Fig. 22.26 The molecular structures of (a) P₄, (b) P₂O₅ and (c) P₄O₁₀. The four P atoms in P₂O₅ and P₄O₁₀ are still in a tetrahedral shape but are not within bonding distance of one another. Colour code: P, brown; O, red.

P−P = 221 pm  
P−O = 165 pm
P−O (cage) = 169 pm  
P−O (terminal) = 143 pm

The oxide is used as a drying and dehydrating agent. If a dish containing phosphorus(V) oxide is exposed to moist air, a brown, viscous layer forms on the surface of the white powder preventing it from absorbing more water.

**Oxoacids of phosphorus**

Phosphorus possesses far more oxoacids than does nitrogen, and Table 22.5 lists selected oxoacids and gives their structures. Each phosphorus atom is tetrahedrally bonded. The basicity of each acid corresponds to the number of OH groups, and not simply to the number of hydrogen atoms. Phosphinic acid, H₂PO₂, is monobasic (equation 22.87) because the two hydrogen atoms which are bonded directly to the phosphorus atom are not lost as protons.

\[ \text{H}_2\text{PO}_2(\text{aq}) + \text{H}_2\text{O}(\ell) \rightarrow [\text{H}_3\text{O}]^+(\text{aq}) + [\text{H}_2\text{PO}_2]^- (\text{aq}) \]  \hspace{1cm} (22.87)

Phosphoric acid, H₃PO₄, is formed by reaction 22.88—the oxide is the anhydride of the acid—or when calcium phosphate (‘phosphate rock’) reacts with concentrated sulfuric acid (equation 22.89). In its pure state, H₃PO₄ forms deliquescent, colourless crystals (mp 315 K) which quickly turn into a viscous liquid. The acid is available commercially as an 85% aqueous solution; even this is viscous, owing to extensive hydrogen bonding.

\[ \text{P}_4\text{O}_{10}(\ell) + 6\text{H}_2\text{O}(\ell) \rightarrow 4\text{H}_3\text{PO}_4(\text{aq}) \]  \hspace{1cm} (22.88)

\[ \text{Ca}_3(\text{PO}_4)_2 + 3\text{H}_2\text{SO}_4 \rightarrow 2\text{H}_3\text{PO}_4 + 3\text{CaSO}_4 \]  \hspace{1cm} (22.89)

Industrially, phosphoric acid is very important and is used on a large scale in the production of fertilizers, detergents and food additives; it is responsible for the sharp taste of many soft drinks. It is also used to remove oxide and scale from the surfaces of iron and steel.

Aqueous H₃PO₄ is a tribasic acid, but the values of pKₐ for equilibria 22.90 to 22.92 show that only the first proton is readily lost. With NaOH, H₃PO₄ can react to give three salts NaH₂PO₄, Na₂HPO₄ and Na₃PO₄.

\[ \text{H}_3\text{PO}_4(\text{aq}) + \text{H}_2\text{O}(\ell) \rightarrow [\text{H}_3\text{O}]^+(\text{aq}) + [\text{H}_2\text{PO}_4]^- (\text{aq}) \]  \hspace{1cm} pKₐ = 2.12 \hspace{1cm} (22.90)

\[ [\text{H}_2\text{PO}_4]^- (\text{aq}) + \text{H}_2\text{O}(\ell) \rightarrow [\text{H}_3\text{O}]^+(\text{aq}) + [\text{HPO}_4]^{2-} (\text{aq}) \]  \hspace{1cm} pKₐ = 7.21 \hspace{1cm} (22.91)

\[ [\text{HPO}_4]^{2-} (\text{aq}) + \text{H}_2\text{O}(\ell) \rightarrow [\text{H}_3\text{O}]^+(\text{aq}) + [\text{PO}_4]^{3-} (\text{aq}) \]  \hspace{1cm} pKₐ = 12.67 \hspace{1cm} (22.92)