44,45]

The formation of 1:1 complexes appears similar to the formation of $[R_3P,AsMe_2]^+Cl^-$ by the reaction of trialkylphosphines and dimethylchloroarsine,[46] however, although the formulation $[R_3X,M^{III}Cl_2]^+Cl^-$ might hold for the 1:1 complexes, it is difficult to extend this to the other complexes. In view of the probable acceptor characteristics of MX_3 molecules other formulations involving p_π–d_π bonding might be expected. A decrease in P–N bond energy from 6·4 kcal. in Me_3N,PCl_3 to 3·1 kcal. in Me_3N,PBr_3 is either the result of the lower electronegativity of the bromine (leading to a lower tendency for the phosphorus to act as acceptor) or the consequence of the greater steric effect of the bromine.

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[41] Holmes, *J. Inorg. Nuclear Chem.*, 1960, **12**, 266.

[42] Greenwood, Perkins, and Wade, *J.*, 1957, 4345.

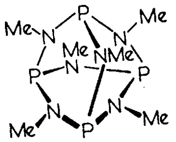
[43] Trost, *Canad. J. Chem.*, 1954, **32**, 356.

[44] Holmes and Bertaut, *J. Amer. Chem. Soc.*, 1958, **80**, 2980, 2983.

[45] Holmes, *J. Amer. Chem. Soc.*, 1960, **82**, 5285.

[46] Coates and Livingstone, *Chem. and Ind.*, 1958, 1366.

Although phosphoryl chloride functions as a donor and arsenic and antimony trichloride as acceptors, complexes between these compounds appear to be best described in terms of purely dipole–dipole interaction (comparable with the solvates referred to earlier). The compounds $AsCl_3,POCl_3$ and $SbCl_3,2POCl_3$ [33] are shown by Raman and infrared spectra not to involve ionic species.[47] Similar observations cover the systems $BiCl_3$–$POCl_3$, $AsCl_3$–Me_2CO, and $SbCl_3$–Me_2CO, in which the compounds $BiCl_3,2POCl_3$, $AsCl_3,Me_2CO$, and $SbCl_3,2Me_2CO$ occur.[48,49] A 1:1 compound between antimony trifluoride and dioxan is reported.[50]



(7) $P_4N_6Me_6$

The adducts of ammonia, primary and secondary amines, and the trihalides cover a wide range of molecular ratios. No systematic investigation has been undertaken. However, in the case of phosphorus trichloride and ammonia at −80° the triamide, $P(NH_2)_3$, is obtained, and at −20° the compound $[\cdot NH\cdot P(NH_2)\cdot]_x$. No evidence of simple addition compounds of the type PCl_3,xNH_3 is found.[51] Phosphorus trichloride with an excess of methylamine yields the compound (7), $P_4N_6Me_6$ [52] and with aniline the compound $[\cdot NPh\cdot P(NHPh)\cdot]_x$.[53] Reaction of the trifluoride and trichloride of arsenic with secondary amines gives simple dialkylamidodihalogenoarsenites $R_2N\cdot AsX_2$; with primary amines, hydrogen halide is readily eliminated from the products to give alkylimidohalogenoarsenites $(\cdot NR\cdot AsX\cdot)_x$.[54]

The list of addition compounds of the trihalides is long and contains many compounds of unexpected composition, whose structures are unknown. The application of modern techniques is of importance in this field; already certain misconceptions have been revealed, for example the reported addition compounds of arsenic trichloride and tribromide with copper and silver metal, *e.g.*, $AsBr_3,3Ag$, $2AsCl_3,7Cu$, have now been shown by *X*-ray diffraction to consist of a mixture of silver(I) or copper(I) halides with amorphous arsenic.[55] The addition compound $2AsF_3,3SO_3$ has been shown by nuclear magnetic resonance to have the complex structure (8).[56]

[47] Kinnell, Lindqvist, and Zackrisson, *Acta Chem. Scand.*, 1959, **13**, 1159.

[48] Zackrisson and Alden, *Acta Chem. Scand.*, 1960, **14**, 994.

[49] Lindqvist and Einarsson, *Acta Chem. Scand.*, 1959, **13**, 420.

[50] Haendeler, Glazier, and Breck, *J. Amer. Chem. Soc.*, 1953, **75**, 3845.

[51] Becke-Goehring and Schulze, *Chem. Ber.*, 1958, **91**, 1188.

[52] Holmes and Forstner, *J. Amer. Chem. Soc.*, 1960, **82**, 5509.

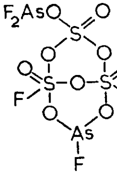
[53] Michaelis and Schroeter, *Ber.*, 1894, **27**, 491; Grimmel, Guenther, and Morgan, *J. Amer. Chem. Soc.*, 1946, **68**, 539; Goldschmidt and Lautenschlager, *Annalen*, 1953, **580**, 68.

[54] Olah and Oswald, *Canad. J. Chem.*, 1960, **38**, 1428, 1431.

[55] Rudörff and Gelinek, *Chem. Ber.*, 1957, **90**, 2654.

[56] Gillespie and Oubridge, *Proc. Chem. Soc.*, 1960, 308.

One aspect of the trihalides of the phosphorus group which has been recently exploited, is their ability to form d_π–d_π bonds leading to compounds such as $Ni(PF_3)_4$, and $Ni(CO)_3(SbCl_3)$. The properties of the trihalides are considerably modified in these compounds, so that, for example, $Ni(PF_3)_4$ can be vaporised in the presence of steam without undue hydrolysis occurring.[57] The phosphorus trihalides are particularly favourable ligands for the platinum metals and many of the adducts have been known for a considerable time. Phosphorus trifluoride and platinum(II) chloride give two volatile compounds dichlorobis(trifluorophosphine)-$\mu\mu'$-dichlorodiplatinum, $(PF_3)_2Pt_2Cl_4$ and dichlorobis(trifluorophosphine)platinum, $(PF_3)_2PtCl_2$.[58] Phosphorus trifluoride exhibits a strong *trans*-effect and in this respect is similar to carbon monoxide. Both of these ligands bind by means of simple σ-bonds and also by a strong π-bond, formed by the overlap of filled *dp*-orbitals of the metal with vacant orbitals on the ligand.



(8)

The pentahalides and related compounds

Certain of the simple pentahalides of this group have been known for a long time; one in particular, phosphorus pentachloride, has played an important part in the development of chemical ideas, first as an example of equilibrium in thermal dissociation, then as a valency problem, and of recent times as an introduction to the extensive ionic chemistry of compounds of this type. Whilst it is common to talk of specific pentahalides this is in many cases merely a reference to the stoicheiometric composition and in no way reflects the structural state. It will be convenient to discuss initially our knowledge of those molecules that are of an unambiguous MX_5 or $MX_{5-n}Y_n$ form and then to survey the various other derived compounds. There are no examples of pentahalides of bismuth other than the fluoride.

Molecular Species.—There is little doubt concerning the molecular existence of the compounds PF_5, PCl_5, PCl_2F_3, PCl_4F, AsF_5, SbF_5, $SbCl_5$, $SbCl_2F_3$, $SbCl_3F_2$, and $SbCl_4F$. That of others, such as PCl_3F_2, PBr_3F_2, PBr_4F, and $SbBr_2F_3$, is less certain. The number of possible species, even excluding stereoisomers, which might be obtained by allowing for simple and mixed fluorides, chlorides, bromides, and iodides of phosphorus, arsenic and antimony, is over 150, only about a tenth having so far been recognised.

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[57] Wilkinson, *J. Amer. Chem. Soc.*, 1951, 73, 5502.
[58] Chatt and Williams, *J.*, 1951, 3061.

The simple halides are prepared by direct reaction of an excess of the halogen with the element. Fluorides are conveniently prepared by fluorination of the chlorides. The mixed halides are prepared by the addition of halogen to the appropriate trihalide, *e.g.*, PCl_2F_3,[59,60] PCl_3F_2,[61] PCl_4F,[61] PBr_2F_3,[62] PBr_3F_2,[19] PBr_4F,[19,63] $SbCl_2F_3$,[64,65] $SbCl_3F_2$,[64,66] $SbBr_2F_3$.[67] Molecular PCl_4F is one of the products of the pyrolysis of $[PCl_4]^+[PF_6]^-$ in arsenic trichloride suspension[68] and molecular $SbCl_4F$ can be obtained by the action of arsenic trifluoride on antimony pentachloride.[69] The direct addition of fluorine to a trihalide has not yet been accomplished. The reaction of fluorine and phosphorus trichloride in the vapour phase leads to appreciable yields of $[PCl_4]^+[PF_6]^-$ together with molecular PCl_4F.[70]

The reaction of halogen with trihalide to give a pentahalide has not been closely studied. It is generally an exothermic reaction, which occurs readily on direct mixing. In the case of phosphorus trifluoride and chlorine the reaction, being homogeneous, proceeds very slowly in the gaseous phase at room temperature.[71] However in the liquid phase the reaction is rapid.[59] In a stainless steel vessel reaction in the gas phase leads to only phosphorus pentafluoride and a large amount of solid probably $[PCl_4]^+[PF_6]^-$.[60]

For most of the compounds above, evidence of the molecular form is largely indirect. Examination of the molecular structure of PF_5,[72] PCl_5,[73] PF_3Cl_2,[72] AsF_5,[74] and $SbCl_5$,[73] in the vapour phase shows all to possess the expected general features of the trigonal bipyramid. In the case of phosphorus pentachloride and antimony pentachloride the apical bonds are longer than the equatorial bonds (PCl_5, apical 2·19 ± 0·02, equatorial 2·04 ± 0·06; $SbCl_5$, apical 2·43 ± 0·06, equatorial 2·31 ± 0·06Å). The extra repulsion exerted on the bonding pairs in the apical positions relative to those in equatorial positions can explain this elongation; alternatively the explanation has been given in terms of incomplete hybridisation leading to a set of three sp^2 equatorial bonds, and a further set of two dp apical bonds. Antimony pentachloride forms a molecular lattice in the solid

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[59] Kennedy and Payne, *J.*, 1959, 1228.
[60] Muetterties, Bither, Farlow, and Coffman, *J. Inorg. Nuclear Chem.*, 1960, **16**, 52.
[61] Booth and Bozarth, *J. Amer. Chem. Soc.*, 1939, **61**, 2927.
[62] Moissan, *Compt. rend.*, 1885, **100**, 1348.
[63] Kolditz and Bauer, *Z. anorg. Chem.*, 1959, **302**, 241.
[64] Ruff, Zedner, Knoch, and Graf, *Ber.*, 1909, **42**, 4021.
[65] Henne and Trott, *J. Amer. Chem. Soc.*, 1947, **69**, 1820.
[66] Swarts, *Bull. Class Sci., Acad. roy. Belg.*, 1895, (3), **29** 874.
[67] Henne, U. S. P., 1,984,480, (1931).
[68] Kolditz, *Z. anorg. Chem.*, 1956, **286**, 307.
[69] Kolditz, *Z. anorg. Chem.*, 1957, **289**, 128.
[70] Payne, unpublished results.
[71] Wilson, *J. Amer. Chem. Soc.*, 1958, **80**, 1338.
[72] Braune and Pinnow, *Z. phys. Chem.*, 1937, *B*, **35**, 239; Brockway and Beach, *J. Amer. Chem Soc.*, 1938, **60**, 1836; Gutowsky and Hoffman, *J. Chem. Phys.*, 1951, **19**, 1259.
[73] Roualt, *Ann. Phys.*, 1940, **14**, 78.
[74] Akers, *Diss. Abs.*, 1955, 1638.

and here Sb–Cl apical = 2·34 Å, Sb–Cl equatorial = 2·29 Å;[75] the elongation appears to be appreciably reduced by crystal-lattice forces. In PCl_2F_3 in accord with the ideas of repulsion of bonded and non-bonded pairs, the chlorine atoms are in the apical positions and the fluorines in the equatorial positions.

The dissociation of the phosphorus pentachloride in the vapour to give phosphorus trichloride and chlorine is familiar and has been studied on many occasions. Antimony pentachloride behaves in a similar way;[76] dissociation in each case at 1 atmosphere amounts to a few per cent at 100°C. PF_5, AsF_5, and SbF_5 have not been observed to undergo such reversible thermal dissociation. PCl_2F_3 shows no dissociation up to 150°, above this temperature disproportionation (partially reversible) occurs. Indirect evidence suggests that PCl_4F dissociates reversibly to phosphorus dichlorofluoride and chlorine.[15] Ready thermal dissociation appears to be restricted to PCl_5, $SbCl_5$ and PCl_4F, in which chlorine atoms are in adjacent positions and hence intramolecular elimination of chlorine is easy. In PCl_2F_3 in which the chlorine atoms are in the apical position the dissociation reactions does not occur. There is no evidence for the existence of phosphorus pentabromide in the vapour.[77] For many of the pentahalides reliable molecular-weight data in the vapour phase are missing. In the case of antimony pentafluoride preliminary results on the molecular weight suggest that appreciable association occurs; values as high as 1230 (SbF_5 = 217) just above the boiling point have been obtained.[78] P_2Cl_{10} species have been recognised mass spectrometrically in the vapour.[15]

Little information on the liquid state is available. All pentahalides so far examined appear to have low or very low electrical conductance and with the exception of antimony pentafluoride are, non-associated, mobile liquids. Antimony pentafluoride is a viscous liquid, shown by nuclear magnetic resonance studies to consist of chains of SbF_6 groups, each sharing two fluorines with two neighbours.[79]

Ionic and other less well-defined Species.—There are now several pentahalides which are recognised as possessing ionic lattices. In only a few cases has the evidence for an ionic lattice been obtained directly from *X*-ray examinations, more often the evidence has been obtained indirectly from conductance or other properties of solutions in solvents known to favour break down of ionic lattices. Phosphorus pentachloride was the first compound in which an ionic lattice ($[PCl_4]^+[PCl_6]^-$) was recognised.[80] Solutions of phosphorus pentachloride in various polar solvents are electrolytic conductors and in methyl cyanide the ions $[PCl_4]^+$ and $[PCl_6]^-$

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[75] Ohlberg, *J. Amer. Chem. Soc.*, 1959, **81**, 811.

[76] Braune and Tiedje, *Z. anorg. Chem.*, 1926, **152**, 39.

[77] Harris and Payne, *J.*, 1958, 3732.

[78] Hubb, Peacock, and Robinson, unpublished results, 1951. See also Dodd and Robinson, "Experimental Inorganic Chemistry," Elsevier, New York, 1954, p. 215.

[79] Hoffman, Holder, and Jolly, *J. Phys Chem*, 1958, **62**, 364.

[80] Clarke, Powell, and Wells, *J.*, 1942, 642.

were identified by transport experiments.[81] The exchange of radioactive chloride ion and the phosphorus pentachloride in methyl cyanide solution shows clearly that the $[PCl_6]^-$ anion is less resistant to attack by chloride ion than the $[PCl_4]^+$ cation.[82] Likewise the ready formation of $[PCl_4]^+[PF_6]^-$ by the action of arsenic trifluoride on a solution of phosphorus pentachloride in arsenic trichloride is evidence for the relative ease of attack on the anion.[83] The P–Cl distances in cation and anion of 1·98 Å and 2·06 Å, respectively, suggest that in the former (tetrahedral form) the binding is stronger. In carbon tetrachloride solution the molecular weight suggests that association may occur ($M = 259$ at a concn. of 0·0241M and 473 at 0·0959M. PCl_5, $M = 208$).[82] Exchange experiments involving molecular chlorine and phosphorus pentachloride in carbon tetrachloride solutions show that the five chlorines attached to phosphorus are not equally reactive. The results can be interpreted to show that three chlorine atoms react more rapidly than the other two. The exchange may involve, as a transition state, the addition of the halogen molecule to the equatorial group.[84]

Although solid phosphorus pentabromide consists of $[PBr_4]^+$ and Br^- ions,[85] in methyl cyanide it is an electrolytic conductor in which the ions, as shown by transport experiments, are $[PBr_4]^+$ and $[PBr_6]^-$. The anion is presumably on the limit of stability, being stabilised only by solvation. Complexes involving the $[PBr_6]^-$ anion have not been reported yet.[86] Conductance, of a lower order, is also observed in solutions in arsenic trichloride,[87] sulphur dioxide,[87] bromine,[88] and nitrobenzene.[89] In nitrobenzene the equilibrium between phosphorus tribromide and bromine appears to involve both undissociated PBr_5 and PBr_7,[86] but there is no indication as to the nature of these species. Fluorination by arsenic trifluoride of phosphorus pentabromide suspended in carbon tetrachloride or carbon disulphide gives $[PBr_4]^+[PF_6]^-$, the reaction being more complex than the fluorination of $[PCl_4]^+[PCl_6]^-$ in arsenic trichloride, but again evidence of the resistance of the cation to attack is obtained.[90]

Pyrolysis of $[PCl_4]^+[PF_6]^-$ leads to both PCl_4F and $[PCl_4]^+F^-$.[68] The change from molecular PCl_4F to ionic $[PCl_4]^+F^-$ has been observed to occur by a first-order reaction.[91] Pyrolysis of $[PBr_4]^+[PF_6]^-$ does not yield $[PBr_4]^+F^-$ which must be prepared by the action of bromine on phosphorus dibromofluoride. In this reaction the molecular form appears to exist at

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[81] Payne, *J.*, 1953, 1052.
[82] Kolditz and Hass, *Z. anorg. Chem.*, 1958, **294**, 191.
[83] Kolditz, *Z. anorg. Chem.*, 1956, **284**, 144.
[84] Downs and Johnson, *J. Amer. Chem. Soc.*, 1955, **77**, 2098.
[85] van Driel and MacGillavry, *Rec. Trav. chim.*, 1943, **62**, 167; Powell and Clark, *Nature*, 1940, **145**, 971.
[86] Harris and Payne, *J.*, 1956, 4617.
[87] Walden, *Z. phys. Chem.*, 1903, **43**, 434.
[88] Plotnikov, *Z. phys. Chem.*, 1904, **48**, 230.
[89] Finkelstein, *Z. phys. Chem.*, 1925, **115**, 306.
[90] Kolditz and Feltz, *Z. anorg. Chem.*, 1957, **293**, 155.
[91] Kolditz, *Z. anorg. Chem.*, 1957, **293**, 147.

—30° and below, but is transformed by heat into the stable ionic form.[63] The compound $[PCl_4]^+[PCl_5F]^-$ contaminated with $[PCl_4]^+F^-$ is the product of the controlled pyrolysis of $[PCl_4]^+[PF_6]^-$ suspended in carbon tetrachloride. Above 110° it disproportionates to PCl_5 and PCl_4F.[15] The analogous compound $[PCl_4]^+[PCl_5Br]^-$ is the product of the addition of bromine to phosphorus trichloride in arsenic trichloride solution. The nature of the anion was established, in addition to evidence from the analytical and conductance data, by direct fluorination with arsenic trifluoride to give $[PCl_4]^+[PF_6]^-$.[92] Despite the considerable amount of work reported above, relatively few of the numerous cations and anions derived from single and mixed pentahalides have been recognised. The $[PCl_4]^+$ cation is clearly a particularly stable species but with a suitable synthetical route substituted $[PX_4]^+$ cations should be obtainable. Amongst the chlorofluoro-anions, $[PCl_4F_2]^-$, $[PCl_3F_3]^-$, $[PCl_2F_4]^-$, and $[PClF_5]^-$ remain to be recognised. No iodide species has yet been encountered. In addition to the large number of species made possible by varying the nature of the attached halogen, there is the added feature of stereoisomerism, which might be encountered in certain of the octahedral anions, to increase still further the total number of individual compounds.

The phosphorus trichloride–bromine system is complicated and many groups of workers have investigated it without complete clarification. Since it was first observed in 1847 that phosphorus trichloride and bromine reacted together exothermically, only one compound of certain constitution has been produced $[PCl_4]^+[PCl_5Br]^-$.[92] Recent Russian work[93] on the system has led to the recognition of two maxima in the phase diagram at the compositions PCl_3Br_4 and PCl_3Br_{18}, and compounds corresponding to these compositions have been reported. A further composition PCl_3Br_8 appeared of significance from viscosity data. In nitrobenzene the compounds behaved as a series of quasiphosphonium compounds $[PCl_3Br]^+[BrBr_{2n}]^-$, with $n = 1$, 3, and 8. In American work no simple solid phase was found. Instead, an unstable aggregate of composition $PCl_{3\cdot0}Br_{5\cdot7}$ which broke down to a compound $PCl_{4\cdot67}Br_{0\cdot33}$, was obtained.[94] A cryoscopic study of phosphorus trichloride and bromine in nitrobenzene shows the existence of PX_5 and PX_7 species.[95] In all the compounds so far reported, only the $[PCl_4]^+[PCl_5Br]^-$ and the more complex $PCl_{4\cdot67}Br_{0\cdot33}$, appear to possess any degree of stability. Even the former breaks down in non-polar solvents to give PCl_5 and PBr_5. The existence of solids containing such a high proportion of bromine as PCl_3Br_{18} may in fact arise from solvation by bromine molecules, or the formation of a type of inclusion compound. Several adducts with carbon tetrachloride have been found, *e.g.* PBr_4F, $2CCl_4$, $PBr_5,2CCl_4$.

With the existence of such an extensive group of ionic compounds in the

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[92] Kolditz and Feltz, *Z. anorg. Chem.*, 1957, **293**, 286.
[93] Kialkov and Kuz'menko, *Zhur obshchei Khim.*, 1951, **21**, 33; 1952, **22**, 1290, 1335.
[94] Popov, Geske, and Baenziger, *J. Amer. Chem. Soc.*, 1956, **78**, 1793.
[95] Harris and Payne, *J.*, 1956, 4613.

case of phosphorus, equally extensive ranges of compounds should be expected for arsenic and antimony, if not bismuth. However, the results to date are somewhat limited, being centred on the $[AsCl_4]^+$ cation.

The failure of numerous attempts to prepare arsenic pentachloride, even in an ionic form, is significant. The $AsCl_5$ molecule and the $[AsCl_6]^-$ ion are presumably inherently less stable than those involving phosphorus or antimony. The core of phosphorus in the quinquevalent state is s^2p^6, whereas in arsenic and antimony it is d^{10}; promotion energy data suggest that the $4s$ and $4p$ and the $4d$ orbitals in arsenic will be separated by an appreciably larger energy difference than the $3s$, $3p$ and $3d$ in phosphorus or the $5s$, $5p$, and $5d$ orbitals in antimony, with a consequent lowering of the stability. The extent of the effect will however depend on the electronegativity of the bonding atom, being less for fluorine than for chlorine. In the tetrahedral state other factors, notably that of π-bonding, are involved and the $[AsCl_4]^+$ cation is comparable to $[PCl_4]^+$ in stability. Compounds such as $AsCl_5,PCl_5$ [96] have been known for a long time and can now be recognised as $[AsCl_4]^+[PCl_6]^-$,[97] others are $[AsCl_4]^+[SbCl_6]^-$,[98] and $[AsCl_4]^+[AsF_6]^-$.[99,100] An attempt to prepare the compound $AsCl_4^+F^-$ by the pyrolysis of $[AsCl_4]^+[AsF_6]^-$ in an analogous way to the disproportionation of $[PCl_4]^+F^-$ failed, the products being only arsenic trifluoride and chlorine.[101] The series of $[AsCl_4]^+$ complexes is extensive, all involving anionic metal halide species, *e.g.*, $[GaCl_4]^-$, $[AlCl_4]^-$, etc. Many similar $[PCl_4]^+$ complex compounds are known.[102]

Only a few derivatives of the pentafluoride and pentachloride of antimony are known. The phase diagram of the SbF_5–$SbCl_5$ systems is complex, with at least six individual phases. $(SbF_5)_3(SbCl_5)_2$ and SbF_3Cl_2 were isolated as crystalline solids, but no further detail is available.[64] Much of this work has centred not on the isolation of the mixed pentachlorides but rather on the preparation and use of these compounds as fluorination catalysts and is reported only in the patent literature. The compound $[SbCl_4]^+F^-$ [69] is prepared by the fluorination of antimony pentachloride by arsenic trifluoride.

Bismuth pentafluoride is the product of the action of fluorine on bismuth trifluoride at 500° and is a black solid with a high melting point. A series of addition compounds with LiF, NaF, KF, and AgF are reported.[103]

The complexes of the pentahalides are numerous; some are clearly of the type $[M^VX_4]^+Y^-$ or $Y^+[M^VX_6]^-$ but many are obviously more complicated, *e.g.*, $(SbF_5)_2Te$ or SbF_5NO_2.[104] No further reference will be made

[96] Cronander, *Bull. Soc. chim. France*, 1873, [2], **19**, 499.
[97] Gutmann, *Z. anorg. Chem.*, 1951, **264**, 151.
[98] Gutmann, *Monatsh.*, 1951, **86**, 473.
[99] Kolditz, *Z. anorg. Chem.*, 1955, **280**, 313.
[100] Dess, Parry and Vidale, *J. Amer. Chem. Soc.*, 1956, **78**, 5730.
[101] Kolditz, *Z. anorg. Chem.*, 1957, **289**, 128.
[102] Groeneveld, *Rec. Trav. chim.*, 1952, **71**, 1152.
[103] Fischer and Rudzitis, *J. Amer. Chem. Soc.*, 1959, **81**, 6375.
[104] Aynsley, Peacock, and Robinson, *Chem. and Ind.*. 1951, 1117.

to the large number of obviously ionic complexes, which have been investigated largely by conductometric methods. Only one structure has been fully determined, namely, that of the complex, $SbCl_5$, $POCl_3$, in which the oxygen of the $POCl_3$ occupies one of the octahedral positions around the antimony:[105] similar complexes are formed with sulphoxides and sulphones.[49]

The tendency of phosphorus pentafluoride to form simple molecular complexes, apart from the $[PF_6]^-$ anion, is exemplified by the compounds PF_5,NMe_3 and $PF_5,CH_3{\cdot}CN$. Phosphorus pentafluoride thus exhibits the general acceptor properties of a Lewis acid with a wide range of bases such as ethers, sulphoxides, amines, amides, and esters.[60,106] This strong acceptor tendency makes phosphorus pentafluoride comparable with boron trifluoride in catalytic activity, *e.g.*, in polymerisations.[106] Adducts of the pentahalides with trimethylamine and trimethylphosphine are $(Me_3P)_2,PCl_5$, $(Me_3N),SbCl_5$, $Me_3P,SbCl_5$, and $(Me_3P)_2,SbCl_5$. Reaction of the pentachlorides with trimethylarsine and trimethylstibine leads to appreciable reduction, often as far as the elements. Phosphorus pentachloride appears to be more readily reduced than antimony pentachloride in these reactions.[44]

The reaction of the pentahalides with ammonia and primary and secondary amines has been reported, but no simple products or a clear picture of the reaction has resulted.[107,108] The reaction of phosphorus pentachloride and ammonium chloride leading to the phosphonitrilic chlorides has been widely examined.[109]

Other halides of the phosphorus group elements

Halides containing bonds between the elements of the group are so far limited to compounds of the form M_2X_4 for phosphorus and arsenic, and to the compound Bi_4Cl_4.

P_2I_4 is readily prepared by the reaction of stoicheiometric amounts of iodine with white phosphorus dissolved in carbon disulphide. Its orange crystals dissociate irreversibly when heated, and are hydrolysed to a variety of products, among them hypophosphoric acid, containing a P–P bond. Solid P_2I_4 consists of a molecular lattice containing non-planar units with $\angle IPI = 102{\cdot}3°$ and $\angle IPP = 93{\cdot}9°$.[110] Its reactions have been very little studied. It is reported to give an adduct with boron tribromide, $P_2I_4,2BBr_3$.[111] P_2Cl_4 is formed when phosphorus trichloride and hydrogen are together submitted to an electrical discharge,[112] or when phosphorus trichloride alone is subjected to a high-voltage discharge between mercury

[105] Lindqvist and Bränden, *Acta Cryst.*, 1959, **12**, 642.
[106] Woolf, *J. Inorg. Nuclear Chem.*, 1956, **3**, 285.
[107] Becke-Goehring and Niedenzu, *Chem. Ber.*, 1957, **90**, 2072.
[108] Audrieth and Sowerby, *Chem. and Ind.*, 1959, 748.
[109] Paddock and Searle, *Adv. Inorg. Chem. Radiochem.*, 1959, **1**, 347.
[110] Leung and Waser, *J. Phys. Chem.*, 1956, **60**, 539.
[111] Tarible, *Comp. rend.*, 1907, **132**, 204.
[112] Besson and Fournier, *Compt. rend.*, 1910, **150**, 102.

electrodes.[113] Fluorination of P_2I_4 by antimony pentafluoride led mainly to phosphorus trifluoride and pentafluoride, however a small amount of a less volatile material of molecular weight approaching that of P_2F_4 was obtained.[114] The compound As_2I_4 is obtained by the reaction of stoicheiometric quantities of arsenic and iodine, and also by heating a mixture of arsenic and arsenic tri-iodide in carbon disulphide.[115] It is soluble in carbon disulphide, in which its molecular weight was determined ebullioscopically.[116] No antimony compounds of this type have been reported. Bismuth has been reported to give a dichloride, a dibromide, and a di-iodide, and also a monochloride. There has always been much doubt as to the dibromide and di-iodide, and discussion must await further investigation. The bismuth–chlorine system has been thoroughly investigated. No evidence of bismuth dichloride was obtained but the existence of a monochloride was confirmed. The monochloride forms shining black, diamagnetic crystals, recognised as containing a tetramer Bi_4Cl_4.[117]

The extent of the contributions to this relatively small field has been enormous, especially within the past decade, even so the subject is very far from complete and the general features are only just beginning to emerge. Considerable technical skill is involved in handling these halides, most of which are readily hydrolysed. That progress has been made in the past is the result of a determination to overcome many difficult problems of technique, and the future must equally depend on such careful, skilled, and determined experimentalists.

[113] Finch, *Canad. J. Chem.*, 1959, **37**, 1793.

[114] Harris, personal communication.

[115] Bamberger and Philipp, *Ber.*, 1881, **14**, 2644; Karantassis, *Bull. Soc. chim. France*, 1925, [4], **37**, 853.

[116] Hewitt and Winmill, *J.*, 1907, **91**, 962.

[117] Corbett, *J. Amer. Chem. Soc.*, 1958, **80**, 4757; *J. Phys. Chem.*, 1958, **62**, 1149.