Chapter 17

THE GROUP VB(15) ELEMENTS: PHOSPHORUS, ARSENIC, ANTIMONY, AND BISMUTH

17-1 Introduction

Phosphorus occurs mainly in minerals of the *apatite* family, $Ca_9(PO_4)_6 \cdot CaX_2$; X = F, Cl, or OH, which are the main components of amorphous phosphate rock, millions of tons of which are processed annually. The elements As, Sb, and Bi occur mainly as sulfide minerals, such as *mispickel* (FeAsS) or *stibnite* (Sb_2S_3).

Some properties of the elements are given in Table 8-5, and some general features and trends are noted in Chapter 8.

The valence shells of the atoms (ns^2np^3) are similar to the electron configuration of N, but beyond the similarity in stoichiometries of compounds such as NH_3 and PH_3, there is little resemblance in the chemistry between even P and N. Phosphorus is a true nonmetal in its chemistry but As, Sb, and Bi show an increasing trend to metallic character and cationic behavior.

The principal factors responsible for the differences between nitrogen and phosphorus group chemistry are those responsible for the C to Si differences, namely, (a) the diminished ability of the second-row element to form $p\pi$-$p\pi$ multiple bonds, and (b) the possibility of utilizing the lower lying $3d$ orbitals.

The first explains features such as the fact that nitrogen forms esters O═NOR, whereas phosphorus gives $P(OR)_3$. Nitrogen oxides and oxoacids all involve multiple bonds (Section 16-1), whereas the phosphorus oxides have single P—O bonds, as in P_4O_6, and phosphoric acid is $PO(OH)_3$ in contrast to $NO_2(OH)$.

The utilization of *d* orbitals has three effects. First, it allows some $p\pi$-$d\pi$ bonding as in $R_3P{=}O$ or $R_3P{=}CH_2$. Thus amine oxides, R_3NO, have only a single canonical structure ($R_3N^+{-}O^-$) and are chemically reactive, while P—O bonds are shorter than expected for the sum of single–bond radii, indicating multiple bonding, and are very strong, about 500 kJ mol^{-1}. Second, there is the possibility of expansion of the valence shell, whereas nitrogen has a covalency maximum of four. Thus we have compounds such as PF_5, $P(C_6H_5)_5$, $P(OCH_3)_6^-$, and PF_6^-.

Notice that for many of the five-coordinate species, especially of phosphorus, the energy difference between the trigonal bipyramidal and square pyramidal configurations is small, and such species are usually stereochemically nonrigid (Section 6-6).

When higher coordination numbers occur for the elements in the III oxidation state, as in $[SbF_5]^{2-}$, the structures take the form of a square pyramid. As discussed in Chapter 3, AB_5E systems such as these accommodate one lone pair (E), in addition to the five peripheral atoms (B), at the central atom (A).

Finally, while trivalent nitrogen and the other elements in compounds such as $N(C_2H_5)_3$, $P(C_2H_5)_3$, and $As(C_6H_5)_3$ have lone pairs and act as donors, there is a profound difference in their donor ability toward transition metals. This follows from the fact that although NR_3 has no low-lying acceptor orbitals, the others do have such orbitals, namely, the empty *d* orbitals. These can accept electron density from filled metal *d* orbitals to form $d\pi$-$d\pi$ bonds, as we shall discuss in detail later (Section 28-15).

17-2 The Elements

Phosphorus is obtained by reduction of phosphate rock with coke and sand in an electric furnace. Phosphorus distills and is condensed under water as P_4. Phosphorus allotropes have been discussed (Section 8-4).

$$2\ Ca_3(PO_4)_2 + 6\ SiO_2 + 10\ C = P_4 + 6\ CaSiO_3 + 10\ CO \qquad (17\text{-}2.1)$$

P_4 is stored under water to protect it from air in which it will inflame. Red and black P are stable in air but will burn on heating. P_4 is soluble in CS_2, benzene, and similar organic solvents; it is very poisonous.

The elements *As, Sb,* and *Bi* are obtained as metals (Section 8-5) by reduction of their oxides with carbon or hydrogen. The metals burn on heating in oxygen to give the oxides.

All the elements react readily with halogens but are unaffected by nonoxidizing acids. Nitric acid gives, respectively, phosphoric acid, arsenic acid, antimony trioxide, and bismuth nitrate, which nicely illustrates the increasing metallic character as the group is descended.

Interaction with various metals and nonmetals gives phosphides, arsenides, and the like, which may be ionic, covalent polymers or metal-like solids. Gallium arsenide (GaAs)—one of the so-called III–V compounds of a Group IIIB(13) and a Group VB(15) element—has semiconductor properties similar to those of Si and Ge.

There are a number of ligands that consist exclusively of Group VB(15) atoms. The P_3 ring forms an η^3 attachment to metals that are also stabilized by tripod ligands (Chapter 6), as in $LCoP_3$, where L = a tripod ligand. The P_4 molecule can serve as an η^1 or an η^2 ligand, for example, in $LNi(\eta^1\text{-}P_4)$ and *trans*-$[RhCl(PPh_3)_2(\eta^2\text{-}P_4)]$. The P_2 and As_2 molecules can bind to metals in a variety of side-on and bridging attachments that resemble those of acetylene (Chapter 29).

17-3 Hydrides (EH_3)

The stability of these EH_3 gases decreases in the series NH_3, PH_3, AsH_3, SbH_3, and BiH_3. The last two in the series are very unstable thermally. The average bond energies are N—H, 391; P—H, 322; As—H, 247; and Sb—H, 255 kJ mol^{-1}.

Phosphine (PH_3) is made by the action of acids on zinc phosphide. Pure PH_3 is not spontaneously flammable, but it often inflames owing to traces of P_2H_4 or P_4 vapor. It is exceedingly poisonous. Because of its poor ability to enter into hydrogen bonding, it is not associated in the liquid state, in contrast to the behavior of ammonia. Phosphine is sparingly soluble in water, and it is a very weak base. The proton affinities of PH_3 and NH_3 differ considerably, as indicated by the relative values of ΔH° for Reactions 17-3.1 and 17-3.2.

$$PH_3(g) + H^+(g) = PH_4^+(g) \quad \Delta H^\circ = -770 \text{ kJ mol}^{-1} \tag{17-3.1}$$

$$NH_3(g) + H^+(g) = NH_4^+(g) \quad \Delta H^\circ = -866 \text{ kJ mol}^{-1} \tag{17-3.2}$$

Although PH_3 is the weaker base, it does react with gaseous HI to give PH_4I as unstable colorless crystals. Phosphonium iodide (PH_4I) is completely hydrolyzed by water, as in Reaction 17-3.3.

$$PH_4I(s) + H_2O = H_3O^+ + I^- + PH_3(g) \tag{17-3.3}$$

It is the low basicity of PH_3 that forces the equilibrium in Reaction 17-3.3 to lie far to the right. Phosphine is used industrially to make organophosphorus compounds (Chapter 29).

17-4 Halides (EX_3, EX_5) and Oxohalides

The trihalides, except PF_3, are obtained by direct halogenation, keeping the element in excess. An excess of the halogen gives EX_5. The trihalides are rapidly hydrolyzed by water and are rather volatile; the gaseous molecules have pyramidal structures. The chlorides and bromides, as well as PF_3 and PI_3, have molecular lattices. The compounds AsI_3, SbI_3, and BiI_3 have layer structures based on hexagonal close packing of iodine atoms with the Group VB(15) atoms in octahedral holes. Bismuth trifluoride (BiF_3) is known in two forms, in both of which Bi has the coordination number eight, while SbF_3 has an intermediate structure in which SbF_3 molecules are linked through F bridges to give each Sb^{III} a very distorted octahedral environment.

Phosphorus trifluoride is a colorless, toxic gas, made by fluorination of PCl_3. It forms complexes with transition metals similar to those formed by CO (Section 28-15). Unlike the other trihalides, PF_3 is hydrolyzed only slowly by H_2O, but it is attacked rapidly by alkalis. It has no Lewis acid properties.

Phosphorus trichloride is a low-boiling liquid that is hydrolyzed by water to give phosphorous acid. It reacts with oxygen to give $OPCl_3$. Figure 17-1 illustrates some of the important reactions of PCl_3. Many of these reactions are typical of other EX_3 compounds and also, with obvious changes in formulas, of $OPCl_3$ and other oxo halides.

Arsenic trihalides are similar to those of phosphorus. Antimony trichloride ($SbCl_3$) differs in that it dissolves in a limited amount of water to give a clear solution that, on dilution, gives insoluble oxo chlorides such as SbOCl and $Sb_4O_5Cl_2$. No simple Sb^{3+} ions exist in the solutions. Bismuth trichloride ($BiCl_3$), a white, crystalline solid, is hydrolyzed by H_2O to BiOCl, but this reaction is reversible.

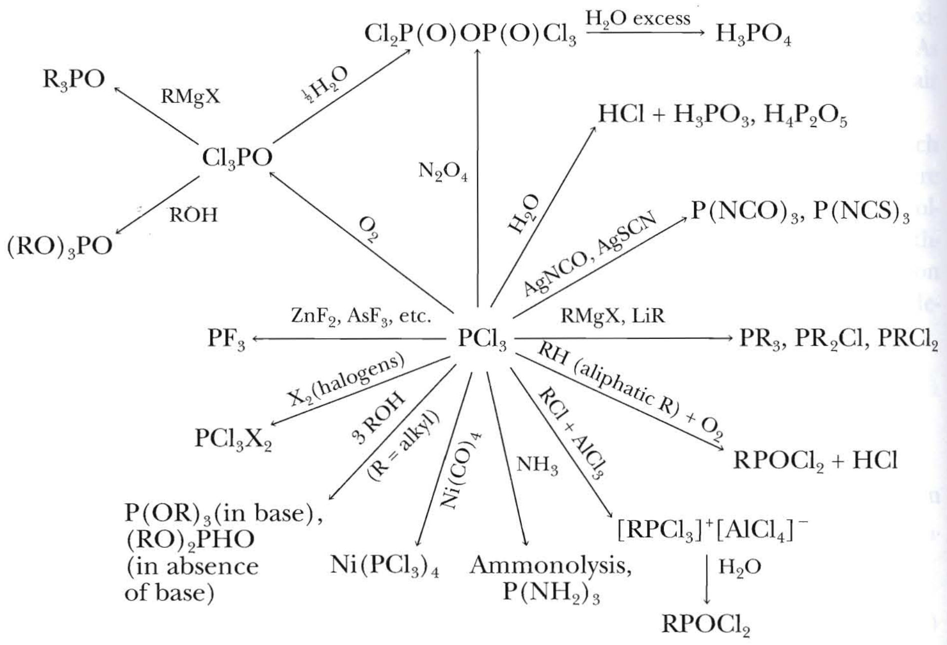


Figure 17-1 Some important reactions of PCl_3. Many of these are typical of other EX_3 and OEX_3 compounds.

$$\mathrm{BiCl_3 + H_2O \rightleftharpoons BiOCl + 2\,HCl} \qquad (17\text{-}4.1)$$

Phosphorus pentafluoride (PF_5) is prepared by the interaction of PCl_5 with CaF_2 at 300–400 °C. It is a very strong Lewis acid and forms complexes with amines, ethers, and other bases, as well as with F^-, in which phosphorus becomes six coordinate. However, these organic complexes are less stable than those of BF_3 and are rapidly decomposed by water and alcohols. Like BF_3, PF_5 is a good catalyst, especially for ionic polymerization. Arsenic pentafluoride (AsF_5) is similar.

Antimony pentafluoride (SbF_5) is a viscous liquid (bp 150 °C). Its association is due to polymerization through fluorine bridging. The crystal has cyclic tetramers. Its main use is in "superacids" (Section 7-13).

The compounds AsF_5, SbF_5, and PF_5 are potent fluoride ion acceptors, forming MF_6^- ions. The PF_6^- ion is a common and convenient *noncomplexing* anion.

Phosphorus(V) chloride has a trigonal bipyramidal structure in the gas, melt, and solution in nonpolar solvents, but the solid is $[PCl_4]^+[PCl_6]^-$, and it is ionized in polar solvents like CH_3NO_2. The tetrahedral PCl_4^+ ion can be considered to arise here by transfer of Cl^- to the Cl^- acceptor, PCl_5. Therefore, it is not surprising that many salts of the PCl_4^+ ion are obtained when PCl_5 reacts with other Cl^- acceptors, namely,

$$\mathrm{PCl_5 + TiCl_4 \longrightarrow [PCl_4^+]_2[Ti_2Cl_{10}]^{2-}} \quad \text{and} \quad \mathrm{[PCl_4]^+[Ti_2Cl_9]^-} \qquad (17\text{-}4.2)$$

$$\mathrm{PCl_5 + NbCl_5 \longrightarrow [PCl_4]^+[NbCl_6]^-} \qquad (17\text{-}4.3)$$

Solid *phosphorus pentabromide* is also ionic, but differs, being $PBr_4^+Br^-$. Antimony forms *antimony pentachloride,* a fuming liquid which is colorless when pure, but usually yellow. While it is a powerful chlorinating agent, it is also useful for removing chloride, as in Reaction 17-4.4.

$$CuCl_2 + 2\ PhCN + 2\ SbCl_5 \longrightarrow Cu(NCPh)_2^+ + 2\ SbCl_6^- \qquad (17\text{-}4.4)$$

Arsenic does not form a pentabromide, and the pentachloride decomposes above −50 °C. The cations AsX_4^+ (X = F, Cl, Br, and I) are all known.

Phosphoryl halides are X_3PO, in which X may be F, Cl, or Br. The most important one is Cl_3PO, which is obtainable by the reactions

$$2\ PCl_3 + O_2 \longrightarrow 2\ Cl_3PO \qquad (17\text{-}4.5)$$

$$P_4O_{10} + 6\ PCl_5 \longrightarrow 10\ Cl_3PO \qquad (17\text{-}4.6)$$

The reactions of Cl_3PO are much like those of PCl_3 (Fig. 17-1). Hydrolysis by water yields phosphoric acid. Cl_3PO also has donor properties and many complexes are known, in which oxygen is the ligating atom.

The oxohalides SbOCl and BiOCl are precipitated when solutions of Sb^{III} and Bi^{III} in concentrated HCl are diluted.

17-5 Oxides

The oxides of the Group VB(15) elements clearly exemplify two important trends that are manifest to some extent in all groups of the periodic table: (1) the stability of the higher oxidation state decreases with increasing atomic number, and (2) in a given oxidation state the metallic character of the elements, and, therefore, the basicity of the oxides, increase with increasing atomic number. Thus, P^{III} and As^{III} oxides are acidic, Sb^{III} oxide is amphoteric, and Bi^{III} oxide is strictly basic.

Phosphorus pentoxide is so termed for historical reasons but its correct molecular formula is P_4O_{10} [Fig. 17-2(*a*)]. It is made by burning phosphorus in excess oxygen. It has at least three solid forms. Two are polymeric but one is a white, crystalline material that sublimes at 360 °C and 1 atm. Sublimation is an excellent method of purification, since the products of incipient hydrolysis, which are the commonest impurities, are comparatively nonvolatile. This form and the vapor consist of molecules in which the P atoms are at the corners of a tetrahedron with six oxygen atoms along the edges. The remaining four O atoms lie along extended threefold axes of the tetrahedron. The P—O—P bonds are single but the length of the four apical P—O bonds indicates $p\pi$-$d\pi$ bonding, that is, P═O.

The compound P_4O_{10} is one of the most effective drying agents known at temperatures below 100 °C. It reacts with water to form a mixture of phosphoric acids whose composition depends on the quantity of water and other conditions. It will even extract the elements of water from many other substances which are themselves considered to be good dehydrating agents; for example, it converts pure HNO_3 into N_2O_5 and H_2SO_4 into SO_3. It also dehydrates many organic compounds, for example, converting amides into nitriles.

The *trioxide* is also polymorphous: one form contains discrete molecules (P_4O_6). The structure [Fig. 17-2(*b*)] is similar to that of P_4O_{10} except that the four nonbridging apical oxygen atoms in the latter are missing. P_4O_6 is a colorless, volatile compound that is formed in about 50% yield when P_4 is burned in

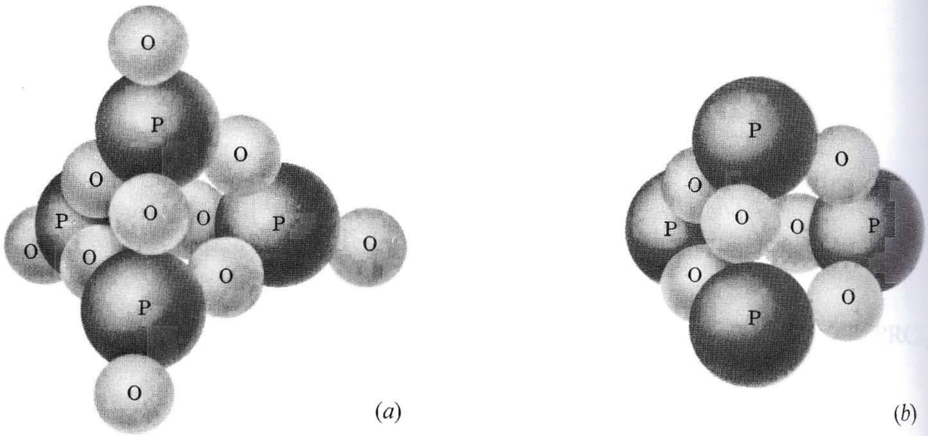


Figure 17-2 The structure of (*a*) P_4O_{10} and (*b*) P_4O_6.

a deficit of oxygen. The compounds As_4O_6 and Sb_4O_6 are similar to P_4O_6 both structurally and in their acidic nature. The compound Bi_2O_3 and the hydroxide, $Bi(OH)_3$, precipitated from bismuth(III) solution have no acidic properties.

17-6 Sulfides

Phosphorus and sulfur combine directly above 100 °C to give several sulfides, the most important being P_4S_3, P_4S_5, P_4S_7, and P_4S_{10}. Each compound is obtained by heating stoichiometric quantities of red P and sulfur. The compound P_4S_3 is used in matches. It is soluble in organic solvents such as carbon disulfide and benzene. The compound P_4S_{10} has the same structure as P_4O_{10}. The others also have structures based on a tetrahedral group of phosphorus atoms with P—S—P bridges or apical P═S groups. P_4S_{10} reacts with alcohols:

$$P_4S_{10} + 8\ ROH \longrightarrow 4(RO)_2P(S)SH + 2\ H_2S \qquad (17\text{-}6.1)$$

to give dialkyl and diaryl dithiophosphates that form the basis of many extreme-pressure lubricants, of oil additives, and of flotation agents.

Arsenic forms As_4S_3, As_4S_4, As_2S_3, and As_2S_5 by direct interaction. The last two can also be precipitated from hydrochloric acid solutions of As^{III} and As^{V} by hydrogen sulfide. As_2S_3 is insoluble in water and acids but is acidic, dissolving in alkali sulfide solutions to give thio anions. As_2S_5 behaves similarly. As_4S_4, which occurs as the mineral *realgar,* has a structure with an As_4 tetrahedron.

Antimony forms Sb_2S_3 either by direct interaction or by precipitation with H_2S from Sb^{III} solutions; it dissolves in an excess of sulfide to give anionic thio complexes, probably mainly SbS_3^{3-}. Antimony trisulfide (Sb_2S_3), as well as Bi_2S_3, possess a ribbonlike polymeric structure in which each Sb atom and each S atom is bound to three atoms of the opposite kind, forming interlocking SbS_3 and SSb_3 pyramids.

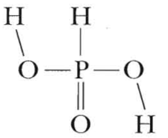
Bismuth gives dark brown Bi_2S_3 on treatment of Bi^{III} solutions with H_2S; it is not acidic.

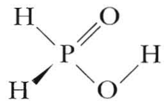
Some of the corresponding selenides and tellurides of As, Sb, and Bi have been studied intensively as semiconductors. (See Section 32-3.)

17-7 The Oxo Acids

The nature and properties of the oxoanions of the Group VB(15) elements have been discussed in Chapter 5. Here we discuss only the important acids and some of their derivatives.

Phosphorous acid is obtained when PCl_3 or P_4O_6 are hydrolyzed by water. It is a deliquescent colorless solid (mp 70 °C, pK = 1.26). The acid and its mono- and diesters differ from PCl_3 in that there are *four* bonds to P, one being P—H. The presence of hydrogen bound to P can be demonstrated by NMR or other spectroscopic techniques. Phosphorous acid is, hence, best written $HP(O)(OH)_2$ as in Structure 17-I. Hypophosphorous acid, H_3PO_2, has two P—H bonds (Structure 17-II). By contrast the triesters have only three bonds to phosphorus, thus being analogous to PCl_3. The trialkyl and aryl phosphites, $P(OR)_3$, have excellent donor properties toward transition metals and many complexes are known.

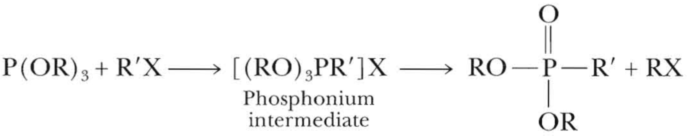

17-I


17-II

Phosphorous acid may be oxidized by chlorine or other agents to phosphoric acid, but the reactions are slow and complex. However, the triesters are quite readily oxidized and must be protected from air.

$$2(RO)_3P + O_2 = 2(RO)_3PO \tag{17-7.1}$$

These compounds also undergo the Michaelis-Arbusov reaction with alkyl halides, forming dialkyl phosphonates:


$$P(OR)_3 + R'X \longrightarrow \underset{\text{Phosphonium intermediate}}{[(RO)_3PR']X} \longrightarrow RO-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle OR}{|}}{P}}-R' + RX \tag{17-7.2}$$

Trimethylphosphite easily undergoes spontaneous isomerization to the dimethyl ester of methylphosphonic acid.

$$P(OCH_3)_3 \longrightarrow CH_3PO(OCH_3)_2 \tag{17-7.3}$$

Orthophosphoric acid, H_3PO_4, commonly called phosphoric acid, is one of the oldest known and most important phosphorus compounds. It is made in vast quantities, usually as 85% syrupy acid, by the direct reaction of ground phosphate rock with sulfuric acid and also by the direct burning of phosphorus and subsequent hydration of P_4O_{10}. The pure acid is a colorless crystalline solid (mp 42.35 °C). It is very stable and has essentially no oxidizing properties below 350–400 °C. At elevated temperatures it is fairly reactive toward metals, which reduce it, and it will attack quartz. *Pyrophosphoric acid* is also produced:

$$2\,H_3PO_4 \longrightarrow H_2O + H_4P_2O_7 \tag{17-7.4}$$

but this conversion is slow at room temperature.

The acid is tribasic: at 25 °C, $pK_1 = 2.15$, $pK_2 = 7.1$, $pK_3 \approx 12.4$. The pure acid and its crystalline hydrates have tetrahedral PO_4 groups connected by hydrogen bonds. Hydrogen bonding persists in the concentrated solutions and is responsible for the syrupy nature. For solutions of concentration less than about 50%, the phosphate anions are hydrogen bonded to the liquid water rather than to other phosphate anions.

Phosphates and the polymerized phosphate anions (for which the free acids are unknown) are discussed in Section 5-4. Large numbers of *phosphate esters* can be made by the reaction

$$OPCl_3 + 3\ ROH = OP(OR)_3 + 3\ HCl \qquad (17\text{-}7.5)$$

or by oxidation of trialkylphosphites. Phosphate esters, such as tributylphosphate, are used in the extraction of certain +4 metal ions (see Section 26-2) from aqueous solutions.

Phosphate esters are also of fundamental importance in living systems. It is because of this that their hydrolysis has been studied. Triesters are attacked by OH^- at P and by H_2O at C, depending on pH.

$$OP(OR)_3 \xrightarrow{^{18}OH^-} OP(OR)_2(^{18}OH) + RO^- \qquad (17\text{-}7.6)$$

$$OP(OR)_3 \xrightarrow{H_2{}^{18}O} OP(OR)_2(OH) + R^{18}OH \qquad (17\text{-}7.7)$$

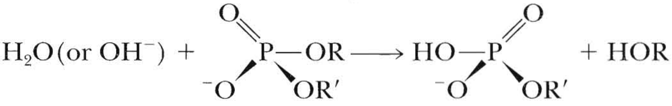
Diesters, which are strongly acidic, are completely in the anionic form at normal (and physiological) pH values.

$$RO{-}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle OH}{|}}{P}}{-}OR' \rightleftharpoons R'OPO_2OR^- + H^+ \qquad K \approx 10^{-1.5} \qquad (17\text{-}7.8)$$

These diesters are thus relatively resistant to nucleophilic attack by either OH^- or H_2O, which is the reason why enzymic catalysis is indispensible if we wish to achieve useful rates of reaction.

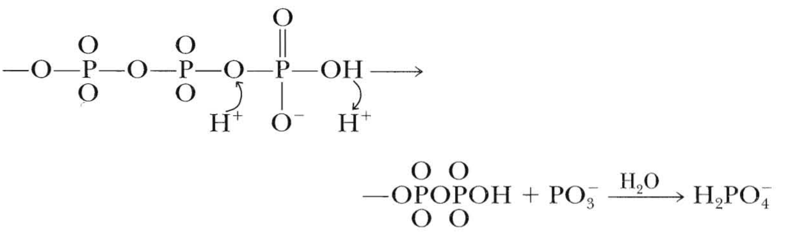
Much remains to be learned concerning the mechanisms of most phosphate ester hydrolyses, especially the many enzymic ones. Two important possibilities are the following:

1. One-step nucleophilic displacement (S_N2) with inversion.



(17-7.9)

2. Release of a short-lived *metaphosphate* group (PO_3^-) which rapidly recovers the four-connected orthophosphate structure.



(17-7.10)

17-8 Complexes of the Group VB(15) Elements

The main aqueous chemistry of Sb^{III} is in oxalato, tartrato, and similar hydroxy acid complexes.

The $[Sb(C_2O_4)_3]^{3-}$ ion forms isolable salts and has been shown to have the incomplete pentagonal bipyramid structure (Fig. 17-3) with a lone pair at one axial position. The tartrate complexes of antimony(III) have been greatly studied, and have been used medicinally as "tartar emetic" for more than 300 years. The structure of the anion in this salt, $K_2[Sb_2(d\text{-}C_4H_2O_6)_2]\cdot 3H_2O$, is shown in Fig. 17-4.

Only for bismuth is there a true cationic chemistry. Aqueous solutions contain well-defined hydrated cations, but there is no evidence for a simple aqua ion $[Bi(H_2O)_n]^{3+}$. In neutral perchlorate solutions the main species is $[Bi_6O_6]^{6+}$ or its hydrated form, $[Bi_6(OH)_{12}]^{6+}$, while $[Bi_6O_6(OH)_3]^{3+}$ is formed at a higher pH. The $[Bi_6(OH)_{12}]^{6+}$ species contains an octahedron of Bi^{3+} ions with an OH^- bridging each edge.

17-9 Phosphorus-Nitrogen Compounds

Many compounds are known with P—N and P=N bonds. The $R_2N—P$ bonds are particularly stable and occur widely in combination with bonds to other univalent groups, such as P—R, P—Ar, and P—halogen.

Phosphazenes are cyclic or chain compounds that contain alternating phosphorus and nitrogen atoms with two substituents on each phosphorus atom. The three main structural types are the cyclic trimer (Structure 17-III), cyclic tetramer (Structure 17-IV), and the oligomer or high polymer (Structure 17-V). The alternating sets of single and double bonds in Structures 17-III to 17-V are written for convenience but, in general, all P—N distances are found to be equal. It appears that they are of the order of about 1.5, since their lengths (1.56–1.61 Å) are appreciably shorter than expected (≈1.80 Å) for P—N single bonds. Hexachlorocyclotriphosphazene, $(NPCl_2)_3$, is a key intermediate in the

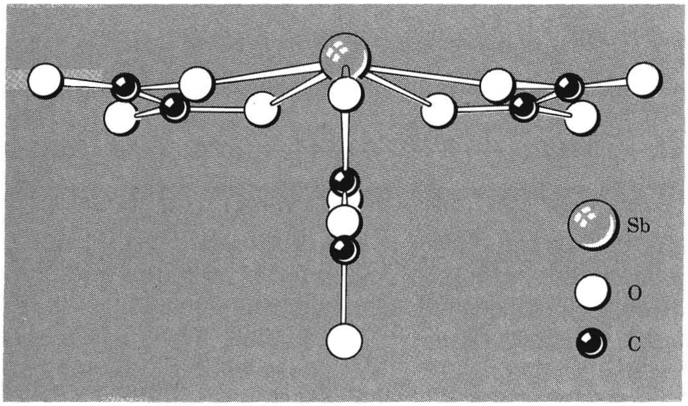


Figure 17-3 The $[Sb(C_2O_4)_3]^{3-}$ ion. Two oxalato, $C_2O_4^{2-}$, ligands are bidentate and one is monodentate. The oxygen donor atoms form a pentagonal base to the pyramid that is capped by Sb^{3+}.

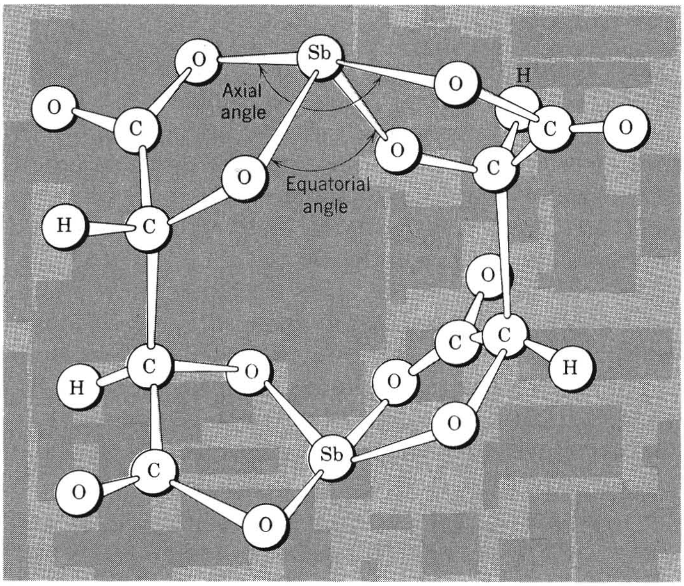
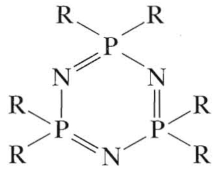
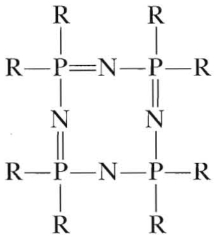


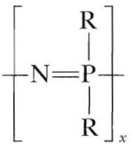
Figure 17-4 Geometry of the anion $[Sb_2(C_4H_2O_6)_2]^{2-}$. Water molecules link the anions into sheets by hydrogen bonding to carboxylate carbon atoms. [Reproduced by permission from Tapscott, R. E., Belford, R. L., and Paul, I. C., *Coord. Chem. Rev.*, **1969,** *4,* 323.]



17-III



17-IV



17-V

synthesis of many other phosphazenes and is manufactured by Reaction 17-9.1:

$$n\,PCl_5 + n\,NH_4Cl \xrightarrow{\text{in } C_2H_2Cl_4 \text{ or } C_6H_5Cl} (NPCl_2)_n + 4n\,HCl \qquad (17\text{-}9.1)$$

Reaction 17-9.1 produces a mixture of cyclic $(NPCl_2)_n$ compounds with $n = 3$, 4, 5, . . ., as well as some low-molecular weight linear polymers. Control of the reaction conditions can give 90% yields of either the compound with $n = 3$ or 4, which can be purified by extraction, recrystallization, or sublimation.

Structures are given in Fig. 17-5 of the cyclic trimer $[NPCl_2]_3$ and the tetramer $[NPClPh]_4$. Most six-membered rings such as $[NPX_2]_3$ are planar, while the larger rings are nonplanar. The fluoroderivatives, $[NPF_2]_n$ are planar, or nearly so, when $n = 3–6$.

The majority of the reactions of phosphazenes involve replacement of the substituents at phosphorus by nucleophiles (e.g., OH, OR, NR_2, or R) to give substituted derivatives, as in Reactions 17-9.2 to 17-9.4.

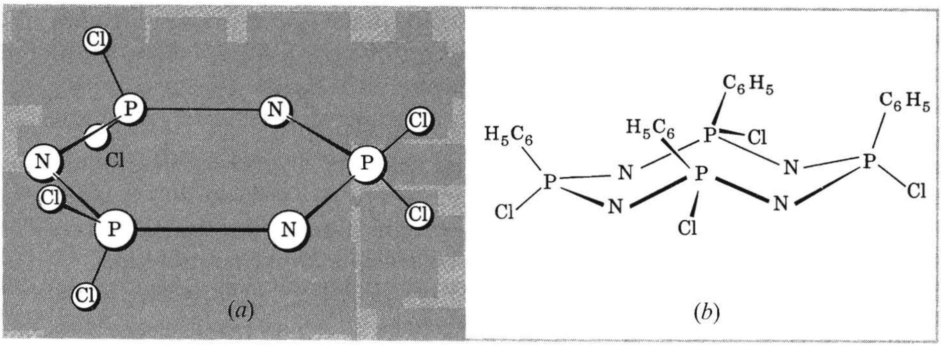


Figure 17-5 The structures of two representative cyclic phosphazenes (*a*) $[NPCl_2]_3$ and (*b*) all-*cis*-$[NPClPh]_4$.

$$[NPCl_2]_3 + 6\ NaOR \longrightarrow [NP(OR)_2]_3 + 6\ NaCl \qquad (17\text{-}9.2)$$

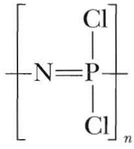
$$[NPCl_2]_3 + 6\ NaSCN \longrightarrow [NP(SCN)_2]_3 + 6\ NaCl \qquad (17\text{-}9.3)$$

$$[NPF_2]_3 + 6\ PhLi \longrightarrow [NPPh_2]_3 + 6\ LiF \qquad (17\text{-}9.4)$$

Hexachlorotriphosphazene, $[NPCl_2]_3$, is especially susceptible to hydrolysis as in Reaction 17-9.5.

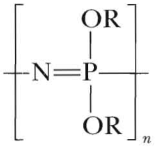
$$[NPCl_2]_3 + 6\ H_2O \longrightarrow [NP(OH)_2]_3 + 6\ HCl \qquad (17\text{-}9.5)$$

Hexachlorotriphosphazene undergoes a ring-opening polymerization above 250 °C to give the linear polydichlorophosphazene represented in Structure 17-VI. Although the dichloro polymer is hydrolytically unstable, it is readily converted, by reactions analogous to those of the cyclic trimer, to derivatives such as Structures 17-VII and 17-VIII. The properties of such polymers depend largely on the nature of the groups attached to phosphorus. Especially stable fibers and useful elastomers are obtained when the substituents are the perfluoroalkoxy groups, such as $CF_3(CF_2)_nCH_2O$, or the amides such as $-NHCH_3$.



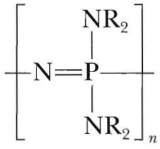
$$\left[-N{=}\overset{Cl}{\underset{Cl}{P}}- \right]_n$$

17-VI



$$\left[-N{=}\overset{OR}{\underset{OR}{P}}- \right]_n$$

17-VII



$$\left[-N{=}\overset{NR_2}{\underset{NR_2}{P}}- \right]_n$$

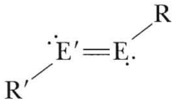
17-VIII

17-10 Compounds with Element-Element Double Bonds

Although N=N double bonds abound, other Group VB(15) E=E bonds were unknown until only recently. Now we have stable compounds that contain P=P, P=As, and As=As bonds. Similar E=E or E=E′ bonds involving antimony or bismuth are still unknown. The best calculations show that the HN=NH and HP=PH π-bond strengths are 256 and 150 kJ mol^{-1}, respectively. Thus the P=P π bond has considerable strength, but is weaker than the N=N π bond.

It is thermodynamics that makes obtaining compounds with E=E bonds difficult. Compounds with such bonds are unstable relative to cyclic oligomers of the type $(RP)_n$ or $(RAs)_n$. It has been found that cyclization can be thwarted by employing large R groups, partly because they diminish the rate of oligomerization, and partly because they reduce the stability of certain cyclic products.

Some of the E═E bond distances of RE═E′R′ molecules (Structure 17-IX)



17-IX

are listed in Table 17-1. The molecules are all planar in their X—E═E′═X portions, and the E═E′ distances are approximately 0.20 Å shorter than the corresponding E—E′ single-bond lengths.

Table 17-1 Bond Distances in Some RE═ER Compounds (Structure 17-IX)

E	E′	R[a]	R′	Distance E═E′ (Å)
P	P	Ar*	Ar*	2.034
P	P	$(Me_3Si)_3C$	$(Me_3Si)_3C$	2.014
P	As	Ar*	$(Me_3Si)_2CH$	2.124
As	As	Ar*	$(Me_3Si)_2CH$	2.224

[a] Ar* = 2,4,6-$(Me_3C)_3C_6H_2$.

Two of the principal methods of preparation are shown in Reactions 17-10.1 and 17-10.2.

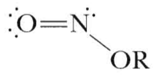
$$2\ RPCl_2 + 2\ Mg \longrightarrow RP{=}PR + 2\ MgCl_2 \tag{17-10.1}$$

$$RECl_2 + H_2E'R' \xrightarrow{\text{base}} RE = E'R' \tag{17-10.2}$$

17-11 Summary of Group Trends for the Elements of Group VB(15)

The list of periodic chemical properties from Section 8-11 can be used now, together with properties mentioned in Chapters 16 and 17, to summarize the periodic trends in the properties and reactivites of the elements of Group VB(15). Among these trends one finds increasing metallic character on descent of the group.

1. Nitrogen
   - (a) Forms covalent compounds almost exclusively, the only important exceptions being simple nitrides, such as Li_3N.
   - (b) Forms oxides that are covalent and serve as acid anhydrides.
   - (c) Forms halides (fluorides predominantly) that are covalent (e.g., NF_3 and NF_4^+).
   - (d) Forms hydrides that are covalent and nonhydridic.
   - (e) Forms esters of the type



   - (f) Frequently forms compounds that are electronically unsaturated, in which the unsaturation is exclusively of the $p\pi$–$p\pi$ type.
2. Phosphorus
   - (a) Forms covalent substances almost exclusively, most of which are electronically saturated.

   (b) Forms electronically saturated covalent oxides that serve as acidic anhydrides.
   (c) Forms low-valent (PX_3) and high-valent (PX_5) molecular halides that are readily hydrolyzed.
   (d) Forms a gaseous hydride, PH_3.
   (e) Forms electronically saturated esters of the type $P(OR)_3$.
   (f) Forms compounds that are electronically saturated, but which contain $p\pi$–$d\pi$ (rather than $p\pi$–$p\pi$) double bonding.
   (g) Compounds with P=P and P=As double bonds are becoming increasingly known.

3. Arsenic, Antimony, and Bismuth
   (a) Increasingly form ionic compounds rather than covalent ones on descent of the group.
   (b) Rather than simple ions such as M^{3+} or M^{5+}, form oxo ions such as SbO^+ and BiO^+.
   (c) Form oxides that are, on descent of the group, increasingly basic, as seen by the following trend: P and As (acidic oxides), Sb (amphoteric oxide), and Bi (basic oxide).
   (d) Form halides that are ionic and increasingly aggregated in the solid state through halide bridges, giving expanded coordination numbers at the metal ion.
   (e) Form increasingly weaker bonds to hydrogen.
   (f) Increasingly form more stable low-valent compounds than is typical of phosphorus, for example, the oxochloride of bismuth, BiOCl.
   (g) Compounds containing As=As and As=P double bonds are known, but the antimony and bismuth analogs are not.

17-12 Descriptive Summary of Reactions

Some of the important reactions of PCl_3 were given in Fig. 17-1. As a study aid, other reactions of phosphorus and its compounds are diagrammed in Figs. 17-6 and 17-7.

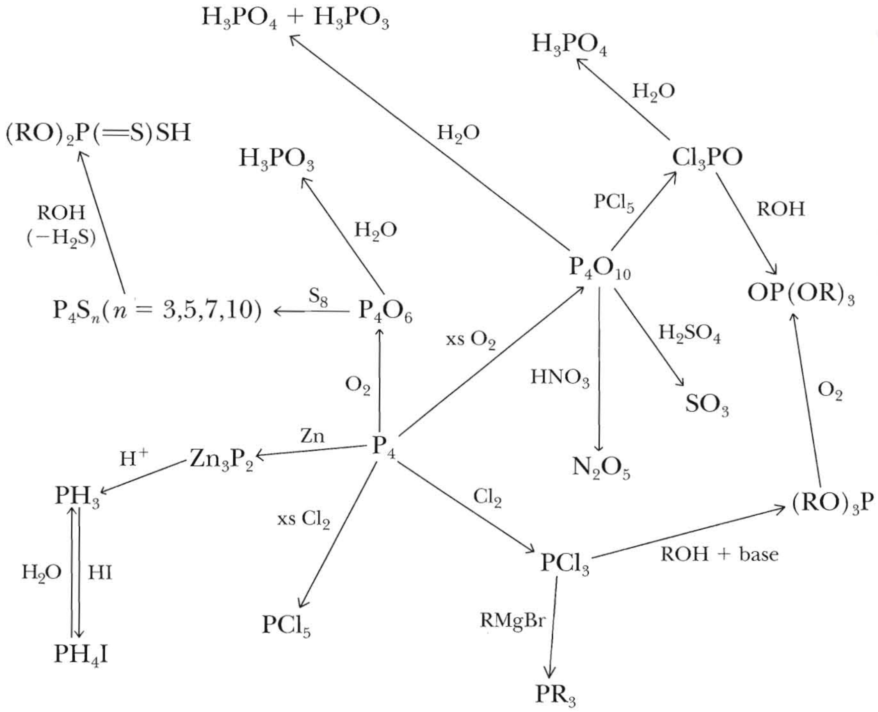


Figure 17-6 Some reactions of P_4 and its derivatives.

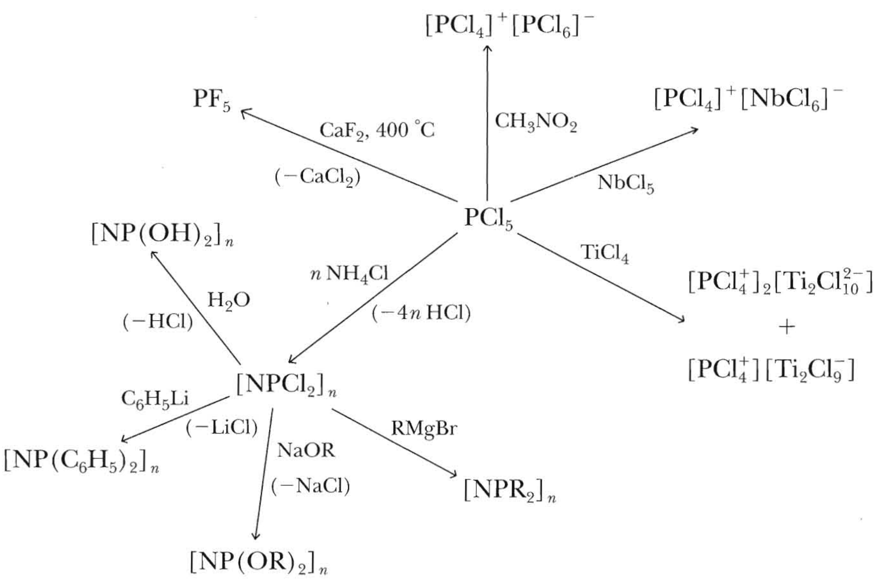


Figure 17-7 Some reactions of PCl_5.

STUDY GUIDE

Study Questions

A. Review

1. Why does phosphorus form P_4 molecules while nitrogen is N_2?
2. How are white and red phosphorus obtained from phosphate rock?
3. What are the principal factors responsible for the differences between the chemistry of nitrogen and the chemistry of phosphorus?
4. Explain the differences in (a) basicity and (b) donor ability toward transition metals of $N(CH_3)_3$ and $P(CH_3)_3$.
5. Write balanced equations for the reactions:
   (a) $P_4 + HNO_3$ (b) $AsCl_3 + H_2O$ (c) $POCl_3 + H_2O$
   (d) $P_4O_{10} + HNO_3$ (e) $P_4O_6 + H_2O$ (f) Zn_3P + dilute HCl
6. How is PCl_5 made? What is its structure in solutions and in the solid state?
7. Draw the structures of P_4O_{10} and As_4O_6.
8. What happens when H_2S is passed into acidic (HCl) solution of trivalent P, As, Sb, and Bi?
9. What are the structures of (a)phosphorous acid and (b) triethylphosphite?
10. What is the Michaelis–Arbusov reaction?
11. Why is pure phosphoric acid syrupy?
12. What is the structure of "tartar emetic"?
13. What are phosphazenes and how are they made?
14. Describe the interaction of water with $SbCl_3$ and $BiCl_3$.
15. How is PF_5 prepared? Give its main chemical properties.
16. Compare the structure and properties of nitric and phosphoric acids.

B. Additional Exercises

1. Discuss the importance of $d\pi$–$p\pi$ bonding for phosphorus. Give examples, with explanations for differences between the chemistries of N and P.
2. The compound NF_3 had no donor properties at all, but PF_3 forms numerous complexes with metals, for example, $Ni(PF_3)_4$. Explain.
3. Both P and Sb form stable pentachlorides but As does not. Why?
4. Compare the oxides of N with those of P.
5. Show with drawings the formation of the π bonds in R_3PO and $R_3P{=}CH_2$. What is the geometry at P in each case?
6. Draw the Lewis diagrams and discuss the geometries in PF_3, PF_5, and PF_6^-.
7. Write balanced equations for the following reactions.
   (a) The hydrolysis of PCl_3.
   (b) Air oxidation of PCl_3.
   (c) The hydrolysis of $BiCl_3$.
   (d) A synthesis of triethylphosphine.
   (e) Oxidation of PCl_3 by F_2.
   (f) Methanolysis of trichlorophosphine oxide.
   (g) Dissolution of PCl_5 in polar solvents.
   (h) Ammonolysis of PCl_3.
   (i) The synthesis of hexachlorotriphosphazene.

8. Suggest a synthesis of $[NP(CH_3)_2]_3$ starting with PCl_5, NH_4Cl, and a Grignard reagent.

9. How many isomers are possible for the partially substituted cyclic trimer $N_3P_3F_2Cl_4$?

10. Discuss the changes in hybridization, oxidation state, and geometry (use the AB_xE_y, classification scheme of Chapter 3 and VSEPR theory) that take place on forming

(a) SbF_6^- from SbF_5 (b) PCl_4^+ from PCl_5

(c) PCl_6^- from PCl_5 (d) $[SbF_5]^{2-}$ from SbF_5

11. Use the Lewis theory of acids and bases to discuss the reactions that are found in Problem 10, part B.

12. Beginning with PCl_5, and using two steps or fewer, list as many derivatives as can be made using the reactions of this chapter.

13. Give the chemical equation that represents each of the following reactions.

(a) Reduction of phosphate rock by carbon and sand.
(b) Hydrolysis of $OPCl_3$, using an excess of water.
(c) Reaction (condensation) of $OPCl_3$ with phenol.
(d) Oxidation of phosphorus with an excess of oxygen.
(e) Air oxidation of $P(OC_6H_5)_3$.
(f) Reaction of PCl_3 with C_2H_5MgBr.
(g) Reaction of PCl_3 with CH_3OH.
(h) $PCl_3 + AsF_3$
(i) $PCl_5 + H_2$

14. Of P_4, Sb_4 and Bi, which is the only element that forms an oxoacid on treatment with HNO_3? Explain.

15. Although compounds such as $OPCl_3$ are properly said to be electronically saturated, the OP linkage possesses considerable double-bond character. Explain.

16. Which elements of Group VB(15) form hydrolyzable halides of both the low- and high-valent variety?

17. Which elements of Group VB(15) form an amphoteric oxide?

18. Give the products to be expected on reaction of P_4 with

(a) A deficiency of oxygen.
(b) An excess of oxygen.
(c) A deficiency of Cl_2.
(d) An excess of Cl_2.
(e) S_8.

19. Give the principal P-containing product for each of the following:

(a) $PCl_5 + NbCl_5$
(b) PCl_5 dissolved in $CH_3NO_2(\ell)$
(c) Metathesis of PCl_5 and CaF_2 at 400 °C
(d) Thermal reaction of PCl_5 and NH_4Cl
(e) $[NPCl_2]_3 + NaOC_2H_5$
(f) $[NPCl_2]_3 + C_6H_5Li$
(g) $[NPCl_2]_3 + C_6H_5MgBr$
(h) $PCl_3 + C_6H_5MgBr$
(i) $PCl_5 + TiCl_4$

20. Explain how the differing reactions of the M_4 elements of Group VB(15) with nitric acid are consistent with increasing metallic behavior on descent of the group.

21. Compare the oxides of phosphorus with those of nitrogen and bismuth.

22. The compound P_4S_{10} is isostructural with P_4O_{10}. It also undergoes the following alcoholysis reaction:

$$P_4S_{10} + 8\ ROH \longrightarrow 4(RO)_2P(S)SH + 2\ H_2S$$

Draw the Lewis diagram of each reactant and product, and give the occupancy notation (AB_xE_y, as in Chapter 3) for each distinct P, O, and S atom.

C. Questions from the Literature of Inorganic Chemistry

1. Consider the paper by B. H. Christian, R. J. Gillespie, and J. F. Sawyer, *Inorg. Chem.*, **1981,** *20,* 3410-3420.

(a) Salts of the cations $As_3S_4^+$ and $As_3Se_4^+$ have been prepared starting with As_4S_4 or As-Se alloys and using (as oxidants) the Lewis acids AsF_5 or SbF_5. Draw Lewis diagrams for the cations and anions that are formed in these reactions.

(b) What (different) products were obtained upon oxidation of As_4F_4 by $SbCl_5$, Cl_2, or Br_2? Why?

(c) How does the structure of the starting material As_4S_4 differ from its oxidized product, $As_3S_4^+$?

2. The dianion $[Sb_2OCl_6]^{2-}$ is described in a paper by M. Hall and D.B. Sowerby, *J. Chem. Soc., Chem. Commun.*, **1979,** 1134–1135.

(a) How is this dianion uniquely different from other antimony chlorides or antimony oxide chlorides?

(b) Show with drawings how each Sb^{III} center can be viewed as an AB_5E system (according to the classification of Chapter 3) in which the "sixth position" of a pseudooctahedron is occupied by a lone electron pair.

(c) Is there evidence among the structural data (either in terms of bond angles or bond lengths) for the presence of a lone pair of electrons on each Sb^{III} center? Answer in terms of VSEPR theory (Chapter 3).

3. The structure of the ion $[SbCl_5]^{2-}$ was reported by R. K. Wismer and R. A. Jacobson, *Inorg. Chem.*, **1974,** *13,* 1678-1680.

(a) Use VSEPR theory and the AB_xE_y classification that was presented in Chapter 3 to discuss the hybridizations and geometries around antimony in the compounds $SbCl_3$, $(NH_4)_2SbCl_5$, $(pyH)SbCl_4$, and $[Co(NH_3)_6][SbCl_6]$.

(b) In the crystals of K_2SbCl_5, the square-pyramidal $[SbCl_5]^{2-}$ units were found to be packed base to base. The short interion Sb-Sb distance indicates little *stereochemical effect* from a localized lone pair of electrons on Sb. Elaborate and explain.

4. Consider the work by P. Wisian-Neilson and R. H. Neilson, *J. Am. Chem. Soc.*, **1980,** *102,* 2848–2849.

(a) What problems normally arise in the syntheses of *fully alkylated* polymeric dialkylphosphazenes, $[NPR_2]_n$, starting with $[NPCl_2]_n$ polymers and using Grignard reagents?

(b) Compound 2 as reported in this work leads to fully alkylated polymers, $[NPR_2]_n$, without the problems mentioned in (a). Why? Show the elimination that must take place upon polymerization.

(c) Draw the Lewis diagrams and discuss the hybridizations and geometries around all atoms in Compounds 1 and 2 of this paper.

(d) Show at each Si, N, and P atom how a *p* or *d* orbital may become involved in a π-bond system in each Molecule 1 and 2.

(e) Elimination reactions of Compound 1 gave a cyclic tetramer, $[NP(CH_3)_2]_4$. Show the necessary elimination reactions and draw the likely structure of the cyclized product.

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