

The chlorination of phosphonic and phosphinic acids and esters are of considerable importance.  $\text{PCl}_5$  can also act as a Lewis acid to give 6-coordinate P complexes, e.g.  $\text{pyPCl}_5$ , and  $\text{pyz-PCl}_5$ , where  $\text{py} = \text{C}_5\text{H}_5\text{N}$  (pyridine) and  $\text{pyz} = \text{cyclo-1,4-C}_4\text{H}_4\text{N}_2$  (pyrazine).<sup>(103)</sup>

### Pseudohalides of phosphorus(III)

Paralleling the various phosphorus trihalides are numerous pseudohalides and mixed pseudohalide-halides of which the various isocyanates and isothiocyanates are perhaps the best known. Most are volatile liquids, e.g.

| Compound | $\text{P}(\text{NCO})_3$ | $\text{PF}(\text{NCO})_2$ | $\text{PF}_2(\text{NCO})$ |
|----------|--------------------------|---------------------------|---------------------------|
| MP/°C    | -2                       | -55                       | ~ -108                    |
| BP/°C    | 169.3                    | 98.7                      | 12.3                      |

| Compound | $\text{PCl}(\text{NCO})_2$ | $\text{PCl}_2(\text{NCO})$ | $\text{P}(\text{NCS})_3$ |
|----------|----------------------------|----------------------------|--------------------------|
| MP/°C    | -50                        | -99                        | -4                       |
| BP/°C    | 134.6                      | 104.5                      | ~120/1 mmHg              |

| Compound | $\text{PF}_2(\text{NCS})$ | $\text{PCl}_2(\text{NCS})$ |
|----------|---------------------------|----------------------------|
| MP/°C    | -95                       | -76                        |
| BP/°C    | 90.3                      | 148(decomp)                |

The corresponding phosphoryl and thiophosphoryl pseudohalides are also known, i.e.  $\text{PO}(\text{NCO})_3$ ,  $\text{PS}(\text{NCO})_3$ , etc. Preparations are by standard procedures such as those on the diagram for  $\text{PCl}_3$  (p. 497). As indicated there,  $\text{P}(\text{CN})_3$  has also been made: it is a highly reactive white crystalline solid mp  $203^\circ$  which reacts violently with water to give mainly phosphorous acid and HCN.

### 12.3.4 Oxohalides and thiohalides of phosphorus

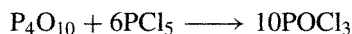
The propensity of phosphorus(III) compounds to oxidize to phosphorus(V) by formation of an additional  $\text{P}=\text{O}$  bond is well illustrated by the

<sup>103</sup> B. N. MEYER, J. N. ISHLEY, A. V. FRATINI and H. C. KNACHEL, *Inorg. Chem.* **19**, 2324-7 (1980) and references therein.

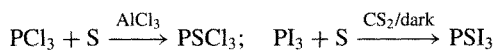
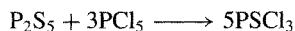
Table 12.4 Some phosphoryl and thiophosphoryl halides and pseudohalides

| Compound             | MP/°C  | BP/°C        | Compound             | MP/°C  | BP/°C      |
|----------------------|--------|--------------|----------------------|--------|------------|
| POF <sub>3</sub>     | -39.1  | -39.7        | POF <sub>2</sub> Cl  | -96.4  | 3.1        |
| POCl <sub>3</sub>    | 1.25   | 105.1        | POFCl <sub>2</sub>   | -80.1  | 52.9       |
| POBr <sub>3</sub>    | 55     | 191.7        | POF <sub>2</sub> Br  | -84.8  | 31.6       |
| POI <sub>3</sub>     | 53     | —            | POFBr <sub>2</sub>   | -117.2 | 110.1      |
| PO(NCO) <sub>3</sub> | 5.0    | 193.1        | POCl <sub>2</sub> Br | 11     | 52/3 mmHg  |
| PO(NCS) <sub>3</sub> | 13.8   | 300.1        | POClBr <sub>2</sub>  | 31     | 49/12 mmHg |
| PSF <sub>3</sub>     | -148.8 | -52.2        | PSF <sub>2</sub> Cl  | -155.2 | 6.3        |
| PSCl <sub>3</sub>    | -35    | -125         | PSFCl <sub>2</sub>   | -96.0  | 64.7       |
| PSBr <sub>3</sub>    | 37.8   | 212 (d)      | PSF <sub>2</sub> Br  | -136.9 | 35.5       |
| PSI <sub>3</sub>     | 48     | decomp       | PSFBr <sub>2</sub>   | -75.2  | 125.3      |
| PS(NCO) <sub>3</sub> | 8.8    | 215          | PO(NCO)FCI           | —      | 103        |
| PS(NCS) <sub>3</sub> | —      | 123/0.3 mmHg | PS(NCS) <sub>2</sub> | —      | 90         |

ease with which the trihalides are converted to their phosphoryl analogues POX<sub>3</sub>. Thus, PCl<sub>3</sub> reacts rapidly with pure O<sub>2</sub> (less rapidly with air) at room temperature or slightly above and this reaction is used on an industrial scale. Alternatively, a slurry of P<sub>4</sub>O<sub>10</sub> in PCl<sub>3</sub> can be chlorinated, the PCl<sub>5</sub> so formed reacting instantaneously with the P<sub>4</sub>O<sub>10</sub>:



POBr<sub>3</sub> can be made by similar methods, but POF<sub>3</sub> is usually made by fluorination of POCl<sub>3</sub> using a metal fluoride (e.g. M = Na, Mg, Zn, Pb, Ag, etc.). POI<sub>3</sub> was first made in 1973 by iodinating POCl<sub>3</sub> with LiI, or by reacting ROPI<sub>2</sub> with iodine (ROPI<sub>2</sub> + I<sub>2</sub> → RI + POI<sub>3</sub>).<sup>(104)</sup> Mixed phosphoryl halides, POX<sub>n</sub>Y<sub>3-n</sub>, and pseudohalides (e.g. X = NCO, NCS) are known, as also are the thiophosphoryl halides PSX<sub>3</sub>, e.g.:



Most of the phosphoryl and thiophosphoryl compounds are colourless gases or volatile liquids though PSBr<sub>3</sub> forms yellow crystals, mp 37.8°, POI<sub>3</sub> is dark violet, mp 53°, and PSI<sub>3</sub> is red-brown, mp 48°. All are monomeric tetrahedral (C<sub>3v</sub>) or pseudotetrahedral. Some physical properties are in Table 12.4. The P–O interatomic

distance in these compounds generally falls in the range 154–158 pm, the small value being consistent with considerable “double-bond character”. Likewise the P–S distance is relatively short (185–194 pm).

The phosphoryl and thiophosphoryl halides are reactive compounds that hydrolyse readily on contact with water. They form adducts with Lewis acids and undergo a variety of substitution reactions to form numerous organophosphorus derivatives and phosphate esters. Thus, alcohols give successively (RO)POCl<sub>2</sub>, (RO)<sub>2</sub>POCl and (RO)<sub>3</sub>PO; phenols react similarly but more slowly. Likewise, amines yield (RNH)POCl<sub>2</sub>, (RNH)<sub>2</sub>POCl and (RNH)<sub>3</sub>PO whereas Grignard reagents yield R<sub>n</sub>POCl<sub>3-n</sub> (n = 1–3). Many of these compounds find extensive use as oil additives, insecticides, plasticizers, surfactants or flame retardants, and are manufactured on the multikilotonne scale.

In addition to the monophosphorus phosphoryl and thiophosphoryl compounds discussed above, several poly-phosphoryl and -thiophosphoryl halides have been characterized. Pyrophosphoryl fluoride, O=PF<sub>2</sub>–O–P(=O)F<sub>2</sub> (mp –0.1°, bp 72° extrap) and the white crystalline cyclic tetramer [O=P(F)–O]<sub>4</sub> were

obtained by subjecting equimolar mixtures of PF<sub>3</sub> and O<sub>2</sub> to a silent electric discharge at –70°. Pyrophosphoryl chloride, O=PCl<sub>2</sub>–O–P(=O)Cl<sub>2</sub> is conveniently prepared by passing Cl<sub>2</sub> into a boiling suspension

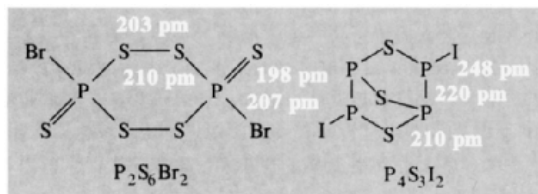
<sup>104</sup> A. V. KIRSANOV, ZH. K. GORBATENKO and N. G. FESHCHENKO, *Pure Appl. Chem.* **44**, 125–39 (1975).

of  $P_4O_{10}$  in  $PCl_3$  diluted with  $CCl_4$ :



It is a colourless, odourless, non-fuming, oily liquid, mp  $-16.5^\circ$ , bp  $215^\circ$  (decomp), with reactions similar to those of  $POCl_3$ . Sealed-tube reactions between  $P_4O_{10}$  and  $POCl_3$  at  $200-230^\circ$  give more highly condensed cyclic and open-chain polyphosphoryl chlorides. A rather different structural motif occurs in  $P_2S_4F_4$ ; this compound is obtained by fluorinating  $P_4S_{10}$  with an alkali-metal fluoride to give the anion  $[S_2PF_2]^-$  which is then oxidized by bromine to  $P_2S_4F_4$  (bp  $60^\circ$  at 10 mmHg). Vibrational and nmr spectra are consistent with the structure  $F_2(S)PSSP(S)F_2$ .

Bromination of  $P_4S_7$  in cold  $CS_2$  yields, in addition to  $PBr_3$  and  $PSBr_3$ , two further thiobromides  $P_2S_6Br_2$  (mp  $118^\circ$  decomp) and  $P_2S_5Br_4$  (mp  $90^\circ$  decomp). The first of these has the cyclic structure shown in which the ring adopts a skew-boat configuration. An even more complex, bicyclic arrangement is found in the orange-yellow compound  $P_4S_3I_2$  (mp  $120^\circ$  decomp) which is formed (together with several other products) when equiatomic amounts of P, S and I are allowed to react. The P and S atoms are arranged in two 5-membered rings having a common P-S-P group as shown; in each there is a P-P group and the I atoms are bonded in *cis*-configuration to the P atoms not common to the two rings. The orange compound  $P_2S_2I_4$  (mp  $94^\circ$ ) was mentioned on p. 498.



<sup>105</sup> H. SCHNÖCKEL and S. SCHUNCK, *Z. anorg. allg. Chem.* **548**, 161-4 (1987); **552**, 155-62 and 63-70 (1987). M. BINNEWIES and H. BORRMANN, *ibid.* **552**, 147-54 (1987).

<sup>106</sup> S. SCHUNCK, H.-J. GÖCKE and H. SCHNÖCKEL, *Z. anorg. allg. Chem.* **583**, 78-84 (1990).

<sup>107</sup> H. BOK, M. KREMER, B. SOLOUKI, M. BINNEWIES and M. MEISEL, *J. Chem. Soc., Chem. Commun.*, 9-11 (1992).

By contrast to the plethora of simple oxohalides and thiohalides of  $P^V$ , the corresponding derivatives of  $P^{III}$  are fugitive species that require matrix isolation techniques for preparation and characterization.<sup>(105)</sup>  $CIPO$ ,  $BrPO$ ,  $FPS$  and  $BrPS$  all form non-linear triatomic molecules, as expected. The corresponding oxosulfide,  $BrP(O)S$ ,<sup>(106)</sup> and its thio-analogue,  $FP(S)S$ ,<sup>(107)</sup> have also recently been isolated.

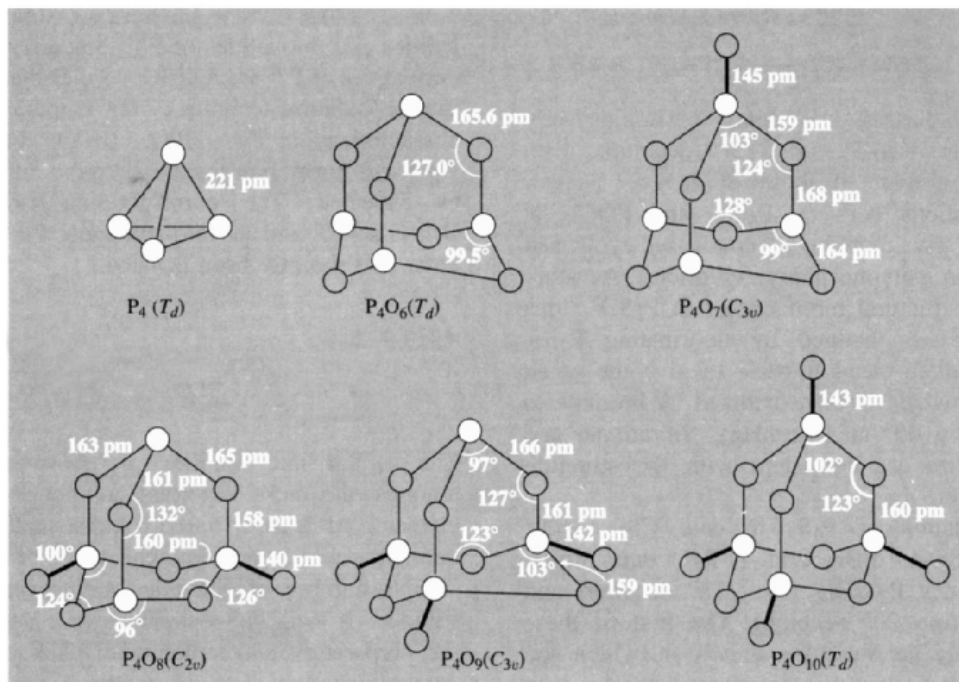
### 12.3.5 Phosphorus oxides, sulfides, selenides and related compounds

The oxides and sulfides of phosphorus are amongst the most important compounds of the element. At least 6 binary oxides and 9 well-defined sulfides are known, together with a similar number of selenides and several oxosulfides. It will be convenient to discuss first the preparation and structure of each group of compounds and then to mention the chemical reactions of the more important members in so far as they are known. It is notable that, in contrast to the ubiquitous  $NO$  and its many complexes (pp. 445 ff), little is known about its analogue,  $PO$  (see p. 506), although it is probably the most abundant P-containing molecule in interstellar clouds.<sup>(108)</sup> The first complex with a  $PO$  ligand was first synthesized as recently as 1991, when dark green crystals of the square-based pyramidal hetero-atom cluster  $[W(CO)_4\{Ni(\eta^5-C_5HPr_4^i)\}_2(\mu:\eta^2,\eta^2-P_2)]$  was oxidized with bis(trimethylsilyl) peroxide,  $(Me_3Si)_2O_2$ , to yield black crystals of the corresponding  $[W(CO)_4\{Ni(\eta^5-C_5HPr_4^i)\}_2(\mu:\eta^2,\eta^2-PO)_2]$ .<sup>(108)</sup>

#### Oxides

$P_4O_6$  is obtained by controlled oxidation of  $P_4$  in an atmosphere of 75%  $O_2$  and 25%  $N_2$  at  $90$  mmHg and  $\sim 50^\circ$  followed by distillation of the product from the mixture. Careful

<sup>108</sup> O. J. SCHERER, J. BRAUN, P. WALTHER, G. HECKMANN and G. WOLMERSHÄUSER, *Angew. Chem. Int. Edn. Engl.* **30**, 852-4. (1991).



**Figure 12.14** Molecular structures, symmetries and dimensions of the 5 oxides  $P_4O_{6+n}$  ( $n = 0-4$ ) compared with  $\alpha$ - $P_4$ . The  $P \cdots P$  distances in the oxides are  $\sim 280-290$  pm, i.e. essentially nonbonding.

precautions are necessary if good yields are to be obtained.<sup>(109)</sup> It forms soft white crystals, mp  $23.8^\circ$ , bp  $175.4^\circ$ , and is soluble in many organic solvents. The molecular structure has tetrahedral symmetry and comprises 4 fused 6-membered  $P_3O_3$  heterocycles each with the chair conformation as shown in Fig. 12.14.<sup>(110)</sup> When  $P_4O_6$  is heated to  $200-400^\circ$  in a sealed, evacuated tube it disproportionates into red phosphorus and a solid-solution series of composition  $P_4O_n$  depending on conditions. The  $\alpha$ -phase has a composition in the range  $P_4O_{8.1}-P_4O_{9.2}$  and comprises a solid solution of oxides in which one or two of the "external" O atoms in  $P_4O_{10}$  have been removed. The  $\beta$ -phase has a composition range  $P_4O_{8.0}-P_4O_{7.7}$

and appears to be a solid solution of  $P_4O_8$  and  $P_4O_7$ , the latter compound having only one O atom external to the  $P_4O_6$  cluster ( $C_{3v}$  symmetry).  $P_4O_7$  is now best prepared from  $P_4O_6$  dissolved in thf, using  $Ph_3PO$  as a catalyst (not an oxidant) at room temperature. The molecular structure and dimensions of  $P_4O_7$  are given in Fig. 12.14 from which it is apparent that there is a gradual lengthening of P-O distances in the sequence  $P^V-O_t < P^V-O_\mu < P^{III}-O_\mu$ . Similar trends are apparent in the dimensions of the other members of the series  $P_4O_{6+n}$  shown in Fig. 12.14.<sup>(110)</sup> In addition, ring angles at P ( $96-103^\circ$ ) are always less than those at O ( $122-132^\circ$ ), as expected.

$P_4O_6$  hydrolyses in cold water to give  $H_3PO_3$  i.e.  $HP(O)(OH)_2$ ; this is interesting in view of the structure of  $P_4O_6$  and implies an oxidative rearrangement of  $\{P-OH\}$  to  $\{H-P=O\}$  (p. 514). The oxide itself ignites and burns when heated in air; the progress of the reaction depends very much on the

<sup>109</sup> D. HEINZE, *Pure Appl. Chem.* **44**, 141-72 (1975).

<sup>110</sup> M. JANSEN and M. VOSS, *Angew. Chem. Int. Edn. Engl.* **20**, 100-1, 965 (1981), and references therein to crystal structure determinations on the other members of the series  $P_4O_{6+n}$ . See also M. JANSEN and M. MOEBES, *Inorg. Chem.* **23**, 4486-8 (1984).

Table 12.5 Some properties of crystalline polymorphs of P<sub>2</sub>O<sub>5</sub>

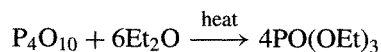
| Polymorph   | Density/g cm <sup>-3</sup> | MP/°C | Pressure at triple pt/mmHg | $\Delta H_{\text{subl}}/\text{kJ (mol P}_4\text{O}_{10})^{-1}$ |
|---|----------------------------|-------|----------------------------|--|
| H: hexagonal P <sub>4</sub> O <sub>10</sub>                 | 2.30                       | 420   | 3600                       | 95   |
| O: metastable (P <sub>2</sub> O <sub>5</sub> ) <sub>n</sub> | 2.72                       | 562   | 437                        | 152  |
| O': stable (P <sub>2</sub> O <sub>5</sub> ) <sub>n</sub>    | 2.74–3.05                  | 580   | 555                        | 142  |

purity of the oxide and the conditions employed, and, when traces of elemental phosphorus are present in the oxide, the reaction is spontaneous even at room temperature. P<sub>4</sub>O<sub>6</sub> reacts readily (often violently) with many simple inorganic and organic compounds but well-characterized products have rarely been isolated until recently.<sup>(109)</sup> It behaves as a ligand and successively displaces CO from [Ni(CO)<sub>4</sub>] to give compounds such as [P<sub>4</sub>O<sub>6</sub>{Ni(CO)<sub>3</sub>}<sub>4</sub>], [Ni(CO)<sub>2</sub>(P<sub>4</sub>O<sub>6</sub>)<sub>2</sub>] and [Ni(CO)(P<sub>4</sub>O<sub>6</sub>)<sub>3</sub>]. With diborane adducts of formula [P<sub>4</sub>O<sub>6</sub>(BH<sub>3</sub>)<sub>n</sub>] (*n* = 1–3) are obtained.

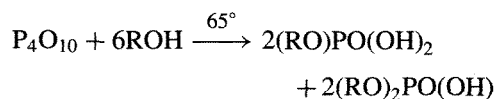
“Phosphorus pentoxide”, P<sub>4</sub>O<sub>10</sub>, is the commonest and most important oxide of phosphorus. It is formed as a fine white smoke or powder when phosphorus burns in air and, when condensed rapidly from the vapour phase in this way, is obtained in the H (hexagonal) form comprising tetrahedral molecules as shown in Fig. 12.14. This compound and the other phosphorus oxides are the first we have considered that feature the {PO<sub>4</sub>} group as a structural unit; this group dominates most of phosphate chemistry and will recur repeatedly during the rest of this chapter. The common hexagonal form of P<sub>4</sub>O<sub>10</sub> is, in fact, metastable and can be transformed into several other modifications by suitable thermal or high-pressure treatment. A metastable orthorhombic (O) form is obtained by heating H for 2 h at 400° and the stable orthorhombic (O') form is obtained after 24 h at 450°. Both consist of extensive sheet polymers of interlocking heterocyclic rings composed of fused {PO<sub>4</sub>} groups. There is also a high-pressure form and a glass, which probably consists of an irregular three-dimensional network of linked {PO<sub>4</sub>} tetrahedra. These polymeric forms are hard and brittle because of the P–O–P bonds throughout the lattice and, as

expected, they are much less volatile and reactive than the less-dense molecular H form. For example, whilst the common H form hydrolyses violently, almost explosively, with evolution of much heat, the polymeric forms react only slowly with water to give, finally, H<sub>3</sub>PO<sub>4</sub>. Some properties of the various polymorphs are compared in Table 12.5. The limpid liquid obtained by rapidly heating the H form contains P<sub>4</sub>O<sub>10</sub> molecules but these rapidly polymerize and rearrange to layer or three-dimensional polymeric forms with a concomitant drop in the vapour pressure and an increase in the viscosity and mp.

Because of its avidity for water, P<sub>4</sub>O<sub>10</sub> is widely used as a dehydrating agent, but its efficacy as a desiccant is greatly impaired by the formation of a crusty surface film of hydrolysis products unless it is finely dispersed on glass wool. Its largest use is in the industrial production of ortho- and poly-phosphoric acids (p. 520) but it is also an intermediate in the production of phosphate esters. Thus, triethylphosphate is made by reacting P<sub>4</sub>O<sub>10</sub> with diethyl ether to form ethylpolyphosphates which, on subsequent pyrolysis and distillation, yield the required product:

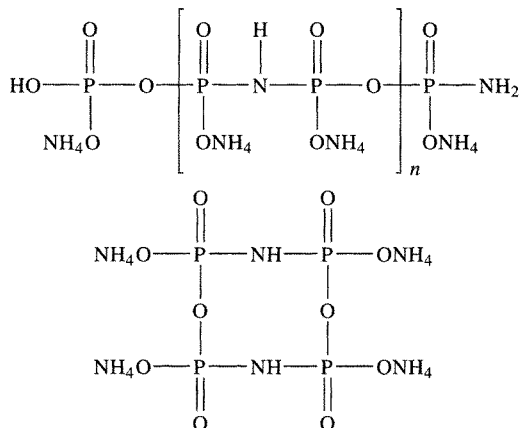


Direct reaction with alcohols gives mixed mono- and di-alkyl phosphoric acids by cleavage of the P–O–P bonds:



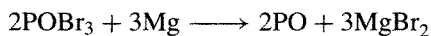
Under less-controlled conditions P<sub>4</sub>O<sub>10</sub> dehydrates ethanol to ethene and methylarylcarbinols to the corresponding styrenes. H<sub>2</sub>SO<sub>4</sub> is dehydrated to SO<sub>3</sub>, HNO<sub>3</sub> gives N<sub>2</sub>O<sub>5</sub> and amides

(RCONH<sub>2</sub>) yield nitriles (RCN). In each of these reactions metaphosphoric acid HPO<sub>3</sub> is the main P-containing product. P<sub>4</sub>O<sub>10</sub> reacts vigorously with both wet and dry NH<sub>3</sub> to form a range of amorphous polymeric powdery materials which are used industrially for water softening because of their ability to sequester Ca ions; composition depends markedly on the preparative conditions employed but most of the commercial products appear to be condensed linear or cyclic amidopolyphosphates which can be represented by formulae such as:



The annual production/consumption of P<sub>4</sub>O<sub>10</sub> in USA and Western Europe totals about 15 000 tonnes.

Other oxides of phosphorus are less well characterized though the suboxide PO and the peroxide P<sub>2</sub>O<sub>6</sub> seem to be definite compounds. PO was obtained as a brown cathodic deposit when a saturated solution of Et<sub>3</sub>NHCl in anhydrous POCl<sub>3</sub> was electrolysed between Pt electrodes at 0°. Alternatively it can be made by the slow reaction of POBr<sub>3</sub> with Mg in Et<sub>2</sub>O under reflux:



Its structure is unknown but is presumably based on a polymeric network of P–O–P links. It reacts with water to give PH<sub>3</sub> and is quantitatively oxidized to P<sub>2</sub>O<sub>5</sub> by oxygen at 300°. The peroxide P<sub>2</sub>O<sub>6</sub> is thought to be the active ingredient in the violet solid obtained when P<sub>4</sub>O<sub>10</sub> and O<sub>2</sub> are passed through a heated

discharge tube at low pressure. The compound has not been obtained pure but liberates I<sub>2</sub> from aqueous KI, hydrolyses to a peroxophosphoric acid, and liberates O<sub>2</sub> when heated to 130° under reduced pressure. Its structure may be (O=)<sub>2</sub>P–O–O–P(=O)<sub>2</sub> or, in view of the variable composition of the product, it may be a mixture of P<sub>4</sub>O<sub>11</sub> and P<sub>4</sub>O<sub>12</sub> obtained by replacing P–O–P links by P–O–O–P in P<sub>4</sub>O<sub>10</sub>.

### Sulfides<sup>(111)</sup>

The sulfides of phosphorus form an intriguing series of compounds which continue to present puzzling structural features. The compounds P<sub>4</sub>S<sub>10</sub>, P<sub>4</sub>S<sub>9</sub>, P<sub>4</sub>S<sub>7</sub>, α-P<sub>4</sub>S<sub>5</sub>, β-P<sub>4</sub>S<sub>5</sub>, α-P<sub>4</sub>S<sub>4</sub>, β-P<sub>4</sub>S<sub>4</sub>, P<sub>4</sub>S<sub>3</sub> and P<sub>4</sub>S<sub>2</sub> are all based on the P<sub>4</sub> tetrahedron but only P<sub>4</sub>S<sub>10</sub> (and possibly P<sub>4</sub>S<sub>9</sub>) is structurally analogous to the oxide. P<sub>4</sub>S<sub>6</sub> is conspicuous by its absence. Structural data are summarized in Fig. 12.15 and some physical properties are in Table 12.6.

P<sub>4</sub>S<sub>3</sub> is the most stable compound in the series and can be prepared by heating the required amounts of red P and sulfur above 180° in an inert atmosphere and then purifying the product by distillation at 420° or by recrystallization from toluene. The retention of a P<sub>3</sub> ring in the structure is notable. Its reactions and commercial application in match manufacture are discussed on p. 509.

The curious phase relations between phosphorus, sulfur and their binary compounds are worth noting. Because both P<sub>4</sub> and S<sub>8</sub> are stable molecules the phase diagram, if studied below 100°, shows only solid solutions with a simple eutectic at 10° (75 atom % P). By contrast, when the mixtures are heated above 200° the elements react and an entirely different phase diagram is obtained; however, as only the most stable compounds P<sub>4</sub>S<sub>3</sub>, P<sub>4</sub>S<sub>7</sub> and P<sub>4</sub>S<sub>10</sub>

<sup>111</sup> H. HOFFMANN and M. BECKE-GOEHRING, *Topics in Phosphorus Chemistry* **8**, 193–271 (1976); J. G. RIESS in A. H. COWLEY (ed.), *Rings, Clusters and Polymers of the Main Group Elements*, ACS Symposium Series No. **232**, 17–47 (1983).

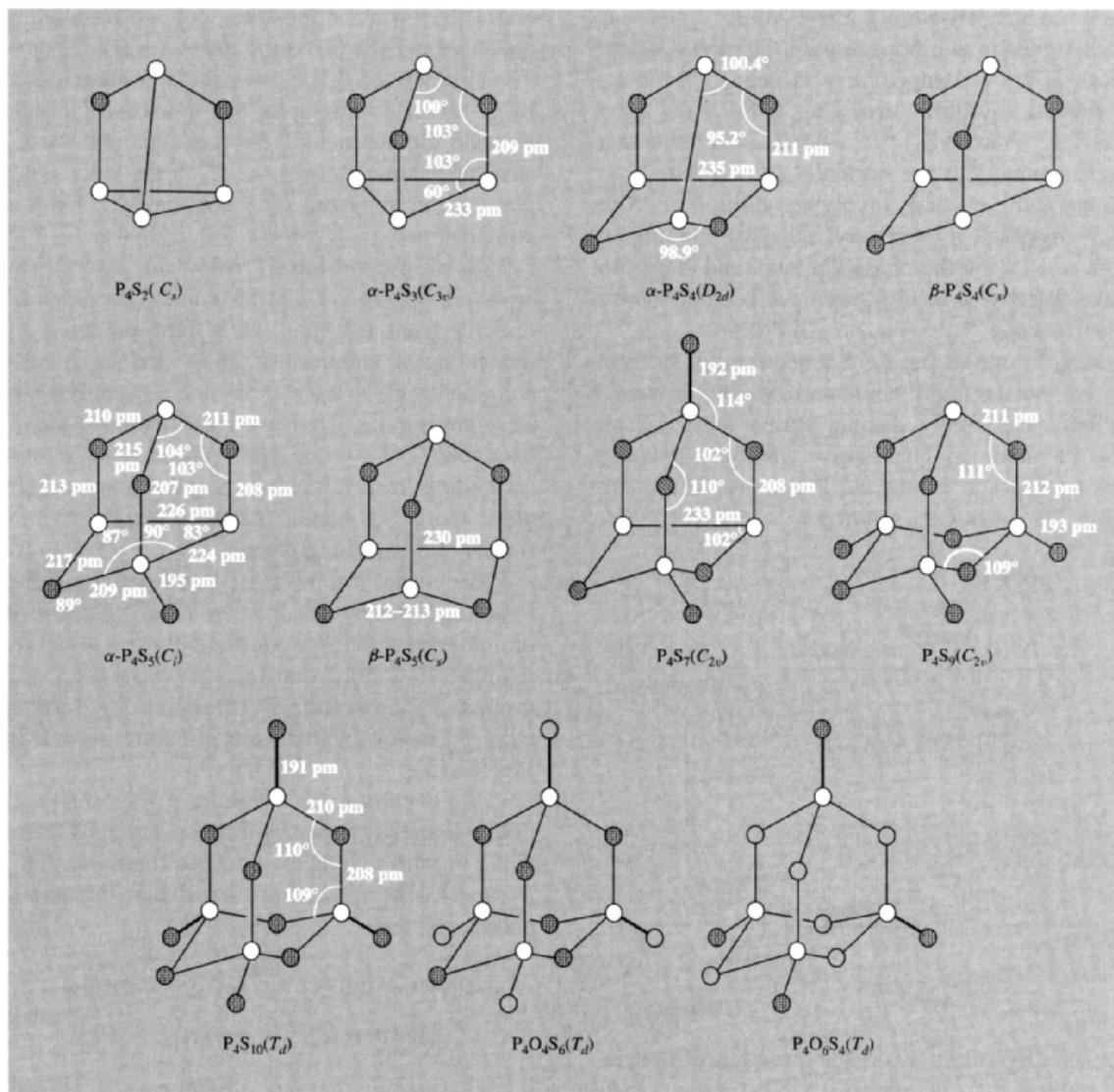


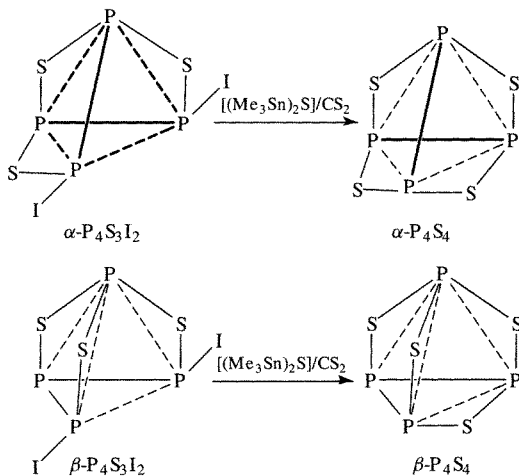
Figure 12.15 Structures of phosphorus sulfides and oxosulfides (schematic).

Table 12.6 Physical properties of some phosphorus sulfides

| Property   | $\alpha$ - $P_4S_3$ | $\alpha$ - $P_4S_4$ | $\alpha$ - $P_4S_5$ | $P_4S_7$         | $P_4S_{10}$ |
|--|---------------------|---------------------|---------------------|------------------|-------------|
| Colour   | Yellow green        | Pale yellow         | Bright yellow       | Very pale yellow | Yellow      |
| MP/ $^{\circ}C$  | 174                 | 230 (d)             | 170–220 (d)         | 308              | 288         |
| BP/ $^{\circ}C$  | 408                 | —                   | —                   | 523              | 514         |
| Density/ $g\ cm^{-3}$                                    | 2.03                | 2.22                | 2.17                | 2.19             | 2.09        |
| Solubility in $CS_2(17^{\circ})$ /<br>g per 100 g $CS_2$ | 100                 | sol                 | 0.5                 | 0.029            | 0.222       |

melt congruently, only these three appear as compounds in equilibrium with the melt. Careful work at lower temperatures is needed to detect peritectic equilibria involving  $P_4S_9$ ,  $P_4S_5$  (and possibly even  $P_4S_2$ ),<sup>(112)</sup> and it is notable that these compounds are normally prepared by low-temperature reactions involving addition of 2S to  $P_4S_7$  and  $P_4S_3$  respectively. Likewise there is no sign of  $P_4S_4$  on the phase diagram, and claims to have detected it in this way have been shown to be erroneous.<sup>(113)</sup>

$P_4S_4$  is one of the most recent binary sulfides to be isolated and characterized and it exists in two structurally distinct forms.<sup>(113,114)</sup> Each can be made in quantitative yield by reacting the appropriate isomer of  $P_4S_3I_2$  (p. 503) with  $[(Me_3Sn)_2S]$  in  $CS_2$  solution:



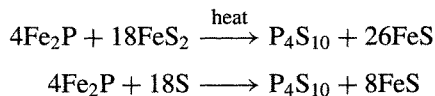
As seen from Fig. 12.15 the structure of  $\alpha\text{-}P_4S_4$  resembles that of  $As_4S_4$  (p. 579) rather than  $N_4S_4$  (p. 723). The 4 P atoms are in tetrahedral array and the 4 S atoms form a slightly distorted square. The 2 P–P bonds are long (as also in  $P_4S_3$

and  $P_4S_7$ ) when compared with corresponding distances in  $P_4S_5$  (225 pm) and  $P_4$  itself (221 pm). The structure of  $\beta\text{-}P_4S_4$  has not been determined by X-ray crystallography but spectroscopic data indicate the absence of P=S groups and the  $C_s$  structure shown in Fig. 12.15 is the only other possible arrangement of 3 coordinate P for this composition.

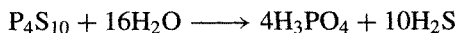
$P_4S_5$  disproportionates below its mp ( $2P_4S_5 \rightleftharpoons P_4S_3 + P_4S_7$ ) and so cannot be obtained directly from the melt. It is best prepared by irradiating a solution of  $P_4S_3$  and S in  $CS_2$  solution using a trace of iodine as catalyst. Its structure is quite unexpected and features a single exocyclic P=S group and 3 fused heterocycles containing, respectively, 4, 5 and 6 atoms; there are 2 short P–P bonds and the 4-membered  $P_3S$  ring is almost square planar.

$P_4S_7$  is the second most stable sulfide (after  $P_4S_3$ ) and can be obtained by direct reaction of the elements. Perhaps surprisingly the structure retains a P–P bond and has two exocyclic P=S groups.  $P_4S_9$  is formed reversibly by heating  $P_4S_7 + 2P_4S_{10}$  and has the structure shown in Fig. 12.15.

$P_4S_{10}$  is commercially the most important sulfide of P and is formed by direct reaction of liquid white  $P_4$  with a slight excess of sulfur above  $300^\circ$ . It can also be made from byproduct ferrophosphorus (p. 480).



It has essentially the same structure as the H form of  $P_4O_{10}$  and hydrolyses mainly according to the overall equation



Presumably intermediate thiophosphoric acids are first formed and, indeed, when the hydrolysis is carried out in aqueous NaOH solution at  $100^\circ$ , substantial amounts of the mono- and di-thiophosphates are obtained. P–S bonds are also retained during reaction of  $P_4S_{10}$  with alcohols or phenols and the products formed are used extensively in industry for a wide variety of

<sup>112</sup> H. VINCENT, *Bull. Soc. Chim. France* 1972, 4517–21; R. FÖRTHMANN and A. SCHNEIDER, *Z. Phys. Chem. (NF)* **49**, 22–37 (1966).

<sup>113</sup> A. M. GRIFFIN, P. C. MINSHALL and G. M. SHELDRIK, *J. Chem. Soc., Chem. Commun.*, 809–10 (1976).

<sup>114</sup> C.-C. CHANG, R. C. HALTIWANGER and A. D. NORMAN, *Inorg. Chem.* **17**, 2056–62 (1978). See also B. W. TATTERSHALL *J. Chem. Soc., Dalton Trans.*, 1515–20 (1987); B. W. TATTERSHALL and N. L. KENDALL, *Polyhedron* **13**, 2629–37 (1994).



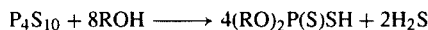
### Phosphorus Sulfides in Industry

The two compounds of importance are  $P_4S_3$  and  $P_4S_{10}$ . The former is made on a large scale for use in "strike anywhere" matches according to a formula evolved by Sévène and Cahen in France in 1898. The ignition results from the violent reaction between  $P_4S_3$  and  $KClO_3$  which is initiated by friction of the match against glass paper (on the side of the box) or other abrasive material. A typical formulation for the match head is:

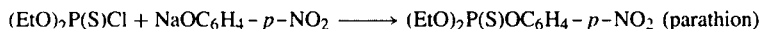
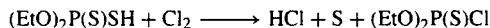
| Reactants |          | Fillers (moderators) |           |     | Adhesives |       |
|-----------|----------|----------------------|-----------|-----|-----------|-------|
| $KClO_3$  | $P_4S_3$ | Ground glass         | $Fe_2O_3$ | ZnO | Glue      | Water |
| 20%       | 9%       | 14%                  | 11%       | 7%  | 10%       | 29%   |

Formulations of this type have completely replaced earlier "strike anywhere" matches based on (poisonous) white  $P_4$ , sulfur, and  $KClO_3$ , though "safety matches" still use a match head which is predominantly  $KClO_3$  struck against the side of the match-box which has been covered with a paste of (non-toxic) red P (49.5%), antimony sulfide (27.6%),  $Fe_2O_3$  (1.2%) and gum arabic (21.7%). About  $10^{11}$  matches are used annually in the UK alone.

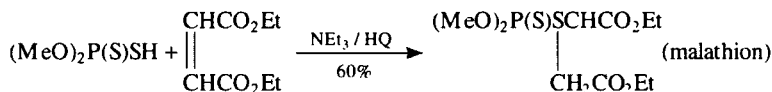
$P_4S_{10}$  is made on an even larger scale than  $P_4S_3$  and is the primary source of a very wide range of organic P-S compounds. World production of  $P_4S_{10}$  exceeds 250 000 tonnes annually of which about half is made in the USA, one-third in the UK/Europe, and the remaining 30 000 tonnes elsewhere (Japan, Romania, the former Soviet Union, Mexico, etc.). The most important reaction of  $P_4S_{10}$  is with alcohols or phenols to give dialkyl or diaryl dithiophosphoric acids:



The zinc salts of these acids are extensively used as additives to lubricating oils to improve their extreme-pressure properties. The compounds also act as antioxidants, corrosion inhibitors and detergents. Short-chain dialkyl dithiophosphates and their sodium and ammonium salts are used as flotation agents for zinc and lead sulfide ores. The methyl and ethyl derivatives  $(RO)_2P(S)SH$  and  $(RO)_2P(S)Cl$  are of particular interest in the large-scale manufacture of pesticides such as parathion, malathion, dimethylparathion, etc.<sup>(83)</sup> For example parathion, which first went into production as an insecticide in Germany in 1947, is made by the following reaction sequence:



Methylparathion is the corresponding dimethyl derivative. Later (1952) malathion found favour because of its decreased toxicity to mammals; it is readily made in 90% yield by the addition of dimethyldithiophosphate to diethylmaleate in the presence of  $NEt_3$  as a catalyst and hydroquinone as a polymerization inhibitor:



The scale of manufacture of these organophosphorus pesticides can be gauged from data referring to the USA annual production in 1975 (tonnes): methylparathion 46 000, parathion 36 000 and malathion 16 000. In addition, some 15 other thioorganophosphorus insecticides are manufactured in the USA on a scale exceeding 2000 tonnes pa each.<sup>(4)</sup> They act by inhibiting cholinesterase, thus preventing the natural hydrolysis of the neurotransmitter acetylcholine in the insect.<sup>(20)</sup>

applications (see Panel).  $P_4S_{10}$  is also widely used to replace O by S in organic compounds to form, e.g., thioamides  $RC(S)NH_2$ , thioaldehydes  $RCHS$  and thioketones  $R_2CS$ . Methanolysis yields  $(MeO)_2P(S)SH$  plus  $H_2S$ ,<sup>(115)</sup> and the related anions  $(RO)_2PS_2^-$  are known as versatile

ligands with a remarkable variety of coordination modes.<sup>(116)</sup>

A rather different series of cyclic thiophosphate(III) anions  $[(PS_2)_n]^{n-}$  is emerging from a study of the reaction of elemental phosphorus with polysulfidic sulfur. Anhydrous compounds

<sup>115</sup> P. BURDAUDUCQ and M. C. DÉMARCO, *J. Chem. Soc., Dalton Trans.*, 1897–900 (1987).

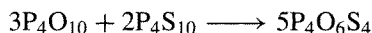
<sup>116</sup> M. G. B. DREW, R. J. HOBSON, P. P. E. M. MUMBA and D. A. RICE, *J. Chem. Soc., Dalton Trans.*, 1569–71 (1987).

$M_5^I[\text{cyclo-P}_5\text{S}_{10}]$  and  $M_6^I[\text{cyclo-P}_6\text{S}_{12}]$  were obtained using red phosphorus, whereas white  $\text{P}_4$  yielded  $[\text{NH}_4]_4[\text{cyclo-P}_4\text{S}_8] \cdot 2\text{H}_2\text{O}$  as shiny platelets. This unique  $\text{P}_4\text{S}_8^{4-}$  anion is the first known homocycle of 4 tetracoordinated P atoms and X-ray studies reveal that the P atoms form a square with rather long P–P distances (228 pm).<sup>(117)</sup>

The new planar anion  $\text{PS}_3^-$  (cf. the nitrate ion,  $\text{NO}_3^-$ ) has been isolated as its tetraphenylarsonium salt, mp  $183^\circ$ , following a surprising reaction of  $\text{P}_4\text{S}_{10}$  with  $\text{KCN}/\text{H}_2\text{S}$  in MeCN, in which the coproduct was the known dianion  $[(\text{NC})\text{P}(\text{S})_2-\text{S}-\text{P}(\text{S})_2(\text{CN})]^{2-}$ <sup>(118)</sup> The first sulfido heptaphosphane cluster anions,  $[\text{P}_7(\text{S})_3]^{3-}$  and  $[\text{HP}_7(\text{S})_2]^{2-}$  (cf.  $\text{P}_7^{3-}$ , p. 491), have also recently been characterized.<sup>(119)</sup>

### Oxosulfides

When  $\text{P}_4\text{O}_{10}$  and  $\text{P}_4\text{S}_{10}$  are heated in appropriate proportions above  $400^\circ$ ,  $\text{P}_4\text{O}_6\text{S}_4$  is obtained as colourless hygroscopic crystals, mp  $102^\circ$ .



The structure is shown in Fig. 12.15. The related compound  $\text{P}_4\text{O}_4\text{S}_6$  is said to be formed by the reaction of  $\text{H}_2\text{S}$  with  $\text{POCl}_3$  at  $0^\circ$  (A. Besson, 1897) but has not been recently investigated. An amorphous yellow material of composition  $\text{P}_4\text{O}_4\text{S}_3$  is obtained when a solution of  $\text{P}_4\text{S}_3$  in  $\text{CS}_2$  or organic solvents is oxidized by dry air or oxygen. Other oxosulfides of uncertain authenticity such as  $\text{P}_6\text{O}_{10}\text{S}_5$  have been reported but their structural integrity has not been established and they may be mixtures. However, the following series can be prepared by appropriate redistribution reactions:  $\text{P}_4\text{O}_6\text{S}_n$  ( $n = 1-4$ ),  $\text{P}_4\text{O}_6\text{Se}_n$  ( $n = 1-3$ ),  $\text{P}_4\text{O}_6\text{SSe}$ ,  $\text{P}_4\text{O}_7\text{S}_n$

<sup>117</sup> H. FALIUS, W. KRAUSE and W. S. SHELDRICK, *Angew. Chem. Int. Edn. Engl.* **20**, 103–4 (1981).

<sup>118</sup> H. W. ROESKY, R. AHLRICH and S. BRODE, *Angew. Chem. Int. Edn. Engl.* **25**, 82–3 (1986)

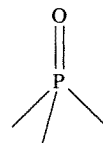
<sup>119</sup> M. BAUDLER and A. FLORUSS, *Z. anorg. allg. Chem.* **620**, 2070–6 (1994).

( $n = 1-3$ ),  $\text{P}_4\text{O}_7\text{Se}$ ,  $\text{P}_4\text{O}_8\text{S}_n$  ( $n = 1, 2$ ).<sup>(120)</sup> The crystal and molecular structures of  $\text{P}_4\text{O}_6\text{S}_2$  and  $\text{P}_4\text{O}_6\text{S}_3$  have recently been determined.<sup>(121)</sup> Two isomers each of  $\beta\text{-P}_4\text{S}_2\text{SeI}_2$  and  $\beta\text{-P}_4\text{SSe}_2\text{I}_2$ , prepared by reaction of  $\text{P}_4\text{S}_{3-n}\text{Se}_n$  with  $\text{I}_2$  in  $\text{CS}_2$  have been structurally identified by  $^{31}\text{P}$  nmr spectroscopy.<sup>(122)</sup>

### 12.3.6 Oxoacids of phosphorus and their salts

The oxoacids of P are more numerous than those of any other element, and the number of oxoanions and oxo-salts is probably exceeded only by those of Si. Many are of great importance technologically and their derivatives are vitally involved in many biological processes (p. 528). Fortunately, the structural principles covering this extensive array of compounds are very simple and can be stated as follows:<sup>†</sup>

- (i) All P atoms in the oxoacids and oxoanions are 4-coordinate and contain at least one P–O unit (1).



(1)

- (ii) All P atoms in the oxoacids have at least one P–OH group (2a) and this often occurs in the anions also; all such groups are ionizable as proton donors (2b).

<sup>120</sup> M. L. WALKER, D. E. PECKENPAUGH and J. L. MILLS, *Inorg. Chem.* **18**, 2792–6 (1979).

<sup>121</sup> F. FRICK and M. JANSEN, *Z. anorg. allg. Chem.* **619**, 281–6 (1993). See M. JANSEN and S. STROJEK, *Z. anorg. allg. Chem.* **621**, 479–83 (1995) for X-ray structures of  $\text{P}_4\text{O}_7\text{S}$ , i.e.  $\text{P}_4\text{O}_6(\text{O})_t(\text{S})_t$ .

<sup>122</sup> P. LÖNNECKE and R. BLACHNIK, *Z. anorg. allg. Chem.* **619**, 1257–61 (1993). See also M. RUCK, *ibid.* **620**, 1832–6 (1994) R. BLACHNIK, A. HEPP, P. LÖNNECKE, J. A. DONKIN and B. W. TATTERSHALL, *ibid.* **620**, 1925–31 (1994).

<sup>†</sup> Heteropolyacids containing P fall outside this classification and are treated, together with the isopolyacids and their salts, on pp. 1010–16. Organic esters such as  $\text{P}(\text{OR})_3$  are also excluded.