

1 Introduction to phosphorus chemistry

1.1 Historical development

Because phosphorus compounds occur in nature both in the biosphere and in minerals, the knowledge of phosphorus compounds (though not of their nature or constitution) is part of the prehistory of chemistry. The old name, microcosmic salt, by which ammonium sodium hydrogenphosphate tetrahydrate, $\text{NaNH}_4\text{HPO}_4 \cdot 4\text{H}_2\text{O}$, was known in late alchemical times, indicates the significance of at least one phosphorus compound to early chemistry. The element itself was also a product of alchemy, having been first produced, by distillation of evaporated urine (presumably involving reduction of phosphate by pyrolytic carbon) by Brand, in Hamburg, in about 1674. Its most spectacular chemical property, that of chemiluminescence during areal oxidation, led to the element being named phosphorus (from the Greek, meaning light-bearer).

The simple inorganic chemistry of phosphorus was developed by a large number of chemists during the eighteenth and nineteenth centuries. The systematic development of organophosphorus chemistry was initially undertaken by A. Michaelis during the latter part of the nineteenth century, and was also pursued by Arbuzov in the early years of the twentieth century.

Phosphorus chemistry developed rapidly in the mid-twentieth century for three main reasons. The discovery by Schrader and by Saunders of the insecticidal and toxic properties of certain esters containing phosphorus on the eve of World War II set in train intensive studies of this area of phosphorus chemistry, and the economic significance of phosphorus-based pesticides continues to stimulate much work. The utility of polyphosphates as builders and sequestering agents in detergents also led to rapid development of this area of phosphorus chemistry. And finally, the resurgence of inorganic chemistry in the 1950s involved, in large measure, organophosphorus compounds as ligands in many of the novel coordination compounds under study.

1.2 Phosphorus in the economy

In 1840 Liebig pointed out that phosphorus is an essential plant nutrient, and indicated the utility of bonemeal in agriculture. By the late 1840s processes for utilizing mineral phosphates as fertilizers had been developed in Britain. This is still by far the predominant use of phosphorus in the economy. Chart 1 gives an approximate breakdown for the United States in the early 1970s of the major classes of industrial phosphorus intermediates, and typical end uses of products containing phosphorus.

1.3 Phosphorus in the ecology

Phosphorus is, on a cosmic basis, a moderately abundant element, among the 20 most abundant in the solar system, for example. In the lithosphere the average amount of phosphorus is about 0.2%; lunar samples and meteorites average about 0.1% phosphorus. In the lithosphere there are many different minerals containing phosphorus, but the form in which the element is found

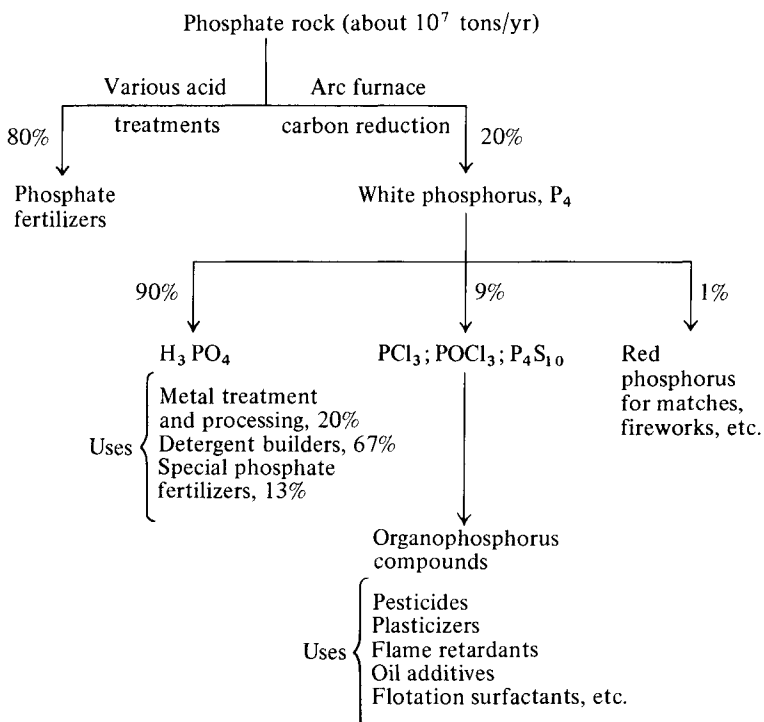


Chart 1. Phosphorus in the economy (figures for U.S. production, early 1970s).

1.3 Phosphorus in the Ecology

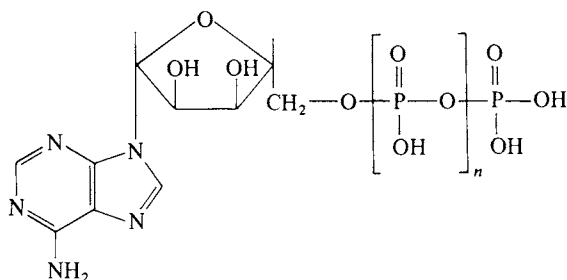
3

is virtually without exception as phosphate, conventionally written as PO_4^{3-} (formal oxidation state V; coordination number 4). The most common single mineral containing phosphorus is fluoroapatite, formula $\text{Ca}_5(\text{PO}_4)_3\text{F}$, but this is an idealized formulation; the class of apatites has the composition $\text{Ca}_5(\text{PO}_4, \text{CO}_3)_3(\text{F}, \text{Cl}, \text{OH})$.

Because phosphorus is so abundant in the earth's crust, it is perhaps not surprising to find that the element has biological functions. These can be divided into two different types. In the first type, phosphorus – in the form of inorganic, primarily calcium, phosphates – is the major structural material in vertebrate bone.

In the second type, phosphate esters provide linkages in biologically important systems. Thus the major energy-storage and -transfer mechanisms in all living systems involve the synthesis and breakdown of phosphate ester linkages such as those present in adenosine diphosphate, ADP, and adenosine triphosphate, ATP (1.1), whereas the storage and transfer of coded genetic information involve nucleic acids (DNA, RNA) that are diesters of phosphoric acid [represented schematically in (1.2)]. Some of the fundamental chemistry of phosphate esters and polyphosphates will be considered later (Section 6.3).

In nature, the phosphorus cycle is different in one respect from the cycles of most other elements of biochemical significance (C, N, S, etc.). Throughout the cycle phosphorus stays in its highest oxidation state, as P(V). Many of the details of the cycle are still obscure, particularly their quantitative aspects, but its main outlines are as indicated in Chart 2.

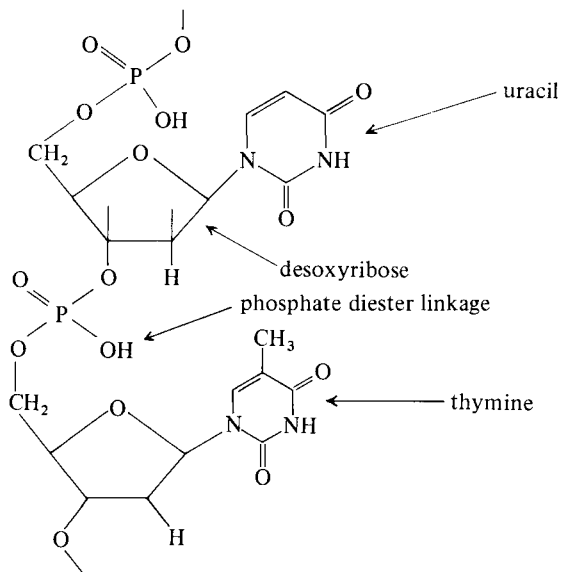


(1.1) Structures of un-ionized forms of adenosine diphosphate (ADP, $n = 1$ and adenosine triphosphate (ATP, $n = 2$)

It is believed that in some ecosystems phosphorus is a limiting basic nutrient. Thus when detergents containing large amounts of phosphate builders became popular in the 1950s, and large amounts of treated sewage containing phosphates began to be released into rivers and lakes, there were severe problems of eutrophication because of an upsurge in growth of algae and other primitive plants. It is only fair to add, however, that the culprit in these examples of ecological imbalance has not always been firmly identified; some

Introduction to Phosphorus Chemistry

4



(1.2) Schematic of phosphate ester linkage in a typical nucleic acid fragment (shown un-ionized)

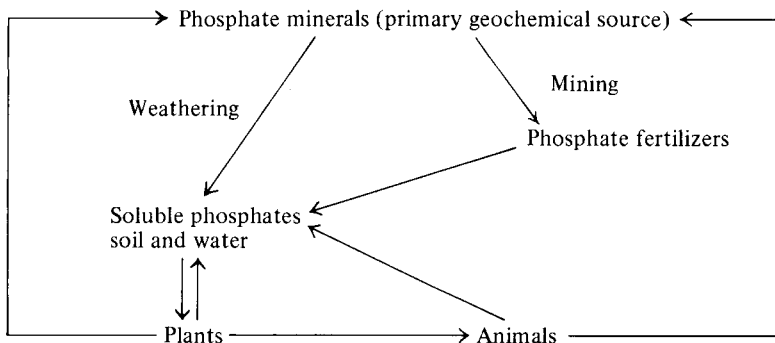


Chart 2. The phosphorus cycle in nature.

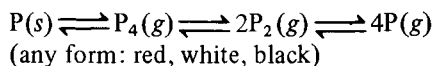
scientists believe that an associated increase in nitrogenous nutrients led to the rapid algal growth. Because of the possibility of phosphates being implicated, however, most detergent manufacturers have reduced the proportion of phosphate builders in detergents.

2 Survey of structural types, geometries, and reactions

When considering the chemistry of those main group elements clustered towards the center of the periodic table (groups III, IV, and V), oxidation state is not a particularly useful method of organizing information. For instance, PF_3 (phosphorus in formal oxidation state +3), PHF_2 (phosphorus in formal oxidation state +1), and PH_3 (phosphorus in formal oxidation state -3) would be separated by an oxidation-state classification, yet the similarities in their structures and chemistry are arguably more important than their differences. Consequently, in this chapter the survey of types of phosphorus compound has been made using coordination number (C.N.) as the unifying principle.

2.1 C.N.1

C.N.1 is a very unusual coordination number for phosphorus, but the few compounds in which it is known are of considerable theoretical significance (see Section 4.3). For example, when elemental phosphorus vapor is heated, the gas-phase molecule P_2 is detectable spectroscopically (2.1). Similarly, the molecule $\text{PN}(g)$ is detectable when phosphorus nitrides are heated.

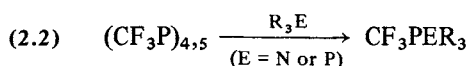


(2.1) Equilibria in elementary phosphorus

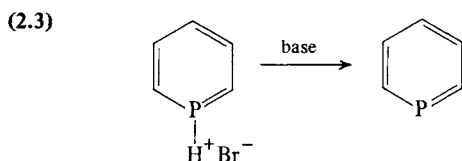
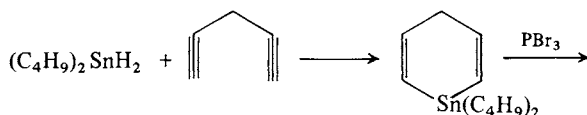
The best-studied molecule of this kind, HCP, has been obtained both in the gas phase and in solution. It is produced when phosphine is passed through a carbon arc. In condensed phases it polymerizes rapidly above 170 K. Spectroscopic study has demonstrated the nature of the carbon-phosphorus multiple bond in HCP as that of a triple bond involving $\text{P}(3p)\text{-C}(2p)\pi$ overlap: H-C:P: .

2.2 C.N.2

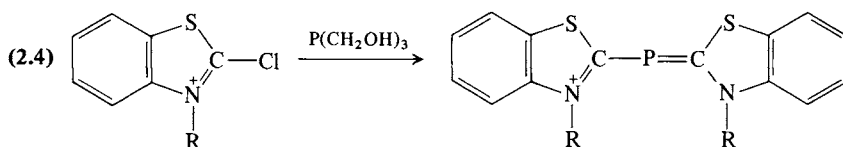
C.N.2 is also an unusual coordination state for phosphorus, although many more compounds with this coordination are known than with C.N.1. For example, reactions between certain cyclopolyphosphines (in which phosphorus has C.N.3) and either tertiary amines or tertiary phosphines give rather labile compounds with one phosphorus atom of C.N.2:



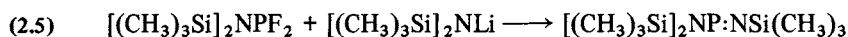
There is also an extensive chemistry of heterocyclic analogs of benzene containing phosphorus atoms, in which phosphorus has C.N.2; for example, the parent phosphabenzene has recently been prepared:



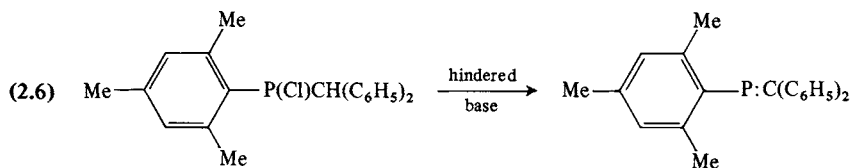
Other two-coordinate phosphorus systems include the phosphacyanins (historically the first of this coordination number to be prepared),



some cationic compounds such as $[(\text{CH}_3)_2\text{N}]_2\text{P}^+\text{AlCl}_4^-$; the very stable silylated phosphazenes,



and some novel stable compounds containing phosphorus-carbon double bonds:

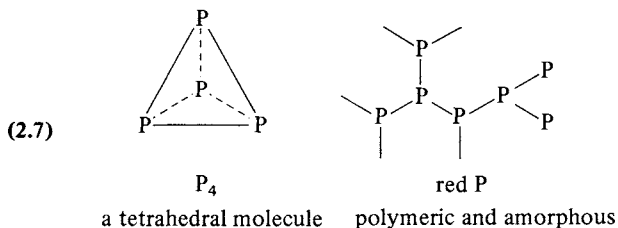


The stability of the 2-C.N. compounds shown in (2.5) and (2.6) is in part due to shielding of the phosphorus atoms by the bulky groups present.

So far there are few structural studies on these 2-C.N. compounds. The CPC skeleton of the phosphacyanins (2.4) is linear, whereas in a phosphazene of the type shown in (2.5) the NPN angle is about 105° .

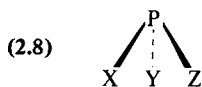
2.3 C.N.3

C.N.3 is one of the most common coordination numbers for phosphorus. An enormous range of compounds of this type, PXYZ, is known, where X, Y, and Z may be H, halogen, organic substituents, OR, NR₂, PR₂, SR, or SiR₃ groups (there are limitations on allowable combinations of groups because of mutual reactivity). The common forms of elemental phosphorus – namely, white phosphorus, P₄, and the polymeric amorphous red phosphorus (2.7) – contain three-coordinate phosphorus atoms.



Chlorination of elemental phosphorus produces phosphorus trichloride, PCl₃, another C.N.3 compound, which is the starting material used in preparation of most other C.N.3 products.

The geometries and structures of many C.N.3 phosphorus compounds have been determined. The almost invariant geometry is that of a trigonal pyramid (2.8), and the angles at phosphorus are normally less than 100° . The stereo-

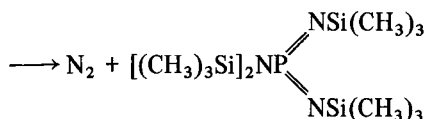
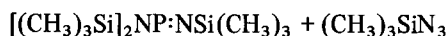


chemical and bonding implications of this structure will be enlarged upon later (section 5.2).

The first exception to the general rule of trigonal pyramidal geometry for C.N.3 was recently reported. The silylated phosphorus-nitrogen compound shown as (2.9), which is an isolable analog of a monomeric metaphosphate (cf. Section 6.2.3), is reported to have a planar trigonal arrangement of the three nitrogen atoms around phosphorus.

Survey of Structural Types, Geometries, and Reactions

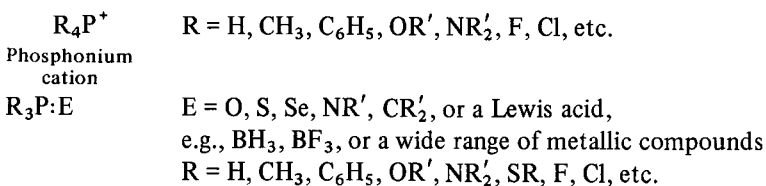
8



(2.9) Trigonal planar coordination about P

2.4 C.N.4

C.N.4 is the most common coordination type for phosphorus compounds, the geometry being that of a tetrahedral arrangement of groups around a central phosphorus atom. An extremely wide range of groups can be attached to phosphorus in this coordination type. Terrestrial naturally occurring phosphorus compounds, both in the lithosphere and the biosphere, are of this coordination number and geometry; (2.10) shows in general terms some of the variations possible on the theme of four coordination. Specific compounds will be discussed in detail in Chapter 6.



(2.10) Some phosphorus compounds of C.N.4

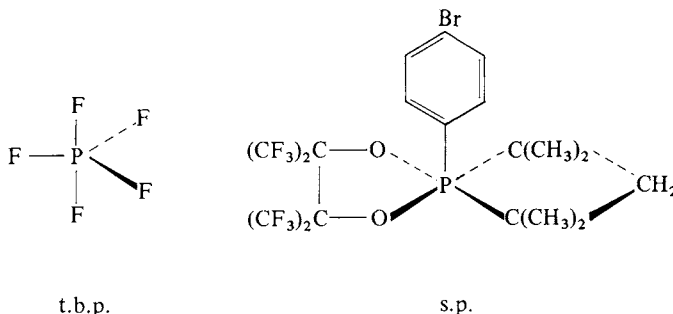
2.5 C.N.5

C.N.5 is not uncommon for phosphorus, with a wider and wider range of examples being reported. The simplest compounds of this type are the gaseous pentahalides PF₅ and PCl₅. (The gaseous pentahydride, PH₅, phosphorane, is as yet unknown). There are now many organophosphorus compounds known with C.N.5. Two idealized geometries have been used to describe compounds in this group. The more common one is trigonal bipyramidal (t.b.p.), such as is found in gaseous phosphorus pentafluoride (2.11); the less common one is square pyramidal (s.p.), and an example of this geometry is also shown in (2.11). An extensive discussion of the stereochemistry of C.N.5 is given in Chapter 7.

It should be mentioned that in the chemistry of phosphorus (as in many other areas of chemistry), stoichiometry is a very shaky guide to constitution or structure. Phosphorus pentachloride is an instructive example. In the gas phase, electron diffraction shows PCl₅ to be t.b.p., a conclusion that is supported by vibrational spectroscopy of the gas phase. Vibrational spectral

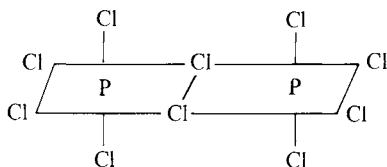
2.7 Reactions by Bond Types

9



(2.11) Geometry of C.N.5

studies of solutions of PCl_5 in benzene or carbon disulfide indicate that it retains its t.b.p. structure (D_{3h} symmetry) in these solvents, but similar studies of dilute solutions in acetonitrile (a much more polar solvent) indicate that PCl_5 is present as the ionized species $\text{PCl}_4^+\text{PCl}_6^-$. Spectroscopic and cryoscopic studies of solutions in carbon tetrachloride indicate the presence of a dimer, P_2Cl_{10} , of unknown structure [although the plausible chlorine bridged structure (2.12) can be suggested]. Finally, X-ray diffraction studies of crystalline PCl_5 show the presence in the structure of equal numbers of tetrahedral PCl_4^+ ions and octahedral PCl_6^- ions.

(2.12) A possible structure for P_2Cl_{10}

2.6 C.N.6

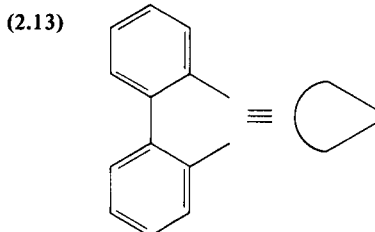
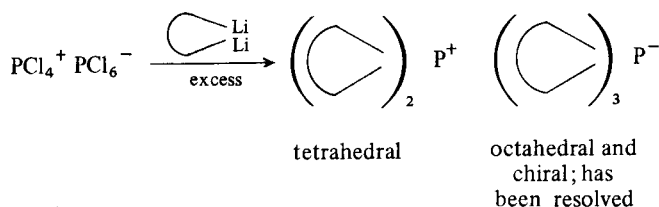
C.N.6 is again a less common C.N. for phosphorus, although there are indications that there is potentially a wide range of compounds available with this coordination. The geometry for all examples studied to date is octahedral. The two best-known compounds of C.N.6 are the anions PF_6^- and PCl_6^- . Organoderivatives have also been prepared, for example, in the elegant synthesis of a chiral derivative shown in (2.13).

2.7 Reactions by bond types

To complete this general survey of phosphorus chemistry, and before going on to a detailed discussion of the physical properties and chemistry of the

Survey of Structural Types, Geometries and Reactions

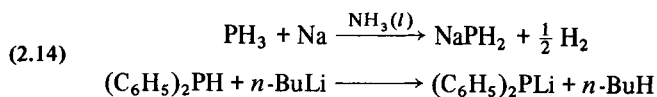
10



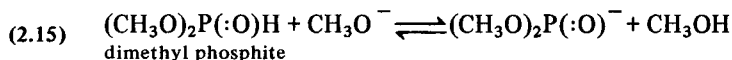
various classes of phosphorus compounds, it will be helpful to provide a brief general discussion of the chemistry of some commonly occurring phosphorus systems. Because the later discussion, in Chapters 5, 6, 7, and 9, is organized in terms of particular coordination numbers or specific reagent types, a different approach is adopted in this section and reactions are grouped according to the type of bond to phosphorus.

2.7.1 Reactions of P-H bonds

Phosphorus and hydrogen have very similar electronegativities, and consequently polar reactions are not much favored at the P-H bond. Hydrogen on phosphorus is only weakly acidic in C.N.3 compounds, although it can be abstracted by alkali metals or metal alkyls:



In C.N.4 compounds, hydrogen on phosphorus is substantially more acidic and can be abstracted by alkoxide ions, as well as the more basic reagents mentioned above:



If this last reaction is carried out in CH_3OD , deuterium is rapidly incorporated into the dimethyl phosphite.

Dialkyl phosphites readily form salts by reaction with alkali metals, and the alkylation of these salts is an important preparative method in phosphorus chemistry (Michaelis-Becker reaction):