PHOSPHORUS COMPOUNDS

1. Introduction

Phosphorus compounds exhibit an enormous variety of chemical and physical properties as a result of the wide range in the oxidation states and coordination numbers for the phosphorus atom. The most commonly encountered phosphorus compounds are oxides, halides, sulfides, hydrides, nitrogen, metal, and organic derivatives, all of which are of industrial importance. The halides, hydride, and metal derivatives (and to a lesser extent the oxides and sulfides) are reactive intermediates for forming phosphorus bonds with other elements.

The largest volume phosphorus compounds are the phosphoric acids and phosphates, ie, the oxide derivatives of phosphorus in the +5 oxidation state. With the exception of the phosphoric acid anhydride, P_4O_{10}, and the phosphate esters, phosphorus compounds with phosphorus in the +5 oxidation state are discussed in another article (see Phosphoric acids and phosphates). This article presents an overview of phosphorus compounds other than the phosphoric acids and phosphates. Elemental phosphorus is covered in a separate article (see Phosphorus).

Kirk-Othmer Encyclopedia of Chemical Technology.

Because of the high stability of the P−O and P=O bonds, the largest group of phosphorus compounds are the oxides. The oxy acids form the basis for the most systematic nomenclature (1,2). Table 1 lists some of the well-characterized lower molecular weight oxy acids and corresponding structures. Whereas phosphonic acid is often referred to as phosphorous acid, the free acid of formula H_3PO_3 exists in the form of the stable, well-characterized phosphinic acid, $HP(=O)(OH)_2$, and not as the structural isomer phosphorous acid [10294-56-1]. Phosphinic acid, H_3PO_2, is often called hypophosphorous acid. Some structures may be found primarily as their salts or esters, the acid forms being encountered infrequently if at all. Examples include the esters of phosphinous acid [2576-87-0], $H_2P{-}OH$, and the phosphite esters, $P(OR)_3$, the latter structurally derived from phosphorous acid. Acids and salts containing more than one phosphorus atom of the same or different oxidation state are known, eg, diphosphoric (III,V) acid, $H_4P_2O_6$ [14902-77-3]. These lower oxidation state acids or salts containing more than one phosphorus atom are encountered infrequently and are often formed, eg, as somewhat metastable intermediates in the hydrolysis of phosphorus halides. They may possess either P−P or P−O −P linkages.

Table 2 provides information for organo derivatives of the phosphorus oxyacids lacking a P−C bond, ie, the esters. Salts and esters described by naming the cations or organic group and changing the suffix from -ic to -ate and -ous to -ite. Compounds are named according to the acids from which they are derived, eg, $(C_2H_5O)_2P(=O)H$ is diethyl phosphonate [762-04-9], and $(C_6H_5O)_3P$ is triphenyl phosphite [101-02-0]. Table 3 lists the structure and names of derivatives having P−C bond(s).

Other phosphorus compounds may also be considered as derivatives of the oxy acids. The P−O or P=O moieties may be replaced with isoelectronic groups to yield halo (P−X), amide ($P(O){-}NR_2$), thio (P=S), imide (P=NH), etc. Many phosphorus compounds are, however, named as salts with phosphorus being the metallic or electropositive element, eg, phosphorus trichloride, PCl_3 [7719-12-2]; phosphorus oxybromide (phosphoryl bromide), $POBr_3$ [7789-59-5]; phosphorus pentafluoride, PF_5 [7647-19-0]; phosphorus triamide, $P(NH_2)_3$ [13566-19-3]; and tetraphosphorus decasulfide, (phosphorus pentasulfide) phosphorus(V) sulfide, P_4S_{10} [1314-80-3]. There is some latitude in describing halo derivatives of oxyacids. For example, diethyl phosphorochloridate $(C_2H_5O)_2P(O)Cl$ [814-49-3] and methylphosphonic dichloride $CH_3P(O)Cl_2$ [676-97-1].

Some compounds are named as derivatives of the simple phosphorus hydrides (phosphines). For example, dimethylphosphine $(CH_3)_3PH$ [676-59-5], triphenylphosphine oxide $(C_6H_5)_3P{=}O$ [791-28-6], 1,2-dimethyldiphosphine $CH_3PHPHCH_3$ [53684-00-7], tetramethylphosphonium chloride $(CH_3)_4P^+Cl^-$ [1941-19-1], phenylphosphonium bromide $C_6H_5PH_3{}^+Br^-$ [55671-96-0].

2. Chemical Properties

2.1. Oxidation States, Coordination Numbers, and Geometries.

Phosphorus bonding is primarily covalent because of the intermediate electronegativity of the phosphorus atom, $X = 2.1$ (equal to that of hydrogen). Oxidation

Table 1. **Major Oxyacids of Phosphorus**

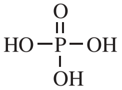
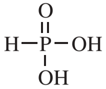
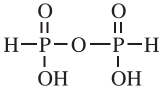
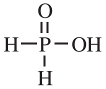
Name	CAS Registry Number	Oxidation state	Molecular formula	Structure	Basicity and salts
(ortho)phosphoric acid	[7664-38-2]	+5	H_3PO_4	 $\mathrm{HO-\underset{\underset{OH}{|}}{\overset{\overset{O}{\|}}{P}}-OH}$	tribasic; salts are called phosphates; also polymeric forms
phosphonic acid (phosphorous acid)	[13598-36-2]	+3	H_3PO_3	 $\mathrm{H-\underset{\underset{OH}{|}}{\overset{\overset{O}{\|}}{P}}-OH}$	dibasic; salts are called phosphites
diphosphonic acid (pyrophosphorous acid)	[36465-90-4]	+3	$H_4P_2O_5$	 $\mathrm{H-\underset{\underset{OH}{|}}{\overset{\overset{O}{\|}}{P}}-O-\underset{\underset{OH}{|}}{\overset{\overset{O}{\|}}{P}}-H}$	dibasic; salts are called pyrophosphites
phosphinic Acid (hypophosphorous acid)	[6303-21-5]	+1	H_3PO_2	 $\mathrm{H-\underset{\underset{H}{|}}{\overset{\overset{O}{\|}}{P}}-OH}$	monobasic; salts are called hypophosphites

Table 2. **Esters of Phosphorus Oxyacids**

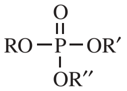
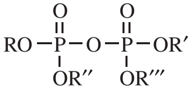
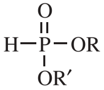
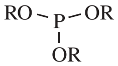
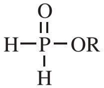
Name	Oxidation state	Molecular formula	Structure	Parent oxyacid
phosphate ester tribasic; salts are (phosphate)	+5	$R_xH_{3-x}PO_4$	 $\mathrm{RO{-}P({=}O)(OR'')}{-}\mathrm{OR'}$	(ortho)phosphoric acid; mono-, di-, and triesters
diphosphate ester (pyrphosphate)	+5	$R_xH_{4-x}P_2O_7$	 $\mathrm{RO{-}P({=}O)(OR''){-}O{-}P({=}O)(OR''')}{-}\mathrm{OR'}$	pyrophosphoric acid; mono-, di-, tri-, and tetraesters
phosphonate ester pyrophosphites (phosphite)	+3	$R_xH_{2-x}PO_3$	 $\mathrm{H{-}P({=}O)(OR')}{-}\mathrm{OR}$	phosphonic acid; mono- and diesters
triphosphite ester (phosphite)	+3	R_3PO_3	 $\mathrm{RO{-}P(OR)}{-}\mathrm{OR}$	hypothetical phosphorous acid, $P(OH)_3$
phosphinite ester	+1	RH_2PO_2	 $\mathrm{H{-}P({=}O)(H)}{-}\mathrm{OR}$	phosphinic acid

Table 3. **Organophosphorus Derivatives with P-C Bonds**

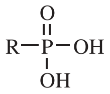
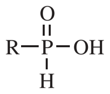
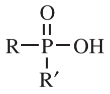
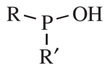
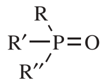
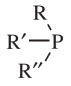
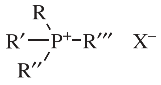
Name	Oxidation state	Acid formula	Structure	Derivatives
Oxyacid derivatives			 $R-\overset{\overset{O}{\|}}{\underset{\underset{OH}{\mid}}{P}}-OH$	
organophosphonic acid (phosphonates)	+3	RH_2PO_3	 $R-\overset{\overset{O}{\|}}{\underset{\underset{H}{\mid}}{P}}-OH$	mono- and diesters
organophosphinic acid; also phosphonous acid (phosphinates)	+1	$R_xH_{2-x}PO_2$	 $R-\overset{\overset{O}{\|}}{\underset{\underset{R'}{\mid}}{P}}-OH$	monoesters
organophosphinous acid (phosphinites)	−1	R_2HPO_2	 $R-\underset{\underset{R'}{\mid}}{P}-OH$	monoesters from hypothetical phosphinous acid, H_2POH
Phosphine derivatives				
organophosphine oxide	−1	$R_xH_{3-x}PO$	 $RR'R''P=O$	

Table 3. (*Continued*)

Name	Oxidation state	Acid formula	Structure	Derivatives
organophosphine	−3	$R_xH_{3-x}P$		
phosphonium Salt	−3	$R_xH_{4-x}P^+X^-$		

states range from -3 to $+5$, but phosphorus exists almost exclusively as phosphates or phosphate derivatives in nature. The $+5$ oxidation state is the most stable for the oxide derivatives in both acidic and basic media (3). Intermediate oxidation states often exhibit a strong tendency to disproportionate.

The most common coordination numbers for the phosphorus atom are 3, 4, or 5 although covalent linkages may range anywhere from 1 to 6. The quadruply connected compounds generally exhibit the highest stability, followed by the coordination numbers 3 and then 5. Singly or doubly connected phosphorus compounds are typically quite unstable, and relatively fewer examples of the five- and six-coordinate compounds are known. The geometries about the phoshorus atom are related to the hybridization and the coordination number. Hybridization may be of mixed character and the bond angles in compounds may vary from the ideal orientations of the pure hybrid.

The coordination number of 4 is the most common for phosphorus compounds containing the first and second row Group 13(III), 14(IV), and 15(V) elements. Bond angles are typically 100–102°, somewhat smaller than the tetrahedral angle of 109°28′ expected for sp^3 hybridization, because of partial of π-bonding character.

The triply connected phosphorus compounds have a lone electron pair that dominates much of the chemistry for these compounds. Examples include phosphorus trihalides, phosphines, and derivatives of phosphorous and phosphinous acids. Formally, they may be considered distorted tetrahedra in each of which an unshared electron pair occupies a fourth coordination position. Bond angles often range near 100 versus 90° theoretical. Tricoordinate compounds typically act as electron donors, forming metal coordination compounds and addition compounds such as $H_3P{*}BF_3$ [41593-56-0].

Substituents on the phosphorus atom can strongly influence the electron donation as trialkyl phosphines are potent electron donors and phosphorus trifluoride is a weak electron donor.

An unshared electron pair on phosphorus reacts with oxidizing agents, eg, hydrogen peroxide, sulfur, or halogens,

$$(RO)_3P: + H_2O_2 \longrightarrow (RO)_3P{=}O + H_2O \tag{1}$$

$$R_3P: + S \longrightarrow R_3P{=}S \tag{2}$$

$$:PCl_3 + Cl_2 \longrightarrow PCl_5 \tag{3}$$

and undergoes quaternization with alkyl halides,

$$R_3P: + R'X \longrightarrow R_3R'P^+X^- \tag{4}$$

The participation of the phosphorus d orbitals in the five- and six-coordinate compounds provides an increased ionic character. Compounds, such as PCl_5 [10026-13-8] are thought to have considerable ionic character. Pentacoordinate phosphorus compounds often act as electron acceptors.

Much effort has been placed on the synthesis of compounds with a chiral center at the phosphorus atom, particularly three- and four-coordinate compounds, such as tertiary phosphines, phosphine oxides, phosphonates, phosphinates, and phosphate esters (4). Some enantiomers exhibit a variety of biological activities and are of interest as agricultural chemicals, pharmaceuticals, etc. Homochiral bisphosphines are commonly used in catalytic asymmetric syntheses.

Phosphorus compounds may also react by free-radical mechanisms. The theoretical and synthetic aspects of the chemistry of phosphorus compounds have been described (5–8). Excellent reviews of low coordinate phosphorus compounds (coordination numbers 1 and 2) are available (9).

2.2. Bond Properties. The bond strengths, bond lengths, and atom electronegativity differences of various phosphorus-atom linkages are given in Table 4.

2.3. Phosphorus–Oxygen and Phosphorus–Sulfur Bonds. Phosphorus formally bonds to oxygen or sulfur as either single or double bonds. More correctly, the P=O bond in phosphoryl compounds is considered to be formed via donation of the electron pair from the phosphorus atom to the oxygen atom. A bond of primarily σ character results that may be more accurately depicted as a coordinate bond, $P\rightarrow O$, or as $P^{+}-O^{-}$. In a species, such as the phosphate ion, $PO_4{}^{3-}$, all phosphorus–oxygen bonds are equivalent, although the ion is customarily depicted as having a single P=O, ie $O{=}PO_3{}^{3-}$. Phosphorus has a strong affinity for oxygen and the great tendency to form a P=O linkage dominates much of phosphorus chemistry.

The O or S atoms in P=O and P=S groups may act as electron donors although they form relatively weak complexes with electron acceptor compounds. They are favored by the nonpolarizable, more electropositive (ie, hard) acids, including protons (11). Use is made of this property in the recovery of uranium from wet-process phosphoric acid by extractants, such as trioctylphosphine oxide [78-50-2] and di(2-ethythexyl) hydrogen phosphate [298-07-7].

The P=S linkage is typically more reactive than the relatively inert P=O linkage. The P–S or P=S bonds are also less stable, hydrolytically and thermally, than their oxygen analogues. The P=S linkages are stronger electron donors and, therefore, form more stable complexes although they are also more

Table 4. **Bonding Properties of Phosphorus**[a]

Bond P–X	Bond energy, kJ/mol	Bond length, nm	Electronegativity difference, $X_X - X_P$
P–O	360	0.15–0.17	1.4
P=O	544	0.141–0.151	1.4
P–H	322	0.140–0.146	0.0
P–C	272	0.183–0.194	0.4
P–F	527	0.150–0.160	1.9
P–Cl	331	0.204–0.205	0.9
P–Br	264	0.215–0.220	0.7
P–I	184	0.248–0.252	0.4
P–N	230	0.17–0.18	0.9
P–P	209	0.217–0.227	0.0
P–S	230	0.200–0.215	0.4
P=S		0.187–0.197	0.4

[a] Refs. 5 and 10.

[b] To convert J to cal, divide by 4.184.

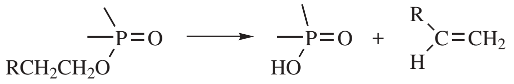
[c] Pauling's electronegativity difference, where X_X represents the electronegativity of atom X.

labile. Thus, they are useful as blocking groups for unshared electron pairs in some sensitive syntheses. The required manipulations are performed on the thio analogue and the electron pair does not become involved with a reactant that would produce a phosphoryl group. The thio group can be removed by a reagent that binds sulfur strongly, eg, triphenylphosphine [603-35-0].

The behavior of the P−O linkage is in many respects intermediate between that of the C−O and S−O bonds. Oxy-acids of phosphorus are intermediate in acid strength between those of carbon and sulfur, and the strong acid function of phosphorus-oxy acids typically exhibiting a pK_a near 2, eg, H_3PO_4 has a pK_a of 2.1; H_3PO_3 a pK_a of 1.5; and $CH_3PO_3H_2$ a pK_a of 2.3. Phosphorus esters are also more labile than carbonates or carboxylates, but less so than sulfates. Although carboxylates hydrolyze by cleavage of the C−O bond and sulfates by cleavage of the O−R bond, phosphorus esters may cleave at either the P−O or O−R bond.

Like P−O−C linkages, P−O−P linkages are susceptible to hydrolytic degradation. Scrambling or interchange usually occurs for phosphorus oxyesters at temperatures and acidities lower than that required for the carbon esters, but greater than that for the sulfur esters.

Esters of phosphorus oxyacids which possess beta hydrogens undergo olefin elimination, usually beginning at 160−200°C.



(5)

The resulting acid function catalyzes the same reaction. It is therefore necessary to distill phosphorus esters < 160°C and if possible preferably in the presence of a mild acid scavenger. Phosphites and hydrogen phosphates are most susceptible to this decomposition. Ester groups lacking a beta hydrogen rearrange to form an anhydride under higher temperatures or dehydrating conditions.

$$2\,(CH_3O)_3P{=}O \longrightarrow CH_3OCH_3 + (CH_3O)_2\overset{O}{\overset{\|}{P}}{-}O{-}\overset{O}{\overset{\|}{P}}(OCH_3)_2 \tag{6}$$

Tetralkyl pyrophosphates are extremely toxic and caution should be used in heating esters (12).

2.4. Phosphorus–Hydrogen Bond. A hydrogen bound to phosphorus has very acidic or hydric character. Most of the reactions of the P−H bond are those of a reducing agent. The P−H bonds are formed by hydrolysis of active metal phosphides or phosphorus halides, by the rearrangement of P−O−H or P−S−H linkages, or hydrolysis of P−P bonds (5,13).

$$PCl_3 + 3\,H_2O \longrightarrow HP({=}O)(OH)_2 + 3\,HCl \tag{7}$$

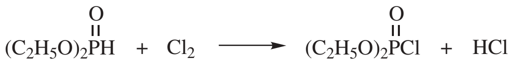
$$Na_3P + 3\,H_2O \longrightarrow PH_3 + 3\,NaOH \tag{8}$$

$$P_4 + 4\,KOH + 2\,H_2O \longrightarrow 2\,K_2HPO_3 + 2\,PH_3 \tag{9}$$

P–H bonds are readily susceptible to acid-, base-, or radical-catalyzed nucleophilic additions to unsaturated centers, such as olefins and ketones, resulting in the concomitant formation of a P–C bond.

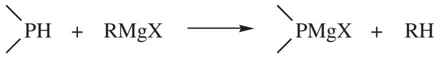
$$RCH{=}CHR' + PH_3 \xrightarrow{\text{catalyst}} RCH_2CHR'PH_2 \qquad (10)$$

A P–H bond is readily attacked by active oxidizing agents. The chlorination of dialkyl phosphonates provides a convenient synthesis of phosphorochloridates:



$$(C_2H_5O)_2P(=O)H + Cl_2 \longrightarrow (C_2H_5O)_2P(=O)Cl + HCl \qquad (11)$$

Phosphorus–hydrogen compounds undergo a metathetical exchange with some Grignard reagents:



$$\rangle PH + RMgX \longrightarrow \rangle PMgX + RH \qquad (12)$$

Some phosphorus–hydrogen compounds are pyrophoric, eg, diphosphine [13445-50-6], P_2H_4, a common impurity in phosphine. Such contaminated phosphine can ignite spontaneously upon contact with air.

2.5. Phosphorus–Carbon Bond. The P–C bond is one of the more stable bonds formed by phosphorus, resistant to both hydrolysis and oxidation (6,7). Unlike the phosphorus–halogen or phosphorus–oxygen bonds, the P–C linkage is inert to exchange. A phosphorus atom connected to carbon behaves similarly to another carbon atom in a hydrocarbon chain.

A general method of forming a phosphorus–carbon bond is by reaction of an organometallic reagent with a phosphorus–halogen link:

$$3\,RM + PCl_3 \longrightarrow R_3P + 3\,MCl \qquad (13)$$

R–M can be a traditional Grignard reagent or an organolithium, zinc, aluminum, or mercury compound. These reactions are subject to many side reactions and yields are often low, eg, 40–50% for $(C_4H_9)_3P$ prepared via a Grignard reaction (14).

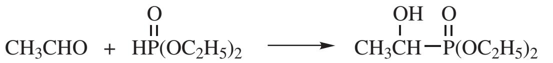
In general, compounds with an active phosphorus–metal linkage react with alkyl halides to form P–C bonds and a metal halide byproduct. Such P–M compounds include alkali or alkaline earth phosphides or phosphine derivatives, eg, Na_3P, PH_2Na [24167-76-8], $XMgPR_2$, or $NaP(=O)(OR)_2$.

A Friedel-Crafts reaction, utilizing phosphorus trichloride or phosphorus tribromide [7789-60-8] in place of an acyl halide, is a convenient route to many arylphosphorus compounds (7):

$$ArH + PCl_3 \xrightarrow{AlCl_3} ArPCl_2 + HCl \qquad (14)$$

Diaryl products are obtained after long reaction times. Other Friedel-Crafts catalysts, eg, $ZnCl_2$, $FeCl_2$, HF, and BF_3 are also effective. In most cases, stoichiometric amounts of catalyst are required. Strong complexation of the phosphine by the catalyst necessitates separation by vacuum distillation, hydrolysis, or addition of reagents, such as $POCl_3$ to form more stable aluminum chloride complexes. Whereas yields up to 70–80% are possible for some aryl derivatives, yields of aliphatic derivatives are generally much less (15).

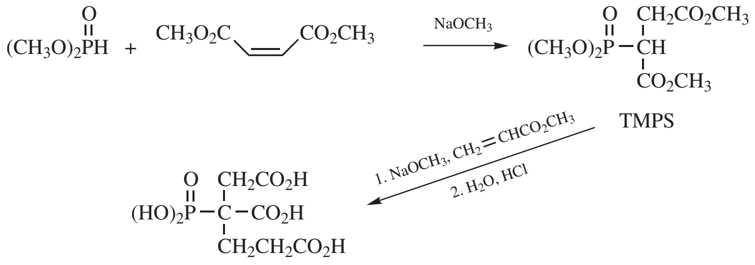
An important feature of the P–H bond is the ready addition across unsaturated groups, such as aldehydes or olefins to form P–C bonds.



$$\mathrm{CH_3CHO} + \mathrm{H\overset{O}{\overset{\|}{P}}(OC_2H_5)_2} \longrightarrow \mathrm{CH_3\overset{OH}{\overset{|}{C}}H{-}\overset{O}{\overset{\|}{P}}(OC_2H_5)_2} \qquad (15)$$

$$3\,\mathrm{C_2H_5CH{=}CH_2} + \mathrm{PH_3} \xrightarrow{\text{base}} (n\cdot \mathrm{C_4H_9})_3\mathrm{P} \qquad (16)$$

Another important P–C bond-forming reaction is the base-catalyzed Michael addition to activated double bonds. For example, dimethyl phosphite can be added to dimethyl maleate to yield tetramethylphosphonosuccinate [2788-26-3] (TMPS), an intermediate in the synthesis of 2-phosphonobutane-1,2,4-tricarboxylic acid [37971-36-1] (PBTC) with 98% yield (16). The PBTC is sold as a water-treatment chemical.

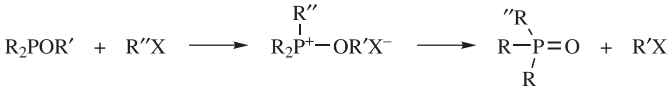


TMPS

PBTC

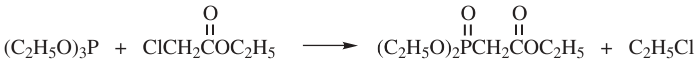
(17)

One of the most useful reactions in forming a P–C bond is the Michaelis-Arbusov reaction, which is characteristic of tricoordinate phosphorus compounds containing an alkoxy group (17). Alkylation of the electron pair is followed by rearrangement of the initial phosphonium salt.



$$\mathrm{R_2POR'} + \mathrm{R''X} \longrightarrow \mathrm{R_2\overset{R''}{\overset{|}{P}}{}^{+}{-}OR'X^-} \longrightarrow \underset{\mathrm{R}}{\overset{''\mathrm{R}}{\mathrm{R{-}P{=}O}}} + \mathrm{R'X} \qquad (18)$$

The Michaelis-Arbusov reaction is especially useful for converting trialkyl phosphites, $(RO)_3P$, to alkylphosphonic esters, and to esters of phosphonocarboxylic acids.



$$\mathrm{(C_2H_5O)_3P} + \mathrm{ClCH_2\overset{O}{\overset{\|}{C}}OC_2H_5} \longrightarrow \mathrm{(C_2H_5O)_2\overset{O}{\overset{\|}{P}}CH_2\overset{O}{\overset{\|}{C}}OC_2H_5} + \mathrm{C_2H_5Cl} \qquad (19)$$

A modified Mannich reaction is useful for the preparation of aminomethylphosphonates used as water treatment chemicals (18).

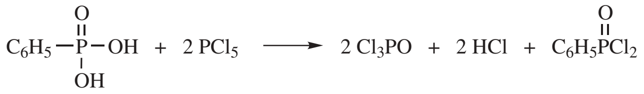
$$2\,H\overset{\overset{O}{\|}}{P}(OR)_2 + 2\,CH_2O + H_2NR' \longrightarrow R'N[CH_2\overset{\overset{O}{\|}}{P}(OR)_2]_2 + 2\,H_2O \qquad (20)$$

This reaction is catalyzed by HCl and yields can be essentially quantitative when using either free or phosphonic acid or its diesters.

2.6. Phosphorus–Halogen Bond. The bond length and energy of phosphorus–halogen compound are presented in Table 4. Bond lengths increase and energies decrease with increasing ionic radii. Phosphorus–halogen bonds are formed by the action of the elements, eg,

$$P_4 + 6\,I_2 \longrightarrow 4\,PI_3 \qquad (21)$$

halogenation of P–H bonds, and the action of common halogenating agents on acids and esters of phosphorus. For example, phenylphosphonic acid [1571-33-1] reacts with phosphorus pentachloride to form phenylphosphonic dichloride [824-72-6].



$$C_6H_5-\underset{\underset{OH}{|}}{\overset{\overset{O}{\|}}{P}}-OH + 2\,PCl_5 \longrightarrow 2\,Cl_3PO + 2\,HCl + C_6H_5\overset{\overset{O}{\|}}{P}Cl_2 \qquad (22)$$

Despite the large energy of formation of many phosphorus–halogen bonds, these are among the most labile phosphorus bonds and participate readily in metathetical reactions. Mixtures of phosphorus halides scramble the halogens to yield mixed halide combinations (5). Thus, mixtures of $POCl_3$ and phosphorus oxybromide [7789-59-5], $POBr_3$, contain not only these two pure materials but also $POCl_2Br$ [13455-03-3] and $POClBr_2$ [13550-31-7]. Other ligands on phosphorus, eg, ester or amide groups, also scramble, but may require thermal excitation for the process.

Phosphorus halides are subject to reactions with active hydrogen compounds and result in the elimination of hydrogen halide. They are convenient reagents in the synthesis of many esters, amides, and related compounds. However, because the involved hydrogen halide frequently catalyzes side reactions, it is usually necessary to employ a hydrogen halide scavenger to remove the by-product.

$$POCl_3 + 3\,ROH + 3\,R'_3N \longrightarrow (RO)_3PO + 3\,R'_3N\cdot HCl \qquad (23)$$

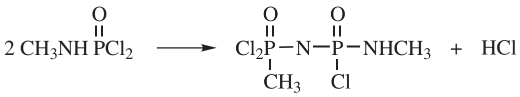
$$CH_3\overset{\overset{O}{\|}}{P}Cl_2 + 4\,(CH_3)_2NH \longrightarrow CH_3\overset{\overset{O}{\|}}{P}[N(CH_3)_2]_2 + 2\,(CH_3)_2NH_2Cl \qquad (24)$$

In some instances, the presence of the acid scavenger affects the nature of the product.

$$PCl_3 + 3\,CH_3CH_2OH \longrightarrow (CH_3CH_2O)_2\overset{\overset{O}{\|}}{P}H + CH_3CH_2Cl + 2\,HCl \qquad (25)$$

$$PCl_3 + 3\,CH_3CH_2OH + 3\,(C_2H_5)_3N \longrightarrow (C_2H_5O)_3P + 3\,(C_2H_5)_3N{\cdot}HCl \qquad (26)$$

When a phosphorus–halogen bond and a active hydrogen occur in the same molecule, such species are subject to thermal rearrangement.



$$2\,CH_3NH\overset{\overset{\large O}{\|}}{P}Cl_2 \longrightarrow Cl_2\overset{\overset{\large O}{\|}}{\underset{\underset{\large CH_3}{|}}{P}}{-}N{-}\overset{\overset{\large O}{\|}}{\underset{\underset{\large Cl}{|}}{P}}{-}NHCH_3 + HCl \qquad (27)$$

The rate of reaction of a phosphorus halogen and an active hydrogen depends on a number of factors, including steric requirements of the reactants, inductive effects on the phosphorus, and size of the halogen, eg, iodine is the most active and fluorine is the least active. Thus, PCl_5 is a highly active phosphorus chloride whereas the chlorocyclophosphazenes are relatively inactive (19). The nearly planar $P_3N_3Cl_6$ is quite inactive but the highly puckered $P_4N_4Cl_8$ [2950-45-9] hydrolyzes slowly on exposure to atmospheric moisture.

3. Phosphorus Halides

Phosphorus forms well-defined halogen compounds of the types PX_3, PX_5, POX_3, and PSX_3, all of which except the pentaiodide and the oxy- and sulfoiodides are known. In addition to the binary halides, a few of the many possible mixed halides, eg, PX_2Y and PX_3Y_2, have been prepared. The commercially important phosphorus halides are phosphorus trichloride [7719-12-2], phosphorus oxychloride [10025-87-3], phosphorus pentachloride [10026-13-8], and phosphorus sulfochloride [3982-91-0]. A few other phosphorus halides, eg, PI_3, PBr_3, PBr_5, PF_3, and PF_5, are marketed as reagent chemicals.

The trihalides of phosphorus usually are obtained by direct halogenation under controlled conditions, eg, in carbon disulfide solution in the case of the triiodide. Phosphorus trifluoride [7647-19-0] is best made by transhalogenation of PCl_3 using AsF_3 or CaF_2. All of the phosphorus trihalides are both Lewis bases and acids. The phosphorus trihalides rapidly hydrolyze in water and are volatile. Examination by electron diffraction has confirmed pyramidal structures for the gaseous trihalide molecules (20). Physical properties and heat of formation of some phosphorus halides are listed in Table 5.

The melting, boiling, and sublimation points of many of the phosphorus halides are well defined and therefore serve for identification. Distillation is the easiest method of purification. Phosphorus-31 nuclear magnetic resonance (nmr) can be used to analyze mixtures of halides that undergo halogen-exchange reactions.

The pentahalides of phosphorus, PX_5, in the gas-phase exhibit varying tendencies to dissociate into trihalide and halogen. Instability increases with increasing ionic radius of the halogen. The pentafluoride appears to be thermally stable. Dissociation of the pentachloride, a few percent at 100°C and 101.3 kPa (1 atm), is essentially completed at 300°C (20). The pentabromide is partially dissociated in the liquid state and totally dissociated above ~35°C (23). The molecules of PF_5 and PCl_5 in the vapor phase are trigonal bipyramids. In the

Table 5. **Physical Properties of Phosphorus Halides**[a]

Compound	CAS Registry Number	Melting point, °C	Boiling point, °C	Specific gravity[b]	Physical state at STP[c]	kJ/mol[d]	kJ/mol[d]	Critical temperature, °C
PCl_3	[7779-72-2]	−93.6	76.1	1.575	liquid	−319.7	30.5	285.5
PCl_5	[10026-13-8]	167[e]	159 subl	2.114	solid[f]	−443.5	64.9	372
$POCl_3$	[10025-87-3]	+1.2	106.5	1.68	liquid	−597.1	34.7	331.8
$PSCl_3$	[3982-91-0]	−36	125	1.668	liquid			
PBr_3	[7789-60-0]	−41.5	173.3	2.880	liquid	−184.5	38.9	
PBr_5	[7789-69-7]	83.8 (subl)	>106 dec		solid[g]	−269.9		
PI_3	[13455-01-1]	61.2	120 dec		solid[h]	−45.6		
P_2I_4	[13455-00-0]	125.5	dec		solid[i]			
PF_3	[7783-55-3]	−151.5	−101	3.907	gas[j]	−918.8	14.6	−2.05
PF_5	[7647-19-0]	−93.7	−84.5	5.84	gas	−1595.8	16.74	
POF_3	[13478-20-1]	−39.4	−39.7	4.65	gas	−1211.3	21.2	73.3
PSF_3	[2404-52-6]	−148.8	−52.3		gas		19.6	72.8
PF_2Cl	[14335-40-1]	−164.8	−47.3		gas		17.6	89.17
PF_3Cl_2	[13454-99-1]	−124	2.5		gas		26.7	
PF_4Cl	[13637-88-2]	−132	−43.4				21.59	
PF_2Br	[15597-40-7]	−133.8	−16.1		gas		23.9	113
PF_2Br_3	[13445-58-4]	−20	−106		liquid			
$PFCl_2$	[15597-63-4]	−144.1	13.9		gas		24.89	
$PFBr_2$	[15597-39-4]	−145	78.4		liquid		31.88	254
PF_2I	[13819-11-9]	−93.8	267					

[a] Refs. 5, 20–23.

[b] At 298.15 K and 101.3 kPa (1 atm).

[c] Colorless unless otherwise noted.

[d] To convert J to cal, divide by 4.184.

[e] At 122 kPa (919 mm Hg).

[f] White to pale yellow.

[g] Red-brown.

[h] Yellow.

[i] Dark red.

[j] Light orange

crystalline state, both pentachloride and pentabromide have ionic structures, ie, $[PCl_4]^+[PCl_6]^-$ and $[PBr_4]^+[PBr_6]^-$, respectively. The PX_4^+ cations are tetrahedral and the PX_6^- anion is octahedral (20,23).

Phosphorus pentafluoride is synthesized easily by transhalogenation of phosphorus pentachloride using arsenic trifluoride at low temperature,

$$3\,PCl_5 + 5\,AsF_3 \longrightarrow 3\,PF_5 + 5\,AsCl_3 \tag{28}$$

by heating hexafluorophosphate of sodium, calcium, and barium, and by

$$NaPF_6 \longrightarrow PF_5 + NaF \tag{29}$$

heating phosphorus pentachloride in the presence of the fluoride of a divalent metal, ie, Cd, Ba, Zn, or Pb, at 300–400°C. Phosphorus pentafluoride, a colorless gas that fumes in air and decomposes in water, is a strong Lewis acid.

$$PF_5 + H_2O \longrightarrow POF_3 + 2\,HF \tag{30}$$

PF_5 forms complexes with amines, ethers, and other bases as well as F^-, with which phosphorus becomes six coordinate. Dry phosphorus pentafluoride does not attack glass. The yellow crystalline phosphorus pentabromide forms from the reaction of PBr_3 and excess bromine.

Phosphorus halides and metals or metal salts form addition complexes. Some typical compounds are PCl_3:$SbCl_5$ and PCl_5:$AlCl_3$ (24). The trivalent complexes contain metal–phosphorus bonds. The pentavalent complexes involve rearrangements to produce assembles of tetrahedral PX_4^- cations and various anions.

3.1. Phosphorus Trichloride. *Properties and Reactions.* Phosphorus trichloride can be prepared either by direct chlorination of elemental phosphorus,

$$P_4 + 6\,Cl_2 \longrightarrow 4\,PCl_3 \tag{31}$$

by reduction of $POCl_3$ by CO,

$$POCl_3 + CO \longrightarrow PCl_3 + CO_2 \tag{32}$$

or by chlorination of ferrophosphide,

$$Fe_3P + 5/2\,Cl_2 \longrightarrow FeCl_2 + PCl_3 \tag{33}$$

Phosphorus trichloride, PCl_3, is a clear, volatile liquid having a pungent, irritating odor. Principal reactions of PCl_3, an excellent chlorination reagent for various hydrocarbons, are summarized in Fig. 1.

The reaction of phosphorus trichloride and water is highly exothermic and vigorous. Depending on the mole ratio of H_2O/PCl_3, three different products can result from hydrolysis. If the ratio is >3, phosphonic acid is

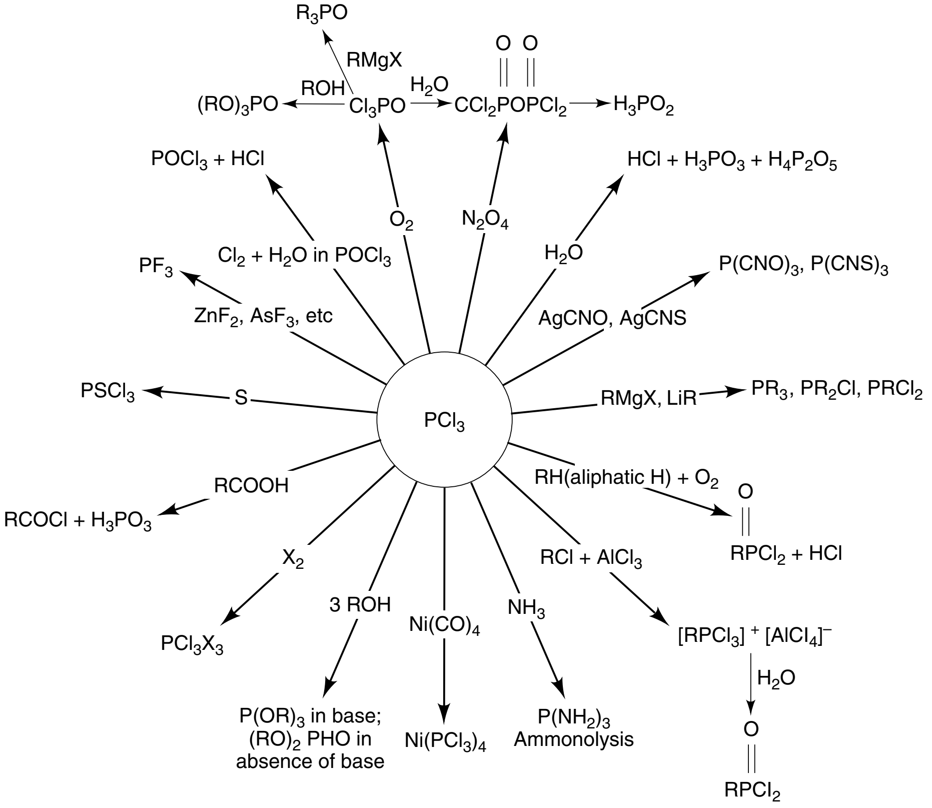
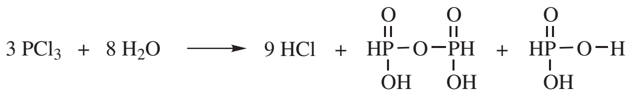


Fig. 1. Important reactions of PCl_3, where X is halogen and R is alkyl. Many of these reactions are typical for other PX_3, as well as POX_3 compounds.

produced

$$PCl_3 + 3\,H_2O \longrightarrow H_3PO_3 + 3\,HCl \qquad (34)$$

If the ratio is 2.5–3, the product is a mixture of phosphonic and pyrophosphonic acids:



$$3\,PCl_3 + 8\,H_2O \longrightarrow 9\,HCl + H\underset{OH}{\overset{O}{\overset{\|}{P}}}-O-\underset{OH}{\overset{O}{\overset{\|}{P}}}H + H\underset{OH}{\overset{O}{\overset{\|}{P}}}-O-H \qquad (35)$$

When the H_2O/ PCl_3 ratio falls < 2.5, a third product of indefinite composition, called lower oxides of phosphorus, is formed. The material ranges from a clear viscous polymer to yellow-to-orange solid flakes of limited solubility in PCl_3. The ^{31}P-nuclear magnetic resonance (nmr) identifies a polymer of randomly disposed P–P and P–O–P linkages. Other groups along the chain consist of –OH, =O, H, and sometimes –Cl or other halides (25). When this compound contacts water, halide groups hydrolyze more rapidly than the rest of the polymer, which leads to the formation of a mixture of phosphinic, phosphonic, and phosphoric acids and the evolution of phosphine and diphosphine gases. The gas evolution can proceed rapidly in the absence of water at elevated ($\geq 150°C$) temperatures. Phosphine, when contaminated with only traces of diphosphine, ignites spontaneously in air. Controlled oxidations by hypochlorite or hydrogen peroxide can consume the yellow-orange solid flakes (26).

Although PCl_3 is nearly insoluble in water, it hydrolyzes rapidly. Unless the addition of the chloride to water is carefully controlled by vigorous agitation, the water concentration in the vicinity of the interface between the PCl_3 and the aqueous solution may be depleted to the point where the ratio falls < 2.5 and formation of the polymer results. The polymer also forms during storage when PCl_3 is in contact with moist air. Such degradation is a problem in tank cars, storage tanks, and other reusable PCl_3 containers. The polymer, which is suspended in PCl_3, can be dissolved by the addition small quantities of PCl_5 or by Cl_2 gas chlorination resulting in the formation of $POCl_3$ and more PCl_3.

Manufacture. Phosphorus trichloride is made by direct union of the elements. The reaction is moderated by combining the chlorine and phosphorus in the presence of a precharge of phosphorus trichloride that is refluxed continuously. A typical manufacturing scheme is shown in Fig. 2. Liquid phosphorus and chlorine gas are continuously introduced into the reaction vessel, which is arranged so that a significant portion of the phosphorus trichloride contained in it undergoes reflux. The remaining phosphorus trichloride is distilled into a pot. A yield of $\sim 99.0\%$ or higher of purified phosphorus trichloride usually is obtained with respect to both the phosphorus and chlorine. The effect of raw material impurities on reactor operations and process waste generations has been evaluated (27). Most raw material impurities remain in the reactor and

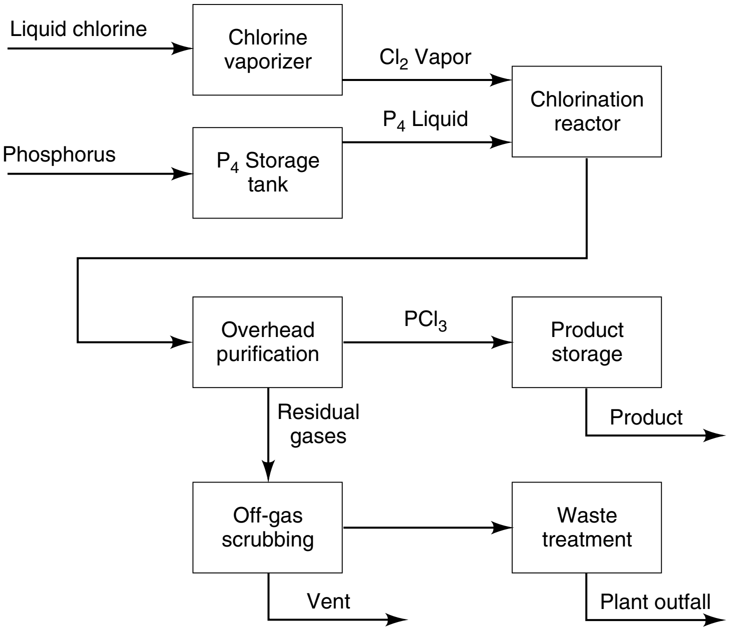


Fig. 2. Manufacturing of phosphorus trichloride.

are removed periodically. Process safety can be improved by using an on-line analyzer and other procedures (28–30).

Specifications and Analytical Methods. Typical analyses for technical grade PCl_3 are as follows (30):

Property	Description or value
appearance	water-white liquid
distillation range, °C	
first drop	74.8
1–96 mL	0.9
dry point	76.0
specific gravity, 15.5/15.5°C	1.586
assay, %	99.75
Fe, ppm	1

Phosphorus oxychloride content and impurities are determined by gas chromatography analyses.

Storage, Shipping, and Handling. Phosphorus trichloride is classified by the ICC as a corrosive liquid and poison inhalation hazard. U.S. Department of Transportation (DOT) white acid label and red poison label are required by law on individual containers: DOT UN No. 1809 (30,31). Alloy or glass-lined vessels are used for storage and reactors. One-gallon (3.8-L) quantities of PCl_3 are stored and shipped in glass containers using specified wooden overpacking (31). Heresite-lined steel drums are for 208-L (55-gal) volume. Bulk PCl_3 shipments are made in Heresite-lined tank cars of 15,000–30,000 L (4000–8000 gal) each, and tank trucks of 15,000–19,000-L (4000–5000-gal) volume. The industrial trend is toward closed-loop loading–unloading operations.

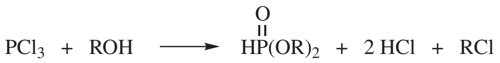
Health and Safety Factors, Toxicology. Phosphorus trichloride severely burns skin, eyes, and mucous membranes. Contaminated clothing must be removed immediately. Vapors from minor inhalation exposure can cause delayed onset of severe respiratory symptoms after 2–24 h, depending on the degree of exposure. Delayed, massive, or acute pulmonary edema and death can develop as consequences of inhalation exposure.

Phosphorus trichloride is highly toxic by ingestion and slightly toxic by single dermal applications. It reacts violently with water and can generate gases sufficient to cause rupture of closed or inadequately vented containers. If the gases contain diphosphine, they can ignite spontaneously. Acids produced in reactions of PCl_3 with water can evolve hydrogen gas on contact with metals. The threshold limit value (TLV) is 0.5 ppm or $3\,mg/m^3$. The oral LD_{50} in rats is 550 mg/kg; the inhalation LC_{50} for rats is 104 ppm/4 h, for guinea pigs, 50 ppm/4 h. The OSHA standard TWA is 0.2 ppm and STEL is 0.5 ppm (30,32).

Uses. The largest usage of PCl_3 is to produce phosphonic acid, H_3PO_3, which in reaction with iminodiacetic acid and formaldehyde forms a glyphosate intermediate that is decarboxymethylated to glyphosate, an effective nonselective herbicide (see Herbicides). Phosphorus trichloride is also a convenient chlorinating reagent for producing various acyl and alkyl chlorides.

$$PCl_3 + 3\,RCOOH \longrightarrow H_3PO_3 + 3\,RCOCl \tag{36}$$

Phosphorus trichloride reacts readily with oxygen, sulfur, chlorine, and water. It serves as an intermediate in the production of phosphorus oxychloride, phosphorus sulfochloride, phosphorus pentachloride, and phosphonic (phosphorous) acids. PCl_3 is also the raw material for the manufacture of dialkyl phosphonates,

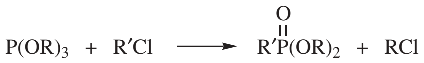


$$PCl_3 + ROH \longrightarrow H\overset{O}{\overset{\|}{P}}(OR)_2 + 2\,HCl + RCl \qquad (37)$$

triarylphosphites,

$$PCl_3 + 3\,ROH + 3\,NR' \longrightarrow P(OR)_3 + 3\,NR'_3{\cdot}HCl \qquad (38)$$

and dialkyl alkylphosphonates.



$$P(OR)_3 + R'Cl \longrightarrow R'\overset{O}{\overset{\|}{P}}(OR)_2 + RCl \qquad (39)$$

Alkyl or aryl phosphonates, which contain a carbon–phosphorus bond, are comparatively more stable. They are of interest as antiscaling additives and corrosion inhibitors for cooling towers and heat exchangers (see Dispersants; Water, Industrial Water Treatment), surfactants (qv), sequestrants, and textile-treating agents. Trialkyl phosphites are useful as esterification (qv) reagents.

The phosphonate esters, $HP(=O)(OR)_2$, of alkylated phenols are used extensively as lubricating-oil additives to control bearing corrosion and oxidation, and to impart antirust properties as stabilizers, as antioxidants (qv) and flame retardants in plastics, as specialty solvents, and as intermediates (see Heat stabilizers).

Phosphite triesters, $P(OR)_3$, form donor complexes with transition metals and other acceptors and are oxidized to the respective phosphates under appropriate conditions.

$$2\,(RO)_3P + O_2 \longrightarrow 2\,(RO)_3PO \qquad (40)$$

Most phosphate esters are made from $POCl_3$ and used as plasticizers (qv) and nonflammable hydraulic fluids (qv).

3.2. Phosphorus Oxychloride. *Properties and Reactions.* Several methods of preparation are available for $POCl_3$, including partial hydrolysis of PCl_5 by heating in the presence of oxalic or boric acid, chlorination and hydrolysis of PCl_3 in the presence of H_3PO_4,

$$H_2O + PCl_3 + Cl_2 \longrightarrow POCl_3 + 2\,HCl \qquad (41)$$

heating a mixture of P_2O_5 and PCl_5,

$$3\,PCl_5 + P_2O_5 \longrightarrow 5\,POCl_3 \qquad (42)$$

controlled oxidation and chlorination of elemental phosphorus,

$$P_4 + 6\,Cl_2 + 2\,O_2 \longrightarrow 4\,POCl_3 \qquad (43)$$

oxidation of PCl_3 using ozone (qv) or oxygen (qv),

$$2\,PCl_3 + O_2 \longrightarrow 2\,POCl_3 \tag{44}$$

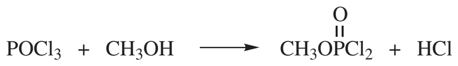
and heating calcium phosphate [7757-93-9] in a mixture of chlorine and carbon monoxide.

$$Ca_3(PO_4)_2 + 6\,CO + 6\,Cl_2 \xrightarrow{300-350^\circ C} 2\,POCl_3 + 3\,CaCl_2 + 6\,CO_2 \tag{45}$$

Phosphorus oxychloride [10021-87-3] (phosphoryl chloride), $POCl_3$, is a colorless fuming liquid having a pungent, disagreeable odor and is reactive with water. The reactions of $POCl_3$ resemble those of PCl_3. By means of Grignard reagents, the halogens can be replaced by alkyl or aryl groups.

$$POCl_3 + 3\,RMgX \longrightarrow OPR_3 + 3\,MgXCl \tag{46}$$

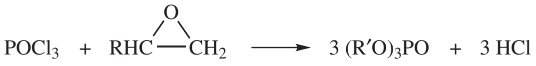
The reaction proceeds in a stepwise fashion and products with only one or two halogens can be produced by suitably limiting the reagent. Using alcohols, alkoxy groups are introduced. Either one or all three halogens can be replaced.



$$POCl_3 + CH_3OH \longrightarrow CH_3O\overset{O}{\overset{\|}{P}}Cl_2 + HCl \tag{47}$$

$$POCl_3 + 3\,CH_3OH \longrightarrow (CH_3O)_3PO + 3\,HCl \tag{48}$$

Adequate yields in this reaction require extremely efficient removal of HCl; otherwise CH_3Cl is formed. Some commercial processes utilize catalytic reactions of epoxy with $POCl_3$ (33):



(49)

Phosphorus oxychloride is stable to $> 300^\circ C$. Hydrolysis with water yields phosphoric acid.

$$POCl_3 + 3\,H_2O \longrightarrow H_3PO_4 + 3\,HCl \tag{50}$$

Phosphorus oxychloride has strong donor properties toward metal ions. The remarkably stable $POCl_3$–$AlCl_3$ complex has been utilized to remove $AlCl_3$ from Friedel-Crafts reaction products. Any POX_3 molecule contains a pyramidal PX_3 group; the oxygen atom occupies the fourth position to complete the distorted tetrahedron (21). Some properties of phosphorus oxyhalides are presented in Table 6.

Manufacture. Phosphorus oxychloride has been manufactured by oxidizing phosphorus trichloride. When oxygen is bubbled through liquid phosphorus trichloride, complete absorption of pure oxygen is effected in a 1-m depth. When there is good heat exchange, the rate of oxygen absorption remains practically

Table 6. **Physical Properties of Phosphorus Oxyhalides**[a]

Parameter	POF_3	$POCl_3$	$POBr_3$	POF_2Cl	$POFCl_2$	POF_2Br	$POFBr_2$
CAS Registry Number	[13478-20-1]	[10021-87-3]	[7789-59-5]	[73769-75-0]	[13769-76-1]	[14014-18-7]	[14014-19-8]
boiling point, °C	−40	107	193	3.1	52.9	30.5	110.1
melting point, °C	−68	1.25	56	−96.4	−80.1	−84.4	−117.2
apical angle,°	107	103.5	108	106	106		
bond length, pm							
P=O	155	145	141	155	154		
P−F	151			151	151		
P−Cl		202		202	200		
P−Br			206				

[a] Ref. 21.

constant until only 3–5 wt % of phosphorus trichloride remains in the oxychloride. The reaction is inhibited by impurities, especially iron and copper, sulfur compounds, or certain impurities from Cl_2 production process. If these impurities are present, the reaction rate between phosphorus trichloride and oxygen exhibits an induction period, and then increases to a maximum, after which it falls steadily as the reaction proceeds. A small amount of dissolved phosphorus in the phosphorus trichloride does not influence the reaction.

Heating a mixture of anhydrous phosphorus pentoxide [1314-56-3] and phosphorus pentachloride produces phosphorus oxychloride. Use of expensive phosphorus pentachloride is obviated by using a mixture of the trichloride and chlorine with the pentoxide. Thus, a manufacturing method consists of the chlorination reaction of the trichloride with the pentoxide:

$$3\,Cl_2 + 3\,PCl_3 + P_2O_5 \longrightarrow 5\,POCl_3 \tag{51}$$

Specifications. Typical analyses for technical-grade $POCl_3$ are as follows (30):

Property	Description or value
appearance	water-white liquid
distillation range, °C	
first drop	106.7
1–96 mL	1.0
dry point	107.9
specific gravity, 15.5°C/15.5°C	1.685
assay, %	99.9
free Cl_2	trace
PCl_3 %	0.10
Fe, ppm	1
crystallizing point, °C	~ 1.1

Storage, Shipping, and Handling. Phosphorus oxychloride is classified by the ICC as a corrosive liquid and a poisonous inhalation hazard. Shipment of $POCl_3$ must be in conformance with ICC regulations, and individual containers must be affixed with the DOT white acid label and red poison label: DOT UN No. 1810 (30). Phosphorus oxychloride is stored and shipped in 3.8-L (1-gal) or smaller glass containers and DOT-specification wooden overpacking. Bulk $POCl_3$ shipments are in nickel-clad tank cars of 15,000–30,000 L (4000–8000 gal) each. Glass and glass-lined steel equipment frequently is used for storage, as well as for reaction vessels (31).

Health and Safety Factors, Toxicology. Phosphorus oxychloride volatilizes readily; its vapors are extremely irritating to the eyes, skin, and mucous membranes (34). Direct contact with the liquid can produce severe burns. Contaminated clothing must be removed immediately. Inhalation of $POCl_3$ vapors can cause pulmonary edema and temporary eyesight problems.

The liquid reacts violently with water, releasing HCl and other gases in sufficient amounts to cause sudden rupture of closed or inadequately vented containers. The acid reaction products can react with metals to generate hydrogen, which is flammable and explosive. The oral LD_{50} in rats is 380 mg/kg; the inhalation LC_{50}

for rats is 48 ppm/4 h, and for guinea pigs, 53 ppm/4 h. The OSHA TWA standard is 0.1 ppm (32).

Uses. Phosphorus oxychloride is used extensively to manufacture alkyl and aryl orthophosphate triesters. A slight excess of the respective alcohol or phenol reacts with $POCl_3$ at elevated temperatures and, if necessary, in the presence of a catalyst.

$$POCl_3 + 3\,ROH \longrightarrow (RO)_3PO + 3\,HCl \tag{52}$$

It is frequently advantageous to favor rapid disengagement of HCl by operating the reaction in an inert solvent such as an alkane. The pure triesters are recovered by a multistep refining process (Fig. 3).

Most of the phosphate esters are used in the production of hydraulic fluids (qv), plastic and elastomer additives, flame retardants (qv), oil stabilizers, pesticides (qv), and medicinal intermediates (see Surfactants). Some trialkyl phosphates, $OP(OR)_3$, are outstanding solvents for nitrates, especially $(UO_2)(NO_3)_2$, and therefore are important in uranium processing (see Extraction).

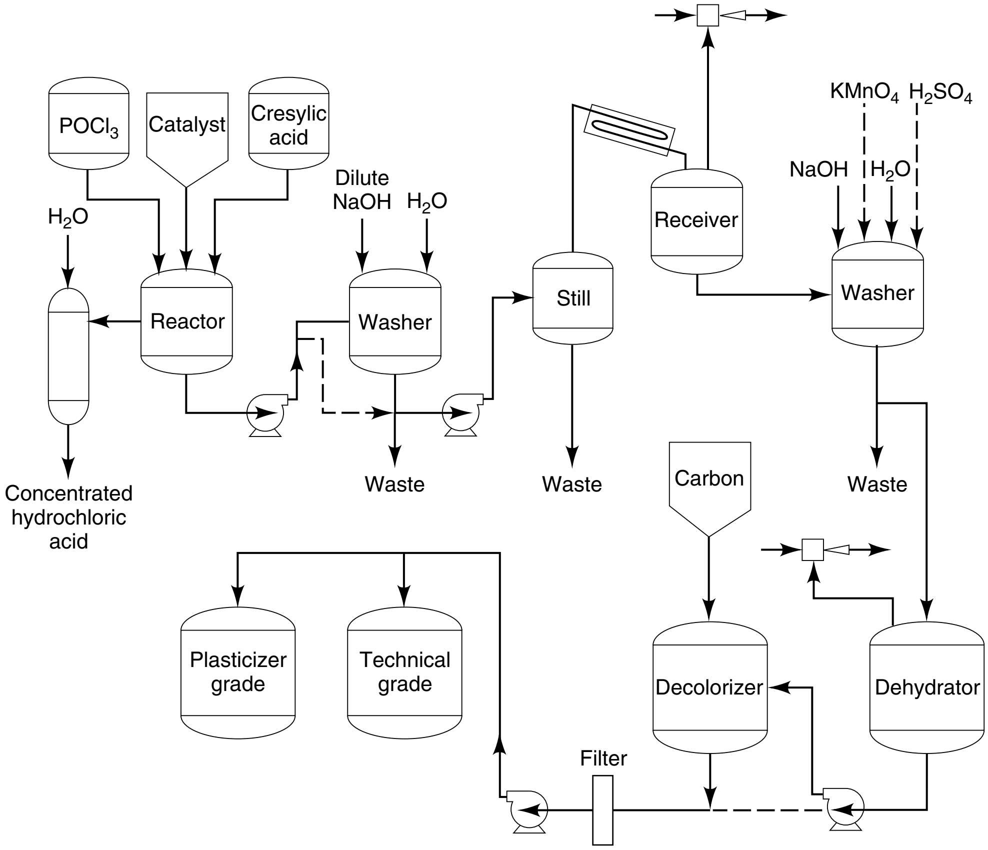
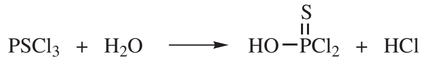


Fig. 3. Manufacturing of triarylphosphates.

Dialkyl phosphorochloridates, $(RO)_2P(=O)Cl$, react with trialkyl phosphate esters to give organic pyrophosphates. Organopyrophosphates are anticholinesterase agents and should be handled with great caution (12). Atropine sulfate is a specific antidote.

3.3. Phosphorus Sulfochloride. *Properties and Reactions.* Phosphorus sulfochloride [3982-91-0] (thiophosphoryl chloride), $PSCl_3$, is a colorless fuming liquid and is made by the reaction of phosphorus trichloride with sulfur and by the reaction of PCl_5 with P_2S_5. Phosphorus sulfochloride is dimorphic in the solid state. It reacts with water, forming either phosphoric acid or dichlorothiophosphoric acid [14500-94-8], depending on the reaction conditions.

$$PSCl_3 + 4\,H_2O \longrightarrow H_3PO_4 + 3\,HCl + H_2S \qquad (53)$$



$$PSCl_3 + H_2O \longrightarrow HO-\overset{\overset{S}{\|}}{P}Cl_2 + HCl \qquad (54)$$

Some physical properties of the phosphorus sulfohalides are summarized in Table 7.

Manufacture. Phosphorus sulfochloride is manufactured by the direct addition of sulfur to phosphorus trichloride (35–37). At ~180°C, the reaction proceeds smoothly. Phosphorus trichloride vapor is passed through an excess of sulfur that is either molten or dissolved in an inert solvent. The use of alkali or alkaline-earth sulfides catalyzes the reaction so that it is complete in a few hours at 150–160°C; use of aluminum chloride as the catalyst gives a comparable reaction rate at 115°C. When an excess of sulfur is used, the product can be distilled out of the reactor, and the residue of sulfur forms part of the charge in the following batch reaction. The reaction is carried out in a stainless steel autoclave, and the yield is better than 98% based on either reactant. Phosphorus sulfochloride is used primarily in the manufacture of insecticides (38–40), such as Parathion.

3.4. Phosphorus Pentachloride. *Properties and Reactions.* Phosphorus pentachloride, PCl_5, is a pale, greenish yellow solid having a pungent odor (see Table 5). It is made from PCl_3 and chlorine. Water attacks PCl_5 and the violent hydrolysis proceeds in two stages.

$$PCl_5 + H_2O \longrightarrow POCl_3 + 2\,HCl \qquad (55)$$

$$POCl_3 + 3\,H_2O \longrightarrow H_3PO_4 + 3\,HCl \qquad (56)$$

Experimental results suggest that PCl_5 is dimeric in CCl_4 solution. The structure consists of two octahedra sharing edges (41). The PCl_5 is monomeric in benzene and apparently is trigonal bipyramidal (20). Solid PCl_5 is ionic, consisting of $[PCl_4]^+$ cations and $[PCl_6]^-$ anions (20).

Manufacture. Phosphorus pentachloride is manufactured by either batch or continuous processing. In the former, the phosphorus trichloride usually dissolves in carbon tetrachloride before being treated with chlorine. A mixture of about one part of phosphorus trichloride to one part of carbon tetrachloride is introduced to a water-jacketed vessel that contains an efficient stirrer and a

Table 7. **Physical Properties of Phosphorus Sulfohalides**[a]

Parameter	PSF_3	$PSCl_3$	$PSBr_3$	PSF_2Cl	$PSFCl_2$	PSF_2Br	$PSFBr_2$
CAS Registry Number	[2404-52-6]	[3982-97-0]	[3937-S9-3]	[2524-02-9]	[2523-93-5]	[73706-09-7]	[73706-70-0]
boiling point, °C	−52.9	125	175 (dec)	6.3	64.7	35.5	125.3
melting point, °C	−148.8	−36.2	39	−155.2	−96.0	−136.9	−75.2
apical angles,° bond length,	100	101	106			106	100
P=S	185	194	189			187	187
P−F	153					145	150
P−Cl		202					
P−Br			213			214	223

[a] Ref. 21.

tight cover with a reflux condenser. The chlorine is passed into the vessel below the liquid level, and crystals of phosphorus pentachloride form in the liquid. When the reaction is completed, the suspension of crystals of phosphorus pentachloride in the carbon tetrachloride is drawn out of the vessel and the crystals are filtered and then dried by circulating hot water through the jacket of the filter. The clarified carbon tetrachloride is returned to the reaction vessel.

Specifications and Analysis. Specifications for PCl_5 are as follows: color, light lemon yellow; PCl_3, trace; Ni, 10 ppm max; Pb, 5 ppm max; and Fe, 5 ppm max. Analysis reveals the following: PCl_3, none; Ni, none; Pb, 1 ppm; and Fe, 2 ppm. Bulk density is $0.9\,g/cm^3$.

Storage, Shipping, and Handling. Phosphorus pentachloride is in the EPA extreme hazardous substance list. It is treated as a flammable solid, and containers in which it is stored or shipped must be affixed with a yellow acid label: DOT UN No. 1806. In general, the pentachloride should be handled with the same precautions that are used with the trichloride. Protective clothing should be worn by workers handling the pentachloride and gas masks should be used when personnel are exposed to the vapors (42).

Health and Safety Factors, Toxicology. Because of its fuming and deliquescent properties, PCl_5 is irritating and corrosive to skin, eyes, and mucous membranes. It reacts with moisture, liberating heat and forming hydrochloric and phosphoric acids which also burn tissue. Inhalation symptoms range from coughing, delayed sneezing, to pulmonary edema. The pentachloride is toxic; its TLV is 1 mg/m^3 of air. The oral LD_{50} in rats is 660 mg/kg; the inhalation LC_{50} for rats is 205 mg/m^3, for mice, 120 ppm/10 min (32). The OSHA standard in air TWA is 1 mg/m^3.

Uses. Phosphorus pentachloride is used in the manufacture of chlorophosphazenes, and serves as a catalyst and a chlorinating agent in organic syntheses.

$$PCl_5 + NH_4Cl \longrightarrow (PNCl_2)_n + 4\,HCl \tag{57}$$

4. Phosphorus Sulfides

4.1. Properties and Reactions.

Phosphorus combines with sulfur to form the binary tetraphosphorus trisulfide [1314-85-8] (phosphorus sesquisulfide), P_4S_3, (**1**); tetraphosphorus pentasulfide [12137-70-1], P_4S_5, (**2**); tetraphosphorus heptasulfide [12037-82-0], P_4S_7, (**3**); and phosphorus(V) sulfide [1314-80-3] (tetraphosphorus decasulfide), P_4S_{10}, (**4**). Further, tetraphosphorus enneasulfide [25070-46-6], P_4S_9, (**5**) has also been reported (43). In addition, a stable oxysulfide, $P_4O_6S_4$ [15780-31-1], exists as a colorless, deliquescent crystalline solid which has a melting point of 102°C. Some physical constants and thermodynamic data for these compounds are presented in Table 8. The structures, determined by x-ray crystallography, are shown in Fig. 4 (43).

The hydrolysis of phosphorus sulfides has been studied quantitatively. A number of products are formed (Table 9). Whereas phosphorus (V) sulfide reacts slowly with cold water, the reaction is more rapid upon heating, producing mainly hydrogen sulfide and orthophosphoric acid, H_3PO_4. At high pH, P_4S_{10} hydrolyzes to a mixture of products containing thiophosphates and sulfides.

Table 8. **Properties of Phosphorus Sulfides**[a]

Property	P_4S_3	P_4S_5	P_4S_7	P_4S_9	P_4S_{10}
CAS Registry Number	[1314-85-8]	[12137-70-1]	[12037-82-0]	[25070-46-6]	[1314-80-3]
mp,°C	173	170–220	307	240–270	285
bp,°C	407	dec[b]	523		515
Density, g/mL	2.03	2.17	2.19	2.08	2.09
color of solid	yellow	light yellow	almost white		yellow
solubility in					
CS_2, g/100 g					
−20°C	11				0.082
0 °C	27		0.005		0.18
17 °C	100[c]	10	0.029		0.22
reactivity					
in cold water	little attack		readily dec	readily dec	slowly dec
in air	slowly oxidize		dec		slowly dec
bond length, pm[d]					
P–P	223	225	233	233	
P–S	209	212	211	212	211
P=S		194	192	192	192
ΔH_f, kJ/mole[e,f]	−154	−207	−272	−292	−309
ΔH_{melt}, kJ/mol					41
ΔH_{vap}, kJ/mol	63.6		93.7		178[g]

[a] Ref. 43.

[b] Decomposes to P_4S_3 and P_4S_7.

[c] The solubility in C_6H_6 at 17°C is 2.5 g/100 g; at 80°C, 17 g/100 g.

[d] Values given are average ones.

[e] From red phosphorus and sulfur.

[f] To convert J to cal, divide by 4.184.

[g] Per mole of P_4S_{10} equivalent; the vapor species is P_2S_5.

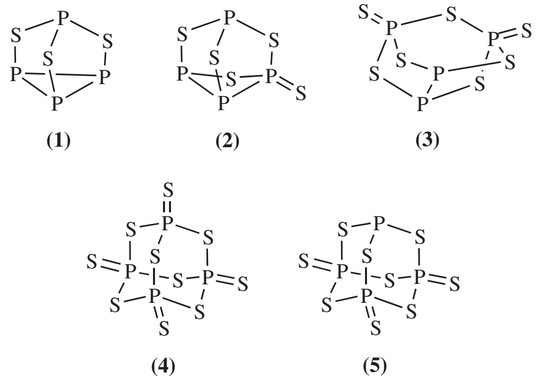
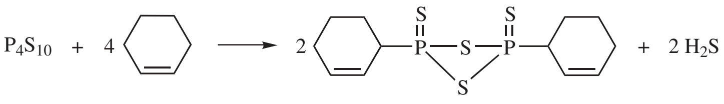


Fig. 4. Structure of phosphorus sulfides.

Phosphorus(V) sulfide reacts with olefins, amines, Grignard reagents, and terpenes (5,43) as follows:



(58)

$$P_4S_{10} + 8\,RNH_2 \longrightarrow 4\,(RNH_2)_2{-}\overset{\overset{\displaystyle S}{\|}}{P}{-}SH \tag{59}$$

$$P_4S_{10} + 4\,RMgX + 8\,H_2O \longrightarrow 4\,R{-}\overset{\overset{\displaystyle O}{\|}}{P}{-}(SH)_2 + 2\,H_2S + 4\,HOMgX \tag{60}$$

O,*O′*-Dialkyl or diaryl dithiophosphoric acids are obtained readily from alcoholysis of phosphorus(V) sulfide. Thus, P_4S_{10} reacts with ethyl alcohol as follows:

$$P_4S_{10} + 8\,C_2H_5OH \longrightarrow 4\,(C_2H_5O)_2{-}\overset{\overset{\displaystyle S}{\|}}{P}{-}SH + 2\,H_2S \tag{61}$$

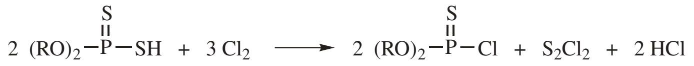
Dialkyl and diaryl dithiophosphoric acids are the bases of many high pressure lubricants, oil additives (see Lubrication and lubricants), and ore flotation chemicals (see Mineral recovery and processing). Organophosphorus insecticides, such as Parathion, are made by chlorination of the appropriate dialkyl

Table 9. **Products from Hydrolysis of Phosphorus Sulfides, %**[a]

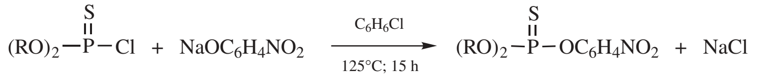
	Alkaline solutions			Acidic solutions			Neutral solutions		
Product	P_4S_3	P_4S_7	P_4S_{10}	P_4S_3	P_4S_7	P_4S_{10}	P_4S_3	P_4S_7	P_4S_{10}
PH_3	5	3			3		3	0	
H_3PO_2	15	2	10		1	10	38	24	
H_3PO_3	75	38			39	0	49	49	
H_3PO_4	0	57	80		57	85	6	6	100

[a] Ref. 5.

dithiophosphate and subsequent reaction of the intermediate dialkyl thiophosphoric chloride with sodium *p*-nitrophenolate according to the following:



$$2\ (RO)_2-\overset{\overset{\displaystyle S}{\|}}{P}-SH + 3\ Cl_2 \longrightarrow 2\ (RO)_2-\overset{\overset{\displaystyle S}{\|}}{P}-Cl + S_2Cl_2 + 2\ HCl \tag{62}$$



$$(RO)_2-\overset{\overset{\displaystyle S}{\|}}{P}-Cl + NaOC_6H_4NO_2 \xrightarrow[\text{125°C; 15 h}]{C_6H_6Cl} (RO)_2-\overset{\overset{\displaystyle S}{\|}}{P}-OC_6H_4NO_2 + NaCl \tag{63}$$

4.2. Manufacture. Phosphorus sulfides are manufactured commercially by direct reaction of the elements. Elemental phosphorus and sulfur are measured into a reaction vessel containing a heel of molten phosphorus sulfide. The reaction can be batch or continuous. The phosphorus/sulfur ratio in the feed determines which phosphorus sulfur compound (Table 8) is formed. The reaction temperature can be the boiling point or lower. For the boiling reactor (44,45), the phosphorus sulfide product is first purified by distillation and then condensed to a liquid. Alternatively, the liquid product can be formed directly in a nondistilled process (46–48), which may involve a subsequent distillation step (46), and in which the phosphorus is often cleaned up prior to use (47–49). For either process, the liquid phosphorus sulfide product is solidified, and usually sized to form a commercial material.

Phosphorus(V) sulfide, an important commodity in the United States since ~1920, is the dominant commercial material. Phosphorus sesquisulfide, P_4S_3, has been made commercially since ~1900. Phosphorus heptasulfide was introduced as a small-scale commercial product in 1940.

4.3. Analyses and Analytical Test Methods for P_4S_{10}. A typical analysis of P_4S_{10} yields the following:

appearance	greenish-yellow powder
phosphorus, wt%	27.4–28.3
color in ethanol, APHA	20–60
iron, ppm	10–20
reactivity, °C/min	
reactive grade	1
very high reactive grade	4–10

Phosphorus content usually is measured by a double end point titration method in which a 1.0-g sample is dissolved in a hot HNO_3–H_2SO_4–$HClO_4$ mixture. The pH is adjusted to 2.5 with NaOH, and the resulting H_3PO_4 is titrated with 0.5 *N* NaOH, using an automatic titrator. The titer between the first and second end points is used to quantify the phosphorus as H_3PO_4.

Reactivity is measured by placing a standard quantity, 100 mL, of isopropyl alcohol in a 500 or 1000-mL Dewar flask equipped with a stirrer and a temperature-measuring device. The temperature of the alcohol is adjusted to 30°C. A 36 g sample is added and the temperature is observed as a function of time from the addition until a maximum is reached. Reactivity is defined as the temperature rise divided by the time interval to reach this maximum. Other alcohols may also be used for measuring reactivity (47).

Reactivity is affected by particle size. Smaller particles react faster. However, the dominant factor for reactivity is the solidification rate. Material that is solidified quicker reacts faster with alcohol (47). Commercial P_4S_{10} is a solid solution containing P_4S_{10}, P_4S_9, P_4S_7, free sulfur, etc (50). Solidification rate also affects the distribution of these compounds. In part because P_4S_9 reacts 10 times faster with alcohol than P_4S_{10} (51). Further, for commercial P_4S_{10}, the P_4S_9/ P_4S_{10} ratio decreases (50) and the reactivity decreases on annealing (45,47).

4.4. Shipping and Storage.

Phosphorus (V) sulfide is stored and shipped in 208-L (55-gal) drums containing 250 kg of product, portable closed aluminum bins containing 1800–3400-kg net weight, and railcars. The P_4S_{10} is classified as a flammable solid having the international shipping code of UN No. 1340.

4.5. Health and Safety Factors, Toxicology.

One source of danger in the handling of phosphorus (V) sulfide is hydrogen sulfide. The OSHA exposure limit to hydrogen sulfide gas, which has a rotten egg odor at 0.1 ppm, is 15 ppm for 15 min or 10 ppm for 8 h. Respiratory problems occur for exposure > 50 ppm; death on exposure to concentration > 1000 ppm. Hydrogen sulfide results from the reaction of the phosphorus (V) sulfide with water or some other chemicals, such as alcohols. Further, phosphorus (V) sulfide combines with atmospheric moisture to release hydrogen sulfide via gradual hydrolysis. Care should be taken (*1*) to store P_2S_5 in well-sealed containers; (*2*) to convey P_2S_5 in well-sealed materials-handling systems containing dry, inert atmospheres; and (*3*) to handle phosphorus (V) sulfide in well-ventilated areas. Another source of danger in handling phosphorus (V) sulfide is fire and explosion. Phosphorus (V) sulfide burns readily to form sulfur dioxide, SO_2, and phosphorus pentoxide, P_4O_{10}, thus P_4S_{10} should be handled in inert atmospheres. Ignition sources, such as spark, static electricity, and heat should also be eliminated.

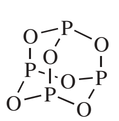
Phosphorus (V) sulfide is a mild skin irritant and may cause dermatitis in sensitive individuals. The primary health hazard results from the liberation of hydrogen sulfide after contact with moisture. Contact with moisture also forms phosphoric acid. A secondary hazard is the formation of sulfur dioxide when phosphorus (V) sulfide burns. The oral LD_{50} of in rats is 389 mg/kg; the OSHA standard time-weighted average (TWA) is 1 mg/m^3 (32).

4.6. Uses.

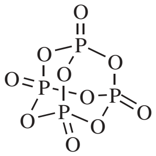
Phosphorus (V) sulfide is used in the manufacture of lubricating oil additives, insecticides, ore flotation agents, and specialty chemicals. Phosphorus sesquisulfide, P_4S_3, has been used extensively in the manufacture of strike-anywhere matches (qv). In addition, small quantities are used in fireworks (see Pyrotechnics).

5. Phosphorus Oxides and Acids

There are five well-defined oxides of phosphorus: phosphorus(III) oxide, P_4O_6 [12440-00-5], phosphorus(V) oxide (phosphorus pentoxide), P_4O_{10} [1314-56-3]; phosphorus tetroxide P_2O_4 [12164-97-5]; tetraphosphorus heptoxide, P_4O_7 [12065-80-4]; and tetraphosphorus nonaoxide, P_4O_9 [12037-11-5]. All are obtained by direct oxidation of phosphorus. The structures of P_4O_6 and P_4O_{10} are related to that of the phosphorus molecule, as shown in **6,7,8**.



(6)



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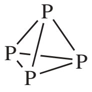


(8)

Other poorly characterized lower oxides of phosphorus ('LOOP') are sometimes formed. These are mixtures of usually water-insoluble, yellow-to-orange polymers (52), which are often formed as disproportionation byproducts in a number of reactions, eg, combustion of phosphorus with an inadequate air supply or hydrolysis of a phosphorus trihalide with less than a stoichiometric amount of water. LOOP may be pyrophoric and may hydrolyze or pyrolyze to yield diphosphine-contaminated phosphine.

5.1. Phosphorus (V) Oxides. *Properties and Structure.* Phosphorus (V) oxide, the extremely hygroscopic acid anhydride of the phosphoric acids, exists in several forms but is often referred to by its empirical formula, P_2O_5, phosphorus pentoxide. Three crystalline polymorphs, two distinct liquids, and several glassy solids are recognized.

The best characterized form of phosphorus pentoxide is the volatile, metastable, crystalline H (hexagonal) modification. It is obtained in tiny hexagonal flakes when phosphorus pentoxide vapor is slowly cooled. The H form consists of individual P_4O_{10} molecules. The standard heat of formation for the H modification of P_4O_{10} is $-3009.9\,\mathrm{kJ/mol}$ (23). The hexagonal form is stable indefinitely at room temperature but it changes to the metastable O (orthorhombic) form on heating to 400°C in a closed system. The orthorhombic modification is polymeric and usually forms as a chalky aggregate of small crystals.

The stable orthorhombic modification, O′ (T or δ-form) may be prepared by heating the other crystalline forms at 450°C for 24 h, producing a horny aggregate of large crystals. Fusion of the material is very slow, and superheating of the crystals occurs easily. The melt is a very viscous fluid and is different from the melt obtained from the hexagonal form. X-ray studies have shown that the O′ form is an infinite polymer of P_2O_5 (as is the other orthorhombic modification). A phase diagram is presented in Fig. 5.

Electron diffraction studies indicate that phosphorus pentoxide vapor consists of P_4O_{10} molecules. The vapor usually condenses to the hexagonal crystalline modification but under rapid cooling can be condensed to an amorphous solid (β-form). The liquid obtained by melting the stable orthorhombic modification cools to form a glass which is the γ-form. The liquid obtained from the H modification also can be supercooled to a glass.

Manufacture. Phosphorus (V) oxide is the only oxide produced commercially. It is made by burning elemental phosphorus in a controlled excess of very dry air in stainless steel externally cooled combustion chamber similar to that for producing thermal phosphoric acid. The combustion gases are then cooled in a large chamber or barn in which the P_4O_{10} gas is condensed. Condensation is promoted by rapid mixing with cooled gases, the barn being externally cooled by air or water. The phosphorus pentoxide consists of the hexagonal crystalline modification with some of the amorphous and O forms. The produc-

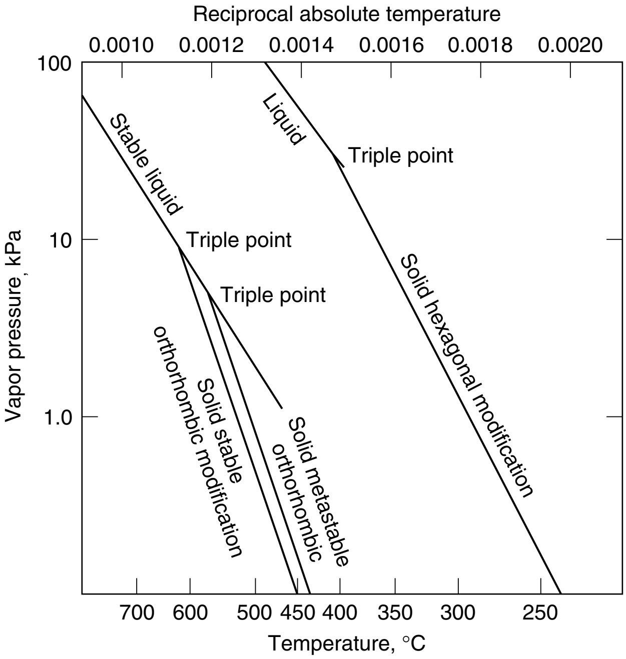


Fig. 5. Phase diagram for three crystalline and two liquid forms of phosphorus (V) oxide.

tion rate and the size, density, and crystallinity of the product are dependent on the cooling rate. Both technical and reagent grade phosphorus pentoxide is typically $> 99\%$ P_2O_5. Lower oxides, which may account for $< 0.3\%$ (as P_4O_6) in technical grade material are present at $< 0.02\%$ in reagent grade phosphorus pentoxide.

Health and Safety: Storage and Handling. Phosphorus (V) oxide is extremely hygroscopic and reacts with explosive violence when in contact with water or aqueous solutions. It is a local corrosive and irritates skin, eyes, and mucous membranes. Ten milligrams per cubic meter causes coughing; the TLV is $1\,mg/m^3$ (32). Phosphorus (V) oxide is sold in small glass bottles contained in boxes or hermetically sealed metal cans. Larger quantities are shipped in metal barrels or drums.

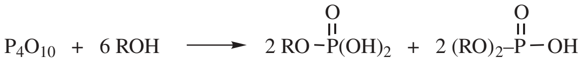
Uses. The most important chemical property of phosphorus pentoxide is its avidity for water. Below 100°C it is one of the most effective dehydrating agents known. The partial water vapor pressure over hydrated pentoxide is $<10^{-4}$ Pa at ambient temperature. It reacts with water to form a mixture of condensed phosphoric acids and extracts water from many substances that are considered good dehydrating agents. For example, phosphorus pentoxide converts pure HNO_3 to N_2O_5 and H_2SO_4 to SO_3, dehydrates amides to nitriles, reacts with alcohols producing phosphate esters, and effects ring closures and other condensation reactions. The main industrial application of phosphorus pentoxide as a drying agent has been in the dehydration step in the manufacture of methyl methacrylate resins. It is used as a drying agent for liquids and gases with which it does not react, especially to remove traces of water from vacuum systems. A drawback in its use as a drying agent is its tendency to coat with a layer of polyphosphoric acid, preventing further moisture absorption.

Phosphorus (V) oxide is used in the manufacture of phosphorus oxychloride, as a catalyst in air blowing of asphalt, and as an intermediate for phosphate esters. Phosphate esters may also be manufactured from $POCl_3$, which in turn may be produced from either PCl_3 or from P_2O_5 and PCl_5. Phosphate esters are used as surfactants, hydraulic fluids, and plasticizers. Organophosphate surfactants are used in industrial and specialty applications, eg, components of dry cleaning compounds, water- and oil-based cutting fluids, emulsifiers and wetting agents in textile manufacturing, emulsifiers in emulsion-polymerization processes, pigment dispersants in oil-based paints, emulsifiers and moisture barrier compounds in cosmetics, and mold-release agents. Liquid phosphate esters, eg, tricresyl phosphate are used as high temperature stable, fire-resistant hydraulic fluids. A large use is the preparation of the plasticizer triethyl phosphate [78-40-0]:

$$\tfrac{1}{2}\,P_4O_{10} + 3\,(C_2H_5)_2O \longrightarrow 2\,(C_2H_5O)_3P{=}O \qquad (64)$$

Phosphorus compounds are effective flame retardants for oxygenated synthetic polymers, such as polyurethanes and polyesters. Aryl phosphates and chloroalkyl phosphates are commonly used. Phosphorus compounds promote char formation, thereby inhibiting further ignition and providing an efficient thermal insulation to the underlying polymer.

Mixed mono- and dialkylphosphates are used as catalysts for resin curing and as intermediates for fire retardants, oil additives, antistatic agents, and extraction solvents. An equimolar mixture of mono- and dialkyl acid phosphates is formed at a 1:6 mole ratio of the oxide to alcohol.



$$P_4O_{10} + 6\,ROH \longrightarrow 2\,RO{-}\overset{\overset{\displaystyle O}{\|}}{P}(OH)_2 + 2\,(RO)_2{-}\overset{\overset{\displaystyle O}{\|}}{P}{-}OH \qquad (65)$$

The aryl phosphate esters are similarly produced from phenols. For example, a mixture of $C_9H_{19}{-}C_6H_4{-}(OCH_2CH_2)_nO{-}P({=}O)(OH)_2$ and $[C_9H_{19}{-}C_6H_4{-}(OCH_2CH_2)_nO]_2P({=}O){-}OH$ are formed from polyethoxylated nonylphenol. The magnesium salts of the ester mixture are soluble in organics and may be used as dry cleaning surfactants.

5.2. Phosphorus (III) Oxide. Phosphorus (III) oxide [12440-00-5], the anhydride of phosphonic acid, is formed along with byproducts such as phosphorus pentoxide and red phosphorus when phosphorus is burned with less than stoichiometric amounts of oxygen (53). Phosphorus (III) oxide, also known as phosphorus trioxide, is a poisonous, white, wax-like, crystalline solid with a melting point of 23.8°C, and a boiling point of 175.3°C. When added to hot water, phosphorus (III) oxide will react violently with the formation of phosphine, phosphoric acid, and red phosphorus. Even in cold water, disproportionation may be observed if the oxide is not well agitated, forming phosphoric acid and LOOP.

Phosphorus (III) oxide is slowly oxidized in the air but when heated above 70°C it can spontaneously ignite as a result of disproportionation to yield elemental phosphorus. Above 210°C, the oxide decomposes into phosphorus and phosphorus tetroxide.

$$4\,P_4O_6 \longrightarrow P_4 + 6\,P_2O_4 \qquad (66)$$

Phosphorus tetroxide is made by heating P_4O_6 in a sealed tube to 440°C.

In both the liquid and vapor states, phosphorus (III) oxide exists as the P_4O_6 molecule and sublimes under vacuum at 180°C and forms colorless, glossy crystals.

5.3. Phosphonic Acid and P (III) Derivatives. Phosphonic or phosphorous acid is a white deliquescent crystalline compound having a melting point of 73.6°C. As evidenced by its structure, $HP(=O)(OH)_2$, phosphonic acid is dibasic. The first hydrogen is strongly ionized, $pK_{a1} = \sim 1.5$, and is therefore a stronger acid than orthophosphoric acid. The second dissociation constant, $pK_{a2} = 6.7$. The third hydrogen does not ionize in aqueous solution. Heating phosphonic acid above ~ 180°C results in an exothermic disproportionation to phosphoric acid, phosphine, and hydrogen. A common accident occurs in overheating reactions in which phosphonic acid or LOOP may be formed, eg, in making alkyl chlorides from PCl_3 at too high a temperature. Phosphonic acid is also referred to as phosphorous acid although technically, the latter is an isomer of phosphonic acid that is not found as the free acid but usually as the triester derivative. The standard heat of formation for phosphonic acid, H_3PO_3 (c) is −964.4/mol (−230.5 kcal/mol) (23).

Phosphonic acid is prepared by the dissolution of phosphorus (III) oxide or more commonly by hydrolysis of phosphorus trichloride:

$$PCl_3 + 3\,H_2O \longrightarrow H_3PO_3 + 3\,HCl \qquad (67)$$

This violent reaction can be tempered by adding PCl_3 to a saturated solution of HCl. Subsequently, the water and hydrogen chloride are boiled out until the temperature reaches 180°C. On cooling, phosphonic acid crystallizes from the melt. Phosphonic acid is typically sold as a 70% solution. Several attempts have been made to produce phosphonic acid by a nonhalide route; however, so far, none of these efforts has been translated into an industrial process.

Phosphonic acid is also derived from byproduct streams. In the manufacture of acid chlorides from carboxylic acids and PCl_3, copious quantities of yellow, polymeric LOOP are frequently also formed. Such mixtures slowly evolve phosphine, particularly on heating and formerly were a disposal problem. Purification of this crude mixture affords commercial phosphonic acid. By-product acid is also derived from acidifying calcium phosphite formed as a by-product in the manufacture of phosphinic acid.

$$H_2SO_4 + CaHPO_3 \longrightarrow H_3PO_3 + CaSO_4 \qquad (68)$$

Phosphonic acid and hydrogen phosphonates are used as strong but slow-acting reducing agents. They cause precipitation of heavy metals from their salt solutions and reduce sulfur dioxide to sulfur, and iodine to iodide in neutral or alkaline solution:

$$HPO_3^{2-} + 3\,OH^- \longrightarrow PO_4^{3-} + 2\,H_2O + 2\,e^- E^\circ = 1.12\,V \qquad (69)$$

In acid solution, the potential of the H_3PO_3-H_3PO_4 couple is +0.20 V. When heated to 200°C, phosphonic acid disproportionates to phosphoric acid and phosphine.

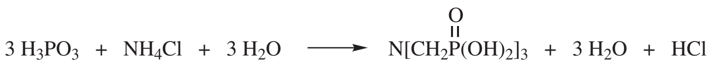
$$4\,H_3PO_3 \longrightarrow 3\,H_3PO_4 + PH_3 \tag{70}$$

The dimer of phosphonic acid, diphosphonic acid (pyrophosphorous acid) $H_4P_2O_5$ [36465-90-4] is formed by the reaction of phosphorus trichloride and phosphonic acid in the ratio of 1:5. It is also formed by the thermal dehydration of phosphonic acid. Unlike the chemistry of phosphoric acid, thermal dehydration does not lead to polymers beyond the dimer; extended dehydration leads to disproportionation to condensed forms of phosphoric acid, such as $H_4P_2O_7$ [2466-09-3] and phosphine.

$$2\,H_3PO_3 \longrightarrow H_4P_2O_5 + H_2O \tag{71}$$

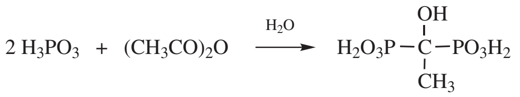
$$2\,H_4P_2O_5 \longrightarrow H_4P_2O_7 + HPO_3 + PH_3 \tag{72}$$

Phosphonic acid is an intermediate in the production of alkylphosphonates that are used as herbicides and as water treatment chemicals for sequestration, scale inhibition, deflocculation, and ion control agents in oil wells, cooling tower waters, and boiler feed waters. For example, aqueous phosphonic acid is reacted with formaldehyde and ammonium chloride in the presence of hydrochloric acid to yield aminotri(methylenephosphonic acid) [6419-19-8]:



$$3\,H_3PO_3 + NH_4Cl + 3\,H_2O \longrightarrow N[CH_2\overset{\overset{\displaystyle O}{\|}}{P}(OH)_2]_3 + 3\,H_2O + HCl \tag{73}$$

1-Hydroxyethane-1,1-diphosphonic acid [2809-21-4] (HEDP) is produced by hydrolysis of the reaction product of phosphonic acid and acetic anhydride:

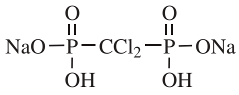


$$2\,H_3PO_3 + (CH_3CO)_2O \xrightarrow{H_2O} H_2O_3P-\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}-PO_3H_2 \tag{74}$$

Glyphosate (*N*-carboxymethylaminomethanephosphonic acid, or *N*-phosphonomethyl glycine [1071-83-6] (**9**), is a large volume biodegradable total herbicide sold as the isopropylammonium salt developed by Monsanto under the trade name of Roundup. 1,1-Bis(phosphonates) are an important class of pharmaceuticals for inhibiting bone resorption (calcium regulator). A commercial example is disodium clodronate [22560-50-5] 10(54).

$$HO-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2NHCH_2-\overset{\overset{\displaystyle O}{\|}}{P}(OH)_2$$

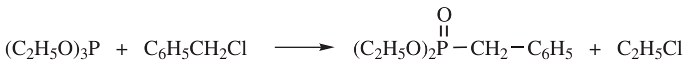
(**9**)



$$NaO-\underset{\underset{\displaystyle OH}{|}}{\overset{\overset{\displaystyle O}{\|}}{P}}-CCl_2-\underset{\underset{\displaystyle OH}{|}}{\overset{\overset{\displaystyle O}{\|}}{P}}-ONa$$

(**10**)

Monoesters of the phosphonic acids are little used in industry. The diesters of phosphonic acid, $O{=}PR(OR)_2$, are commonly prepared in industry from trialkyl phosphites in a Michaelis-Arbusov reaction:



$$(C_2H_5O)_3P + C_6H_5CH_2Cl \longrightarrow (C_2H_5O)_2\overset{O}{\overset{\parallel}{P}}-CH_2-C_6H_5 + C_2H_5Cl \tag{75}$$

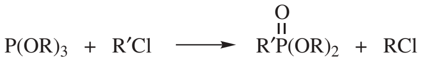
The Michaelis-Arbusov reaction is very exothermic and can be explosive; therefore, it is preferable to initiate the reaction with an alkyl halide at a lower temperature where the reaction rate is controlled by the halide concentration.

Trialkyl esters of phosphonic acid exist in two structurally isomeric forms. The trialkylphosphites, $P(OR)_3$ are isomers of the more stable phosphonates, $O{=}PR(OR)_2$, and the former may be rearranged to the latter with catalytic quantities of alkylating agent. The dialkyl alkylphosphonates are used as flame retardants, plasticizers, and as intermediates. The Michaelis-Arbusov reaction may be used for a variety of compound types, including mono- and diphosphites (17). Triaryl phosphites do not readily undergo the Michaelis- Arbusov reaction, although there are a few special cases.

Phosphorus trichloride may also be used directly in the production of trialkyl phosphites, dialkyl phosphonates, and dialkyl alkylphosphonates.

$$PCl_3 + 3\,ROH \longrightarrow H\overset{O}{\overset{\parallel}{P}}(OR)_2 + 2\,HCl + RCl \tag{76}$$

$$PCl_3 + 3\,ROH \longrightarrow + 3\,NR'_3 \longrightarrow P(OR)_3 + 3\,NR'^{*}_3HCl \tag{77}$$



$$P(OR)_3 + R'Cl \longrightarrow R'\overset{O}{\overset{\parallel}{P}}(OR)_2 + RCl \tag{78}$$

The phosphite triesters are useful in esterifying carboxylic acids. The triesters are readily oxidized to the respective phosphates.

5.4. Phosphinic Acid. Phosphinic acid (hypophosphorous acid) is a deliquescent crystalline solid that melts at 26.5°C. It is a monobasic acid having a pK_a of 2.1. Its metal salts generally exhibit a high solubility. Phosphinic acid disproportionates upon heating $> 133°C$ to generate phosphoric and phosphonic acids, hydrogen, and phosphine.

$$2\,H_3PO_2 \longrightarrow H_3PO_4 + PH_3 \tag{79}$$

The standard heat of formation for crystalline H_3PO_2 is -604.6 kJ/mol (-144.5 kcal/mol) (23).

The acid can be prepared by the oxidation of phosphine with iodine and water.

$$PH_3 + 2\,I_2 + 2\,H_2O \longrightarrow H_3PO_2 + 4\,HI \tag{80}$$

The reaction is quantitative and byproduct hydroiodic acid is removed by repeated distillation at 5.3 kPa (40 mmHg), leaving pure H_3PO_2 as the product. Phosphinic acid may also be prepared by the treatment of barium hypophosphite [14871-79-5] with a stoichiometric quantity of sulfuric acid to precipitate barium sulfate.

Commercially, phosphinic acid and its salts are manufactured by treatment of white phosphorus with a boiling slurry of lime. The desired product, calcium phosphinite [7789-79-9], remains in solution and insoluble calcium phosphite [21056-98-4] is precipitated.

$$P_4 + 2\,Ca(OH)_2 + 3\,H_2O \longrightarrow PH_3 + H_2 + Ca(H_2PO_2)_2 + CaHPO_3 \qquad (81)$$

Phosphine and hydrogen are also formed, the gas-containing sufficient diphosphine to make it spontaneously flammable. Under some conditions equal amounts of phosphorus appear as phosphine and as phosphite, and the volume of the hydrogen liberated is nearly proportional to the hypophosphite that forms.

$$P_4 + 4\,OH^- + 4\,H_2O \longrightarrow 4\,H_2PO_2^- + 2\,H_2 \qquad (82)$$

$$P_4 + 4\,OH^- + 2\,H_2O \longrightarrow 2\,HPO_3^{2-} + 2\,PH_3 \qquad (83)$$

In addition, a small amount of decomposition of hypophosphite by alkali occurs.

$$H_2PO_2^- + OH^- \longrightarrow HPO_3^{2-} + H_2 \qquad (84)$$

Excess calcium hydroxide is precipitated using carbon dioxide and the calcium carbonate, calcium hydroxide, and calcium phosphite are removed by filtration. The filtered solution is treated with an equivalent amount of sodium sulfate or sodium carbonate to precipitate calcium sulfate or carbonate. Sodium hypophosphite monohydrate [10039-56-2] is recovered upon concentration of the solution. Phosphinic acid is produced from the sodium salt by ion exchange. The acid is sold as a 50 wt%, 30–32 wt%, or 10 wt% solution.

Phosphinic acid and its salts are strong reducing agents, especially in alkaline solution (55).

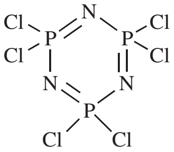
$$H_3PO_2 + H_2O \longrightarrow H_3PO_3 + 2\,H^+ + 2\,e^- + 0.50\,V \qquad (85)$$

$$H_2PO_2^- + 3\,OH^- \longrightarrow HPO_3^{2-} + 2\,H_2O + 2\,e^- + 1.56\,V \qquad (86)$$

A principal commercial application of the hypophosphites is in the electroless plating process. Nickel salts are chemically reduced by hypophosphites to form a smooth adherent nickel plating to protect the interiors of large vessels and tank cars. The coating, which can be hardened by heat treatment, usually contains 8–10 wt% phosphorus and is highly impervious.

6. Phosphazenes and Other Phosphorus–Nitrogen Compounds

6.1. Phosphazenes. Phosphazenes, $(NPX_2)_n$, are a class of linear and cyclic compounds with an unsaturated skeleton of alternating phosphorus and nitrogen atoms (56,57). Hexachlorocyclotriphosphazene [940-71-6] $(NPCl_2)_3$ (**11**) and Octachlorocyclotetraphosphazene [2950-45-0] $(NPCl_2)_4$, are made by the slow addition of phosphorus pentachloride to an excess of ammonium chloride in a solvent, such as chlorobenzene or tetrachloroethane. Addition of suitable anhydrous metal chlorides, such as $SnCl_4$, $MgCl_2$, $ZnCl_2$, $MnCl_2$, and $TiCl_4$ at 1–10 wt% reduces the reaction time to 5–10 h. Other catalysts are also known. The most serious problem is the isolation and purification of the products. Crude mixtures of chlorophosphazenes can be produced quite inexpensively, but the pure cyclic trimer is expensive. The lower cyclic species can be extracted from the reaction mixture using low boiling petroleum ether; the trimer then is separated by vacuum distillation.



(**11**)

Heating the lower cyclic halophosphazenes results in the formation of linear high polymers, such as poly(dichlorophosphazene) [25034-79-1] (**12**). The high polymeric polyphosphazenes are also known as inorganic rubber because of their with elastomeric properties.

The halophosphazenes are hydrolyzed by water. The most reactive species are hydrolyzed upon contact with atmospheric moisture at room temperature, but more stable species are hydrolyzed by boiling acid or caustic. The halophosphazenes are degraded to halide ion, phosphoric acid or phosphate, and ammonia or ammonium ion. Some properties of chlorophosphazenes are listed in Table 10. The lower linear chlorophosphazenes are oily substances, whereas most of the cyclic members are crystalline white solids. The lower chlorophosphazenes are characterized by high vapor pressures at room temperature and small concentrations cause prolonged irritation of eye membranes. Temporary throat and lung irritation following inhalation of these compounds also occurs.

The cyclic halides can be converted to discrete substitution products by reaction with amines, alcohol, or alkylating agents. For example, $(NPCl_2)_3$ reacts with ammonia to form $(NP(NH_2)_2)_3$ [13597-92-7], with p-$NaOC_6H_4CH_3$ to form $(NP(OC_6H_4CH_3)_2)_3$ [27122-73-2], or with CH_3MgCl to form $(NP(CH_3)_2)_3$ [6607-

Table 10. **Physical Properties of Phosphazenes**[a]

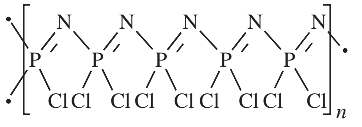
Compound formula	CAS Registry Number	Melting point, °C	Boiling point, °C
	Cyclic phosphazenes		
$(NPCl_2)_3$	[940-71-6]	114[b]	256
$(NPCl_2)_4$	[2950-45-0]	123.5[b]	328.5
$(NPCl_2)_5$	[14596-41-3]	41.3[c]	223–224
$(NPCl_2)_6$	[2851-52-7]	92.3[c]	281–282
$(NPCl_2)_7$	[13827-30-0]	8–18[c]	289–294
$(NPCl_2)_8$	[14514-98-8]	57–58[c]	
	Linear phosphazenes		
$Cl_3P{=}NPCl_2N\text{-}POCl_2$	[36778-94-6]	32–33	
$[Cl(PCl_2{=}N)_3PCl_3]^+(PCl_6)^-$	[21246-63-9]	95–96	
$[Cl(PCl_2{=}N)_4PCl_3]^+(PCl_6)^-$	[21283-49-8]	98–100	

[a] Ref. 56.

[b] At 101.3 kPa (1 atm.).

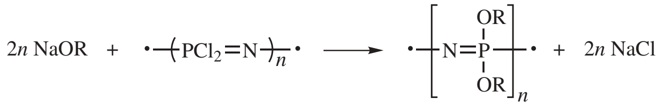
[c] At 1.7 kPa (13 mmHg).

30-3]. Among the cyclic members, the trimeric halides are the most inert toward substitution and tetrameric halides the most active.



(**12**)

Poly(dichlorophosphazene), Cl-(PCl_2=N)$_n$-$PCl_3{}^+X^-$, where X= Cl or PCl_6, is formed by heating purified hexachlorocyclotriphosphazene in the molten state at 210−250°C while protecting the reaction from moisture. The time, temperature, and extent of polymerization to $< 70\%$ are carefully regulated. An uncross-linked high polymer is formed that is soluble in solvents, such as toluene or tetrahydrofuran (thf). The chlorine atoms of the dissolved polymer can be effectively substituted by nucleophiles to form alkoxy, amino derivatives, etc. For example,



$$2n\,\mathrm{NaOR} + \cdot\!\left(\mathrm{PCl_2{=}N}\right)_n\!\cdot \longrightarrow \cdot\!\left[\mathrm{N{=}}\overset{\mathrm{OR}}{\underset{\mathrm{OR}}{\mathrm{P}}}\right]_n\!\cdot + 2n\,\mathrm{NaCl} \tag{87}$$

Continued heating of the unsubstituted polymer also yields insoluble cross-linked elastomeric polyphosphazenes. The rubber-like material may possess molecular weights on the order of 10^6–10^7.

Although polyphosphazenes exhibit interesting properties as elastomers, commercial importance of the unsubstituted chloro polymers has been limited by hydrolytic instability. Polymers substituted with organic side groups are however generally stable toward water. Properties of the substituted polymers include low temperature flexibility and elasticity, thermal stability in excess of 200°C, high stability to various kinds of radiation, resistance to water, solvents, and oils, and nonflammability and flame retardancy. Polymer properties, such as crystallinity, hydrophilicity, and electrical conductivity can be controlled over a wide range through selection of the substituted side groups. Hydrocarbon-resistant fluoroalkyloxy elastomers have been fabricated for automotive applications, aryloxy foams were developed for flame resistance, as well as heat and sound insulation, and poly(bis(methoxyethoxyethoxy)phosphazene) [98973-15-0] has been proposed as a solid electrolyte for rechargeable batteries. Biomedical applications, such as heart valves and controlled-release drug delivery systems have also been proposed. In spite of the variety of controllable properties, phosphazene polymers have not yet achieved widespread commercial application.

6.2. Other Phosphorus–Nitrogen Compounds. Of the binary phosphorus-nitrogen compounds, only triphosphorus pentanitride [12136-91-3], P_3N_5, has been obtained in a pure state. It can be prepared by treating P_2S_5 with ammonia and subsequent heating of the intermediate product to 850°C in a stream of NH_3. Triphosphorus pentanitride is a colorless solid, tasteless, odor-less, insoluble in common solvents, and stable in ambient atmosphere. Upon being heated under vacuum, the compound decomposes $>760°C$ into the elements, whereas heating in a stream of hydrogen yields P_4 and NH_3. The unstable trichlorophosphineimide [14700-11-9], $Cl_3P{=}NH$, results from the reaction of PCl_5 with ammonia. However, if the interaction product of phosphorus pentachloride and ammonia is heated *in vacuo*, phospham [22722-08-3], $[PN_2H]_n$ forms. Phospham is a white, loose powder and is insoluble in water. It appears to have potential utility as a flame retardant, eg, for nylon (58).

6.3. Inorganic Phosphines and Phosphides. *Phosphine.* Phosphine, PH_3, is an extremely toxic gas. Phosphine can be produced in a number of ways, but the inadvertent evolution of phosphine in an otherwise-safe reaction is another element of hazard in many procedures involving phosphorus chemicals. Phosphine can be conveniently produced by the hydrolysis of an active metal phosphide, eg, Ca_3P_2 [1305-99-3] or AlP [20859-73-8] (5). By using aluminum phosphide, AlP, the yields are high and contamination by diphosphine are minimal.

Phosphine is prepared commercially by the acid- or base-catalyzed reaction of elemental phosphorus with water. In the acid-catalyzed reaction, white phosphorus (P_4) converts in part to red phosphorus; the latter is the main reactant (59).

$$P_4 + 12\,H_2O \xrightarrow[\text{polyphosphoric acid}]{280°C} 5\,PH_3 + 3\,H_3PO_4 \qquad (88)$$

Phosphine is also made as a by-product of the commercial production of sodium hypophosphite [7789-79-9] from elemental phosphorus and a base such as lime or caustic. Compared with the acid process, the base-catalyzed process has the disadvantage of generating large quantities of hydrogen along with the phosphine and a lower yield of phosphorus as phosphine.

Phosphine is usually contaminated to varying degrees with diphosphine which renders it spontaneously flammable. Pure phosphine can be produced by hydrolysis of phosphonium iodide [12125-09-6] PH_4I. Phosphine is purified commercially for electronics use by pressure distillation to remove hydrogen, air, arsine, water, etc. Electronics grade phosphine is typically >99.999% pure. Phosphine is used in gallium phosphide and indium phosphide semiconductor devices, such as light-emitting diodes (LED) and laser diodes, and as an n-type dopant for silicon. Phosphine is also used as a grain fumigant. The standard heat of formation of PH_3 (g) is 5.4 kJ/mol (1.3 kcal/mol) (23).

Phosphides. Compounds of phosphorus with the more electropositive elements are generally called phosphides. A large number of binary phosphides are known, as well as many ternary mixed-metal phosphides, metal phosphide nitrides, etc. Some binary phosphides, such as those of nickel exhibit a variety of stoichiometries (Ni_3P, Ni_5P_2, $Ni_{12}P_5$, Ni_2P, Ni_5P_4, NiP, NiP_2, NiP_3), while others such as aluminum form only one, AlP [20859-73-8]. Metalloids such as B and Si also form phosphides.

The phosphides are usually made by the direct combination of the elements at elevated temperature. Lithium phosphide Li_3P [12057-29-3], Sodium phosphide Na_3P [12058-85-4], potassium phosphide KP_{15} [12260-14-9], as well as iron (III) phosphide FeP [26508-33-8], and diiron phosphide Fe_2P [1310-43-6], are made in this manner.

Some phosphides such as titanium phosphide TiP [12037-65-9] can be prepared by passing phosphine over the metal or its halide. Phosphides may also be prepared by reducing phosphorus-containing salts with hydrogen, carbon, etc, at high temperatures, the main example being the byproduct formation of ferrophosphorus in the electric furnace process for elemental phosphorus. Phosphrus-rich phosphides such as vanadium diphosphide [12037-77-3] may be converted to lower phosphides, eg, vanadium phosphide [12066-53-4] by thermal treatment:

$$VP_2 \longrightarrow VP + P \tag{89}$$

Phosphides have varying degrees of metallic, covalent, and ionic character to the bonding. Strongly electropositive metals, eg, alkali metal, alkaline earth, and lanthanides, yield ionic phosphides that react readily with water to generate phosphine. The usual alkali metai phosphides are reddish-brown to black and are stable up to 650°C but react instantly with moisture to form phosphine. Magnesium phosphide Mg_3P_2 [12057-74-8], and AlP, are stable in dry air, but decompose upon contact with water. These compounds are used with an igniting agent, eg, 1 wt% nitric acid or nitric oxide, in sea flares to produce a dense cloud of phosphoric acid mist and a highly luminous flame. Aluminum phosphide has been used since the 1930s for the generation of phosphine in grain fumigation. Magnesium phosphide, calcium phosphide Ca_3P_2 [1305-99-3], and zinc phosphide, Zn_3P_2 [1314-84-7] are also used as fumigants and/or rodent poisons. Calcium phosphide is prepared commercially by heating quick lime in phosphorus vapor.

The alkali metal phosphides of formula M_3P and the alkaline earth phosphides of formula M_3P_2 contain the P^{3-} anion. Calcium diphosphide, CaP_2 [81103-86-8], contains the ${P_2}^{4-}$ ion and reaction with water liberates diphosphine, maintaining the P–P linkage intact.

$$2\,CaP_2 + 4\,H_2O \longrightarrow P_2H_4 + 2\,Ca(OH)_2 \tag{90}$$

The existence of a variety of other polyphosphide anions has been demonstrated, eg, ${P_3}^{5-}$ and ${P_5}^{7-}$ have been identified in LaP_2 (60).

The phosphides of the less electropositive metals and the metalloids may be considered more as metal–phosphorus alloys. They are thermally stable and are typically resistant to attack by water, even at 100°C. Some are resistant to dilute acids or bases, but most are decomposed by stronger oxidizing acids or by bases. The transition metal-rich phosphides are comparable in structure and properties to the transition metal borides and silicides.

The phosphides are sometimes classified according to stoichiometry into metal-rich phosphides ($M/P > 1$), monophosphides ($M/P = 1$), and phosphorus-rich phosphides ($M/P < 1$). The metal-rich phosphides are typically hard and brittle, having a metallic luster and possessing high electrical and thermal conductivities. The monophosphides are typically also hard, chemically inert, and possess a luster. Many of the monophosphides and the phosphorus-rich phosphides are semiconductors. Gallium phosphide, GaP [12063-98-8], and indium phosphide, InP [22398-80-7], are specialty semiconductors having a high electron-hole mobility. These phosphides and related ternary compounds are used in light emitting diodes, solar energy conversion panels, field effect transistors, photodetectors, etc. The structures of the phosphorus-rich phosphides are made of increasingly polymerized polyphosphide anions as the M/P ratio decreases.

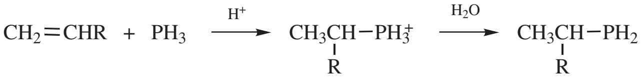
Ferrophosphorus is produced as a by-product in the electrothermal manufacture of elemental phosphorus, the iron being present as an impurity in the phosphate rock raw material. The commercial product contains ~23–29% P and is composed primarily of Fe_2P and Fe_3P [12023-53-9]. Ferrophosphorus is used in metallurgical processes for the addition of phosphorus content. Low concentrations of phosphorus (up to ~0.1%) in wrought and cast iron and steel increases the strength, hardness, and wear resistance and improves the flow properties.

Copper and tin phosphides are used as deoxidants in the production of the respective metals, to increase the tensile strength, and corrosion resistance in phosphor bronze [12767-50-9], and as components of brazing solders.

6.4. Health and Safety Factors, Toxicology. Phosphine is one of the most toxic of the simple gases. Phosphine is lethal to adults in a 0.5–1 h exposure at 0.05 mg/L (7). Phosphine acts as a central nervous system and liver toxin. The corresponding value for H_2S is 9.6 mg/L and, for HCN, 0.12 mg/L. Federal specifications regarding exposure are 400mg/m^3 TWA and a TLV of 0.3 ppm (32). Handling on a large scale requires detection monitoring, personal protective equipment, air-breathing stations, and flame retardant. Phosphine is unacceptable for transport on either passenger or cargo aircraft. Phosphine is pyrophoric, exhibiting a wide flammability range. The lower explosion limit for phosphine is 1.6% and the upper limit is near 100% (61).

6.5. Organophosphines and Derivatives. *Organophosphines. Preparation and Properties of Organophosphines.* Aliphatic phosphines can be gases, volatile liquids, or oils. Aromatic phosphines frequently are crystalline, although many are oils. Some physical properties are listed in Table 11. The most characteristic chemical properties of phosphines include their susceptibility to oxidation and the availability of the unshared electron pair for coordination. The most common derivatives of the phosphines include the halophosphines, phosphine oxides, metal complexes of phosphines, and phosphonium salts. Phosphines are also raw materials in the preparation of P^I derivatives, ie derivatives of the tautomers phosphinic acid, $HP(OH)_2$, and phosphonous acid, $H_2P(=O)OH$.

There are a few economical routes that can be employed for production of the largest volume phosphines. The preparation of alkyl phosphines where $R \geq C_2H_5$ employs the addition of lower phosphines across an olefinic double bond. The reaction may be either acid, base, or radical catalyzed. The acid-catalyzed addition probably proceeds through generation of a carbonium-ion intermediate which is attacked by the unshared electron pair on phosphorus. A typical Markovnikov distribution of products occurs.



$$CH_2{=}CHR + PH_3 \xrightarrow{H^+} \underset{\displaystyle R}{CH_3CH}-PH_3^+ \xrightarrow{H_2O} \underset{\displaystyle R}{CH_3CH}-PH_2 \qquad (91)$$

The free phosphine is liberated upon removing the acid catalyst with water.

In the presence of strong bases, the reaction is thought to proceed via formation of a negatively charged phosphide in a Michael mechanism. Free-radical initiators are also effective at reduced temperatures. Free-radical reactions proceed through ready homolysis of the P−H bonds. At $>300°C$, there appears to be sufficient dissociation of PH_3 to initiate a free-radical addition in the absence of a catalyst. If low molecular weight olefins are present, some carbon-chain growth also may occur. Linear trialkyl phosphines are the usual products in base- or radical-catalyzed additions as they are thermodynamically favored. Tri-*n*-butylphosphine [998-40-3] is prepared by the radical-catalyzed addition of 1-butene to phosphine.

In the presence of a large excess of PH_3, primary phosphines (RPH_2) are formed predominantly. Secondary phosphines, R_2PH, must be either isolated from mixtures with primary and tertiary products or made in special, multistep procedures. Certain secondary phosphines can be produced if steric factors preclude conversion to a tertiary product. Both primary and secondary phosphines can be substituted with olefins. With the proper selection of substituents, mixed phosphines of the type $RR'PH$ or $RR'R''P$ can be made.

Primary, secondary, and tertiary aryl phosphines are conveniently prepared by in Friedel-Crafts reactions. For example, triphenylphosphine [603-35-0] is prepared from benzene and phosphorus trichloride.

$$3\,C_6H_6 + PCl_3 \xrightarrow{AlCl_3} (C_6H_5)_3P + 3\,HCl \qquad (92)$$

Halophosphines can be reduced to phosphines. Various methods have been employed to recover the product, but yields are only fair. The crude products can be purified by distillation. Highly pure triphenylphosphine can be obtained by recrystallization. Stoichiometric amounts of $AlCl_3$ are generally required because of the complexation by the phosphorus compound.

In general, if the desired carbon−phosphorus skeleton is available in an oxidized form, reduction with lithium aluminum hydride is a powerful technique for the production of primary and secondary phosphines. The method is applicable to halophosphines and phosphonic and phosphinic acids as well as their esters, and acid chlorides. Tertiary and secondary phosphine oxides can be reduced to the phosphines:

$$RPCl_2 \xrightarrow{LiAlH_4} RPH_2 \qquad (93)$$

$$R_2P({=}O)\ OR' \xrightarrow{LiAlH_4} R_2PH \qquad (94)$$

$$R_3P{=}O \xrightarrow{LiAlH_4} R_3P \qquad (95)$$

Halophosphines can be treated with organometallic reagents, eg, Grignard reagents, organomercuries, and organolithiums, to produce tertiary phosphines.

$$RPCl_2 + 2\,C_6H_5Li \longrightarrow RP(C_6H_5)_2 + 2\,LiCl \qquad (96)$$

Yields are best in the case of aromatic metallic reagents. Use of aliphatic reagents favors low molecular weight products. Products often are recovered by water addition followed by separation and distillation of the organic layer. Such procedures inevitably lead to acidic byproducts when there is incomplete replacement of the halogens on phosphorus. A modification of the Wurtz reaction sometimes is used.

$$PX_3 + 3\,RX' + 6\,Na \longrightarrow R_3P + 3\,NaX + 3\,NaX' \tag{97}$$

The addition of alkyl halides to phosphines is analogous to the reactions with amines. Because primary phosphonium salts are highly dissociated, the reaction proceeds to the tertiary or quaternary salts.

$$PH_3 + RX \rightleftharpoons RPH_3^+X^- \rightleftharpoons RPH_2 + HX \tag{98}$$

$$RPH_2 + RX \rightleftharpoons R_2PH_2^+X^- \rightleftharpoons R_2PH + HX \tag{99}$$

$$R_2PH + RX \rightleftharpoons R_3PH^+X^- \rightleftharpoons R_3P + HX \tag{100}$$

$$R_3P + RX \rightleftharpoons R_4P^+X^- \tag{101}$$

Alkylation of phosphines by alkyl halides exhibits reactivity relative to the base strength, ie, PH_3 being the least reactive and tertiary phosphines the most. This reactivity reflects the difficulty in using alkylation to prepare anything except quaternary phosphonium halides.

Metal phosphides may be employed to direct the action of alkyl halides more towards primary and secondary phosphines.

$$NaPH_2 + RX \longrightarrow NaX + RPH_2 \tag{102}$$

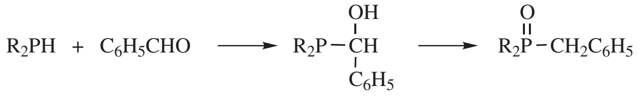
$$KRPH + R'X \longrightarrow KX + RR'PH \tag{103}$$

Products are contaminated with more highly alkylated compounds but less so than without the active metal. The metal phosphide can be generated from a Grignard or organolithium reagent.

The addition of P–H bonds across a carbonyl function leads to the formation of 2-hydroxy-substituted phosphines. The reaction is acid catalyzed and appears to be quite general with complete reaction of each P–H bond if linear aliphatic aldehydes are used. Steric considerations may limit the product to primary or secondary phosphines. In the case of formaldehyde, a quaternary phosphonium salt [124-64-1] is obtained.

$$PH_3 + 4\,CH_2O + HCl \longrightarrow (HOCH_2)_4P^+Cl^- \tag{104}$$

If aromatic aldehydes or ketones are used, the tertiary phosphine product sometimes rearranges to a mixed phosphine oxide.



$$R_2PH + C_6H_5CHO \longrightarrow R_2P-\underset{C_6H_5}{\overset{OH}{CH}} \longrightarrow R_2\overset{O}{\overset{\|}{P}}-CH_2C_6H_5 \tag{105}$$

Other methods of preparation are described in detail (7,64,65).

Phosphines readily coordinate with typical Lewis acids, eg, the proton, BF_3, and metals to form compounds such as PH_4I, the adduct $(CH_3)_3PBF_3$ [1898-77-7], and the complex $[(C_6H_5)_3P]_2NiC_8H_{12}$ [36510-64-2], respectively. Phosphines usually are considered soft bases and interact most strongly with soft acids or highly polarizable electron-pair acceptors (11). Complexation is facilitated by the back-donation of electrons from the acceptor to the unfilled *d* orbitals of phosphorus (66). Aromatic phosphines are therefore much better ligands than would be anticipated from the relatively poor coordinating ability of the anilines and other aromatic amines. With respect to the proton, the base strength of phosphines increases with the degree of substitution: $PH_3 < CH_3PH_2 < (CH_3)_2PH < (CH_3)_3P$. The quaternary phosphonium hydroxide $(CH_3)_4P^+OH^-$ [4814-27-8], is a strong base and essentially is ionized 100% in water. Representative pK_a values are listed in Table 11.

Because of the wide-ranging ability of phosphines to bond with electron acceptors, eg, metals, they are broadly used ligands in the construction of catalysts. For example, $[(n\text{-}C_4H_9)_3PPtCl_2]_2SnCl_2$ is a useful hydroformylation catalyst for alpha olefins (67). Catalysts derived from cobalt carbonyl and tributylphosphine and convert internal olefins to linear alcohols (68). Rhodium complexes of chiral phosphines, eg, methylpropylphenylphosphine [4653-62-7] may be used as stereoselective hydrogenation catalysts (69). The use of tertiary alkylphosphines in conjunction with the reaction reduces the formation of by-products (70).

$$CO + 2\,H_2 + CH_3OH \xrightarrow{\text{catalyst}} CH_3CH_2OH + H_2O \qquad (106)$$

Catalysts employing phosphines are also used in olefin hydrogenation (71), homologation (72), and polymerization (73,74).

Reactions of Organophosphines. Phosphines are generally subject to air oxidation at ambient temperatures via a free radical mechanism. Because of their higher stability, tertiary aryl phosphines are the slowest to air oxidize but undergo oxidation readily at higher temperatures. Phosphines also react with elemental sulfur and other common oxidizing agents such as H_2O_2 or HNO_3. Secondary or tertiary phosphines yield the corresponding oxides or sulfides, eg, triphenylphosphine yields triphenylphosphine oxide [791-28-6].

$$2\,(C_6H_5)_3P + O_2 \longrightarrow 2\,(C_6H_5)_3P = O \qquad (107)$$

The secondary phosphine oxides or sulfides can be oxidized to phosphinic acids or thiophosphinic acids.

$$R_2\overset{\overset{S}{\|}}{P}H + S \longrightarrow R_2\overset{\overset{S}{\|}}{P}SH \qquad (108)$$

Table 11. **Physical Properties of Phosphines**[a]

Compound	CAS Registry Number	Boiling point, °C	Denisty at 20°C, g/cm^3	Dipole moment, 10^{-30} Cm[c]	Index of refraction, n_D^{20}	pK_a	nmr Parameters[b]	
							^{31}P chemical shift, ppm	$J_{P\text{-}H}$ Hz[d]
PH_3	[7803-51-2]	−88	1.529[e]				238–241	180–182
CH_3PH_2	[593-54-4]	−14		3.7			163	188
$(CH_3)_2PH$	[676-59-5]	21		4.10			100	188–191
$(CH_3)_3P$	[594-09-2]	38–41			1.192	8.65[f]	62, 63	
$C_2H_5PH_2$	[593-68-0]	25		3.87			128	185
$(C_2H_5)_2PH$	[627-49-6]	85–86	0.7862	4.7	1.447	33.7[j]	56	190
$(C_2H_5)_3P$	[554-70-1]	129–130	0.7999	4.7–9.7	1.456	8.8[f]	20, 21	
n-$C_4H_9PH_2$	[1732-74-7]	86–88	0.7693	4.54	1.4372	−0.03[f]	135	195
(*n*-$C_4H_9)_2PH$	[1732-72-5]	178–186	0.8083		1.456	4.51[f]	70	180
(*n*-$C_4H_9)_3P$	[998-40-3]	240–242	0.817–0.82	5.0–7.3	1.4635	8.43[f]	32	
iso-$C_4H_9PH_2$	[4023-52-3]	60–80				−0.02[f]		
tert-$C_4H_9PH_2$	[2501-94-2]	66–67					120	182
(*n*-$C_8H_{17})_3P$	[4731-53-7]	291[g]			1.4683		32, 33	
CF_3PH_2	[420-52-0]	−25.5		6.41			129	201
$HOCH_2CH_2PH_2$	[16247-01-1]	139–140	1.004		1.4950			
$HO_2CCH_2PH_2$	[4757-26-0]	85–86[h]					143	198
$H_2NCH_2CH_2PH_2$	[14085-97-3]	110					150	194
$C_6H_5PH_2$	[638-21-1]	157–160	1.001[i]	3.70	1.5796	24.5[j]	119–124	195–201
$(C_6H_5)_2PH$	[829-85-6]	280				0.03[f]	41.4	214–239
$(C_6H_5)_3P$	[603-35-0]	384[k]		4.74–5.14		2.73[f]	6–8	

[a] Refs. 7, 62, and 63.

[b] Nuclear magnetic resonance = nmr.

[c] To convert Cm to debye, divide by 3.336×10^{-30}.

[d] The parameter $J_{P\text{-}H}$ is the coupling constant between the phosphorus and hydrogen atoms.

[e] Value is in g/L at 0°C and 101.3 kPa (1 atm).

[f] In water.

[g] At 6.7 kPa (50 mmHg); melting point = 48°C.

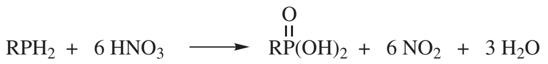
[h] At 1.3 kPa (10 mmHg).

[i] At 15°C.

[j] In methanol.

[k] Melting point = 79–81°C.

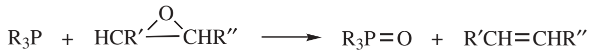
Primary phosphines are oxidized as intermediates in the syntheses of phosphonic acids and phosphonates.



$$RPH_2 + 6\,HNO_3 \longrightarrow RP(=O)(OH)_2 + 6\,NO_2 + 3\,H_2O \tag{109}$$

Secondary phosphines are likewise intermediates in the syntheses of phosphonic acids. Bis(2,4,4-trimethylpentyl) phosphinic acid [100786-00-3] (Cyanex 272, Cytec) is an extractant with high selectivity for Co over Ni. The primary and secondary phosphines can also be used to make other mixed phosphines.

Because relatively mild oxidizing agents react with phosphines, the latter are convenient deoxidizers (75) or desulfurizers (76).



$$R_3P + HCR'\overset{O}{\frown}CHR'' \longrightarrow R_3P{=}O + R'CH{=}CHR'' \tag{110}$$

$$R_3P + C_4H_9SH \longrightarrow R_3P{=}S + C_4H_{10} \tag{111}$$

Functional groups within the substituents in a phosphine usually behave similarly to a hydrocarbon, provided that they do not react with the phosphine group.

Pentavalent phosphorus derivatives can be converted to phosphonyl halides or phosphine oxides by partial hydrolysis or by other oxygen donors.

$$R_3PX_2 + H_2O \longrightarrow R_3P{=}O + 2\,HX \tag{112}$$

$$C_6H_5PX_4 + CH_3CO_2H \longrightarrow C_6H_5{-}P(=O)X_2 + HX + H_3C{-}C(=O)X \tag{113}$$

Primary and secondary phosphines can be treated with halogenating agents to produce halophosphines.

$$RPH_2 + 2\,COCl_2 \longrightarrow RPCl_2 + 2\,HCl + 2\,CO \tag{114}$$

Phosgene, $COCl_2$, is a useful chlorinating reagent, but PCl_5, $SOCl_2$, SO_2Cl_2, $ClSO_3$, and $SiCl_4$ also are used. The activity of elemental halogens must be limited by low temperatures, dilute reactions, and carefully controlled additions so that only trivalent derivatives form.

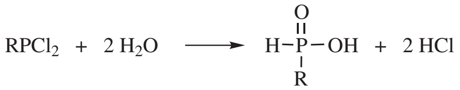
Tertiary phosphines and primary and secondary phosphines can be oxidized by elemental halogen to halophosphine halides.

$$R_3P + Cl_2 \longrightarrow R_3PCl_2 \tag{115}$$

$$R_2PCl + Br_2 \longrightarrow R_2PClBr_2 \tag{116}$$

The reactions are general for chlorine and bromine. Iodine does not react to form pentavalent phosphorus compounds. Fluorides are best formed with less active fluorinating agents.

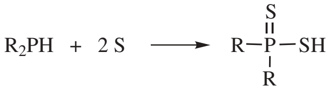
Dihalophosphines or halophosphites, prepared from phosphorus trichloride, are used in the synthesis of organophosphinates.



$$RPCl_2 + 2\,H_2O \longrightarrow H{-}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle R}{|}}{P}}{-}OH + 2\,HCl \qquad (117)$$

$$Cl{-}P(OR)_2 + R'MgCl \longrightarrow R'P(OR)_2 + MgCl_2 \qquad (118)$$

Organophosphinates (77) may also be prepared by the oxidation of secondary phosphines or halophosphines with hydrogen peroxide or sulfur.

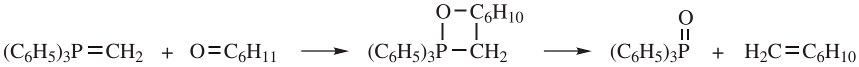


$$R_2PH + 2\,S \longrightarrow R{-}\overset{\overset{\displaystyle S}{\|}}{\underset{\underset{\displaystyle R}{|}}{P}}{-}SH \qquad (119)$$

A useful application of phosphines for replacing a carbonyl function with a carbon–carbon double bond is the Wittig reaction (78). A tertiary phosphine, usually triphenylphosphine, is treated with the appropriate alkyl halide that must include at least one α-hydrogen. The quaternary salt [1779-49-3] is dehydrohalogenated to form the Wittig reagent, methylenetriphenylphosphorane [19943-09-5], an ylide:

$$(C_6H_5)_3P + CH_3Br \longrightarrow [(C_6H_5)_3PCH_3]^+Br^- \xrightarrow{n\text{-BuLi}} (C_6H_5)_3P = CH_2 + C_4H_{10} + LiBr \qquad (120)$$

Sodium hydride, sodium amide, or other strong bases also can be used. The reagent can be generated in the presence of an appropriate carbonyl compound that reacts directly.



$$(C_6H_5)_3P{=}CH_2 + O{=}C_6H_{11} \longrightarrow (C_6H_5)_3\overset{\overset{\displaystyle O-C_6H_{10}}{|\quad\;\; |}}{P{-}CH_2} \longrightarrow (C_6H_5)_3\overset{\overset{\displaystyle O}{\|}}{P} + H_2C{=}C_6H_{10} \qquad (121)$$

Although the reaction is most general for aldehydes and ketones, in certain instances esters, anhydrides, and nitrites are attacked by these reagents (7,79).

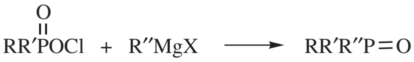
6.6. Health and Safety Factors, Toxicology. Because low molecular weight phosphines generally are spontaneously flammable, they must be stored and handled in a inert atmosphere. For dibutylphenylphosphine [6372-44-7], a lowest reported LC_{50} is 1100mg/m^3 in 10 min.

6.7. Phosphine Oxides. Controlled oxidation of secondary or tertiary phosphines with H_2O_2 yields the corresponding phosphine oxides. Control of the reaction temperature must be maintained to prevent further oxidation to phosphinic acids. Trioctylphosphine oxide [78-50-2] (TOPO) may be manufactured by the radical-catalyzed addition of 1-octene to phosphine followed by peroxide oxidation.

$$(C_8H_{17})_3P + H_2O_2 \longrightarrow (C_8H_{17})_3P{=}O + H_2O \qquad (122)$$

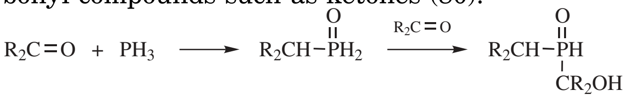
TOPO is used in extraction of uranium from wet-process phosphoric acid. Phosphine oxides having higher alkyl substituents are also prepared industrially using Grignard reagents.

$$(RO)_2\overset{O}{\overset{\|}{P}}H + 3\,R'MgX \longrightarrow R'_2\overset{O}{\overset{\|}{P}}H \qquad (123)$$



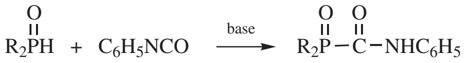
$$RR'\overset{O}{\overset{\|}{P}}OCl + R''MgX \longrightarrow RR'R''P{=}O \qquad (124)$$

Phosphine oxides may be prepared by the acid-catalyzed reaction of phosphine with carbonyl compounds such as ketones (80).



$$R_2C{=}O + PH_3 \longrightarrow R_2CH{-}\overset{O}{\overset{\|}{P}}H_2 \xrightarrow{R_2C=O} R_2CH{-}\underset{CR_2OH}{\underset{|}{\overset{O}{\overset{\|}{P}}}}H \qquad (125)$$

Because of their relative instability, primary phosphine oxides may not be isolated, but converted directly to derivatives. Primary and secondary phosphine oxides undergo reactions characteristic of P–H bonds, eg, the base-catalyzed nucleophilic addition to unsaturated compounds, such as olefins, ketones, and isocyanates (81).



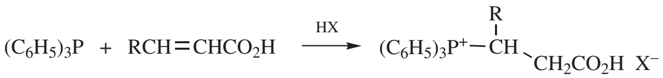
$$R_2\overset{O}{\overset{\|}{P}}H + C_6H_5NCO \xrightarrow{\text{base}} R_2\overset{O}{\overset{\|}{P}}{-}\overset{O}{\overset{\|}{C}}{-}NHC_6H_5 \qquad (126)$$

Tertiary phosphine oxides are very stable. The temperatures required for thermal decomposition are ~300°C higher than the corresponding amine oxides (82). Trimethyl phosphine oxide is stable to 700°C.

6.8. Phosphonium Salts. The most common route to phosphonium salts is the reaction of tertiary phosphines with alkyl or aryl halides in polar solvents.

$$R_3P + RX \longrightarrow R_4P^+X^- \qquad (127)$$

Phosphonium salts may also be prepared by the addition of tertiary phosphines to carbonyl compounds or olefins (83).



$$(C_6H_5)_3P + RCH{=}CHCO_2H \xrightarrow{HX} (C_6H_5)_3P^+{-}\overset{R}{\overset{|}{C}}H{\diagdown}CH_2CO_2H\ X^- \qquad (128)$$

Tetrakis(hydroxymethyl)phosphonium hydroxide, used for flameproofing cellulosic fabrics, is manufactured in a two-step process.

$$PH_3 + CH_2O + HCl \xrightarrow{H_2O} (HOCH_2)_4P^+Cl^- \xrightarrow{NaOH} (HOCH_2)_4P^+OH^- \qquad (129)$$

The corresponding sulfate has replaced much of the hydroxide because under certain conditions of manufacture or use the carcinogen bis(chloromethyl) ether may form.

Phosphonium salts are typically stable, crystalline solids with high water solubility. Uses include phase-transfer catalysts (84) and biocides (eg, tributyl(tetradecyl)phosphonium chloride [8741-28-8] for cooling water systems) (85). Although their thermal stability is quite high, tertiary phosphines can be obtained from pyrolysis of quaternary phosphonium halides. The hydroxides undergo thermal degradation to phosphine oxides.

$$R_4P^+OH^- \longrightarrow R_3P=O+RH \tag{130}$$

7. Economic Aspects

Phosphorus compounds are manufactured for a variety of uses, either directly or as intermediates in the production of other compounds. Manufacturing of the largest-volume products is summarized in Table 12, and prices are given in Table 13. Phosphorus trichloride is the compound in highest demand. Phosphorus trichloride production increased steadily from 1985 to 2005. Up to 75% of PCl_3 is used for pesticide products due to Monsanto's phenomenal success of herbicide, glyphosate.

Eleven percent of PCl_3 is used for the manufacture of surfactants and sequestrants, which are used widely in industrial and specialty applications, eg, heavy-duty liquid detergents, components of dry cleaning compounds, water- and oil-based cutting fluids, emulsifiers, and wetting agents in textile manufacturing, emulsifiers in emulsion–polymerization processes, pigment dispersants in oil-based paints, emulsifiers and moisture barrier compounds in cosmetics (qv), and mold-release agents (see Dispersants). In Europe, phosphonate surfactants have been used in some household detergent formulations (88).

Organophosphorus compounds, primarily phosphonic acids, are used as sequestrants, scale inhibitors, deflocculants, or ion-control agents in oil wells, cooling-tower waters, and boiler-feed waters. Organophosphates are also used as plasticizers and flame retardants in plastics and elastomers, which accounted for 10% of PCl_3 consumed. Phosphites, in conjunction with liquid mixed metals, such as calcium–zinc and barium–cadmium heat stabilizers, function as antioxidants and stabilizer adjutants. In 2001, such phosphorus-based chemicals amounted to slightly $>6\%$ of all such plastic additives and represented 8500 t of phosphorus.

Phosphonic (phosphorous) acid, produced by hydrolysis of PCl_3, is for the most part consumed captively. Phosphonic acid is also formed as a by-product

Table 12. **U.S. Production of Phosphorus Compounds**[a,b]

Year	PCl_3	P_2S_5	$POCl_3$	P_2O_5
1980	87	73	31	6.4
1985	85	73	27	6.0
1990	140	70	30	5.1
1995	186	63	40	7.9
2000	294	60	40	6.6
2004 est.	245	55	40	7.2

[a] Ref. 86.
[b] $t \times 10^3$.

Table 13. **U.S. Prices of Phosphorus Compounds**[a,b]

Year	PCl_3	P_2S_5	$POCl_3$	P_2O_5
1970	0.23	0.29	0.25	0.38
1975	0.73	0.66	0.82	0.60
1980	0.97	0.88	1.06	0.86
1985	0.71	1.15	0.95	0.82
1990	0.90	1.35	1.10	0.85
1995	1.03	1.57	1.27	0.93
2000	1.07	–	1.47	1.10
2005	1.08	–	1.48	2.43

[a] Ref. 87.
[b] $/kg.

from manufacturing carboxylic acid chlorides and alkali peroxides. Additional by-product phosphonic acid is recovered in the manufacture of phosphinic acid.

Phosphorus trichloride is also used in the manufacture of antifoam agents, catalysts, dyes and pigments, as well as pharmaceutical and quaternary compounds, and is commonly used as a chlorinating agent. Phosphorus trichloride is used to make phosphorus oxychloride, which is used in the manufacture of adsorbents for air filters, antifoam agents, dyes and pigments, mineral-processing materials, pharmaceuticals (qv), and solvents.

Liquid phosphate esters, eg, tricresyl phosphate [1330-78-5], are one of two types of fire-resistant hydraulic fluids. Fire-resistant fluids are used, eg, in aircraft. Phosphorus-based fluids are generally stable at high temperature as well. Approximately 10,000 t organophosphorus compounds, prepared from $POCl_3$, were used as hydraulic fluids in 1994.

Approximately 50% or 220,000 t of the total U.S. 1999 pesticide production were phosphorus-containing products. These were based on the primary products, PCl_3 and P_2S_5, and on the secondary products, $POCl_3$, $PSCl_3$, and H_3PO_3. The pesticide market is estimated to account for about 13,000 t (25%) of the U.S. P_2S_5 production in 2004. This is a decline from ~36,000 t in 1980. Organophosphate insecticides offer broad spectrum pest control. For this reason, organophosphate insecticides, eg, Malathion, Parathion are under environmental pressure. Further, organophosphate insecticides face strong competition from pest control agents having higher specificity and much lower application rates, such as synthetic pyrethroids. Synthetic pyrethroids are chemical equivalents of natural pyrethrins, which are toxins produced in plants and insects that provide defense against (other) insects (see Pesticides). As a result, the use of P_2S_5 for insecticides is expected to be flat or declining in the United States. Because of the success in variuos plant genetic engnnering against pest infections, the comsumption of perticides has been decreased significantly since 2000.

Detergents, dispersants, antiwear agents, extreme pressure agents, corrosion inhibitors, oxidation inhibitors, and viscosity-index improvers are all classified as lubricating oil additives (LOAs). The lubricating oil additive market is estimated to account for ~39,000 t (70%) of the United States P_2S_5 production in 2004, an increase from ~32,000 t in 1980. The bulk of organophosphate oil additives are zinc and other metal dialkyl and diaryl phosphorodithioates, $Zn[(RO)_2PS_2]_2$. These compounds provide antiwear, anticorrosion, and antioxidant properties to the oil. No other compound has been identified that performs all three functions. Further, there is no known substitute for crankcase antiwear. However, there is some concern for the effect of organophosphate oil additives on catalytic converters in automobiles. Consequently, in 2005, the level of phosphorus in motor oil is limited to 0.08 wt%, a decrease from the chemical limit of 0.10 wt% in 2003.

Over 99% of the phosphorus pentoxide produced is not collected as such, but is immediately converted into phosphoric acid. The amount of phosphorus pentoxide produced as such in the United States in 2001 was 7400 short tons. The only U.S. producer is Innophos (formerly Rhodia Inc.) at Nashville, TN. Clariant and ATOFINA produce phosphorus pentoxide in Western Europe. In 2001, phosphorus pentoxide production in Western Europe was ~ 10000 metric tones. Phosphorus pentoxide is used as a catalyst, a blowing agent for asphalt, a condensing agent for organic reactions, and a raw material for the manufacture of organic phosphate esters and a drying agent for gases.

Approximately 5000 tons of sodium hypophosphite [7681-53-0], NaH_2PO_2, was produced in 2000. It is used primarily in electroless nickel plating of plastic objects. Of the secondary products made from primary phosphorus compounds, phosphorus oxychloride is manufactured in the largest volume. Phosphorus pentachloride and phosphorus sulfochloride are made from phosphorus trichloride.

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