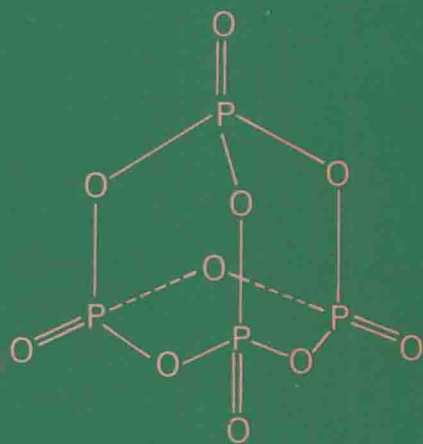


Introduction to phosphorus chemistry

HAROLD GOLDWHITE



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Introduction to phosphorus chemistry

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Preface

This book presents an introduction to the chemistry of a single element, phosphorus, as an example of a range of topics of interest in the whole of chemistry. The chemistry of phosphorus involves many of the major themes of modern chemistry – for example, bonding; physical techniques; and structure, both static and dynamic. In surveying the chemistry of phosphorus, it is necessary to cross and recross the boundaries of the various subdisciplines of chemistry that are today beginning to erode. There is an “inorganic” chemistry of phosphorus; organophosphorus chemistry is a large and expanding domain; phosphorus is an economically important element, and a vitally important element in the biosphere.

Many books have already been devoted, in whole or in part, to this important and interesting element. There are, however, few recent brief and introductory surveys, of the type this book attempts, of the major points of interest in the chemistry of this element. This book is intended for the chemist at an advanced undergraduate or graduate level who is interested in learning the fundamentals of the chemistry of phosphorus. Because an attempt is made at conciseness, the book cannot claim to be comprehensive or entirely current. The most significant developments in phosphorus chemistry through the end of June 1979 have been included. The critical bibliography and suggestions for further reading list the most useful secondary and tertiary sources in phosphorus chemistry. The primary literature is not included, because that would greatly expand the bibliography with little added utility for the intended reader of this work. Fortunately for those working in phosphorus chemistry, the major developments are rapidly made accessible in reviews and specialist reports, as indicated.

Chemists in the United States are, in the main, reluctant to adopt *Système Internationale* (SI) units. However the SI system's consistency and ease of use will certainly lead to a steady increase in its adoption by chemists. In this book I have given both SI and the more familiar cgs units where appropriate.

I carried out my original investigations in phosphorus chemistry under the direction of Dr. B. C. Saunders at Cambridge University, and later worked

collaboratively in a very different area of phosphorus chemistry with Professor R. N. Haszeldine at the University of Manchester Institute of Science and Technology. I owe much to these chemists, and to my undergraduate, graduate, and postdoctoral collaborators over the years.

The present text had its origin in courses given at California State University, Los Angeles; at the University of Strasbourg; and at the National University of Mexico. I thank my colleagues and students at all three institutions for their valued contributions to the development of this material.

Finally, I thank my parents, my wife, and my children for their continuous strong support and help; their contributions to my work have been of inestimable value.

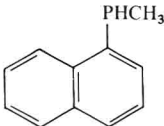
Harold Goldwhite

Los Angeles

Notes on nomenclature

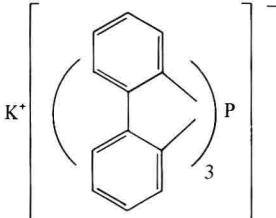
The nomenclature of phosphorus chemistry is in a somewhat confused (and confusing) state. Although an "agreed" system of naming phosphorus compounds was put forward jointly by the Chemical Society of London and the American Chemical Society in 1952, it was not adopted wholeheartedly by authors or editors and in the present literature the same phosphorus compound may be given several different names. This is a fundamentally undesirable situation, but it seems unlikely to change in the near future, in view of the already existing proliferation of names. The International Union of Pure and Applied Chemistry (IUPAC) has, in its latest proposals on the nomenclature of organic compounds containing phosphorus (Tentative Nomenclature of Organic Chemistry, Section D, Bulletin No. 31, August 1973) explicitly endorsed the naming of such compounds in three different ways: (1) as substitution products of parent hydrides, for example, of PH_3 , phosphine; (2) as derivatives of parent compounds, for example, H_2POH , phosphinous acid; (3) by coordination nomenclature as compounds of phosphorus, with an oxidation state affixed, if the author desires.

The proposals for phosphorus nomenclature (and that of analogous arsenic, antimony, and bismuth compounds) occupy 27 text pages in the IUPAC monograph and will not be reproduced here. Instead examples of alternative names for some common structural types will be presented, so that the reader will be able to follow not only the text of this book, but also the current literature of the subject.

Compound	Acceptable name(s) (and comments)
PH_3	Phosphine (a parent compound)
	Methyl(1-naphthyl)phosphine (alphabetic ordering of radicals)

Compound	Acceptable name(s) (and comments)
$\begin{array}{c} \text{CH}_3 - \text{CH} - \text{CH}_2\text{OH} \\ \\ \text{PH}_2 \end{array}$	2-Phosphino-1-propanol (using phosphino as a name for the $-\text{PH}_2$ substituent)
$\text{HP}(\text{CH}_2\text{CH}_2\text{COOH})_2$	3,3'-Phosphinediyldipropionic acid (phosphinediyl is the recommended name for HP as a substituent)
$\begin{array}{ccccccccccccccc} 11 & 10 & 9 & & 8 & 7 & 6 & & 5 & 4 & 3 & 2 & 1 \\ \text{CH}_3 & \text{CH}_2 & \text{P} & - & \text{CH}_2 & \text{CH}_2 & \text{P} & - & \text{CH}_2 & \text{CH}_2 & \text{CH}_2 & \text{P} & \text{CH}_3 \\ & & & & & & & & & & & & \\ & & \text{CH}_3 & & & & \text{C}_2\text{H}_5 & & & & & \text{H} & \end{array}$	6-Ethyl-9-methyl-2,6,9 triphosphaundecane (using substitution nomenclature with the suffix <i>-a</i> for a chain compound with several phosphorus atoms)
$\text{CH}_3\text{COP}(\text{CH}_3)_2$	Acetyldimethylphosphine (acyl compounds are named as phosphine derivatives)
$(\text{C}_6\text{H}_5)_2\text{PLi}$	Lithium diphenylphosphide (the suffix <i>-ide</i> indicates the negative character of the phosphorus atom)
$(\text{C}_2\text{H}_5)_2\text{POCH}_3$	Diethylmethoxyphosphine (as a phosphine derivative) Methyl diethylphosphinite [as an ester of diethylphosphinous acid, $(\text{C}_2\text{H}_5)_2\text{POH}$] Diethylmethoxophosphorus (III) (coordination nomenclature)
CH_3PCl_2	Dichloro(methyl)phosphine [the (methyl) is in parentheses to avoid confusion with CHCl_2PH_2 , (dichloromethyl) phosphine] Methylphosphinous dichloride Dichloro(methyl) phosphorus

Compound	Acceptable names(s) (and comments)
$\begin{array}{c} \text{OCH}_3 \\ \diagup \\ \text{C}_6\text{H}_5\text{P} \\ \diagdown \\ \text{N}(\text{CH}_3)_2 \end{array}$	Dimethylamino(methoxy) (phenyl)phosphine Phenyl N,N,P-trimethyl- phosphonamidite [as a de- rivative of phosphonamid- ous acid, $\text{HP}(\text{OH})\text{NH}_2$] Dimethylamido(methoxo) phenylphosphorus
$(\text{CH}_3)(\text{C}_2\text{H}_5)(\text{C}_6\text{H}_5)(\text{C}_6\text{H}_5\text{CH}_2)\text{P}^+\text{Cl}^-$	Benzylethylmethylphenyl- phosphonium chloride (the suffix <i>-onium</i> indicates four- coordinate positive charac- ter for phosphorus)
$(\text{C}_6\text{H}_5)(\text{CH}_3)_2\text{PO}$	Dimethyl(phenyl)phosphine oxide Dimethyl(oxo)phenylphos- phorane (phosphorane de- notes the five-coordinate state of phosphorus with, in this example, the oxo sub- stituent formally occupying two coordination sites; see below for other examples) Dimethyl(oxo)phenylphos- phorus
$(\text{C}_6\text{H}_5)_3\text{PCH}_2$	Methylene(triphenyl)phos- phorane Methylene(triphenyl)phos- phorus (Triphenylphosphonio) methylide (when the con- tribution P^+-C^- is to be stressed)
$(\text{CH}_3)_2\text{PO}(\text{OH})$	Dimethylphosphinic acid Dimethyl(hydroxo) (oxo) phosphorane Dimethyl(hydroxo) (oxo) phosphorus

Compound	Acceptable names(s) (and comments)
$\text{ClCH}_2\text{PO}(\text{OH})_2$	(Chloromethyl)phosphonic acid Chloromethyl(dihydroxo)(oxo)phosphorane Chloromethyl(dihydroxo)(oxo)phosphorus
$\text{C}_6\text{H}_5\text{P}(\text{:O})(\text{Cl})(\text{OCH}_3)$	Methyl phenylchlorophosphonate [ester of phenylchlorophosphonic acid, $\text{C}_6\text{H}_5\text{P}(\text{O})(\text{Cl})\text{OH}$] Methyl phenylphosphonochloridate [ester of acid chloride of phenylphosphonic acid, $\text{C}_6\text{H}_5\text{P}(\text{O})(\text{OH})_2$] Chloro(methoxo)(oxo)phenylphosphorus
$(\text{C}_6\text{H}_5)_3\text{PBr}_2$	Dibromotriphenylphosphorane Dibromotriphenylphosphorus
	Potassium tris(2,2'-biphenylene) phosphate(V) (Stock system) Potassium tris(2,2'-biphenylene)phosphate(I-) (ion-charge system)
$\text{H}_2\text{P}-\text{PH}_2$	Diphosphane (the old name, diphosphine, is strongly discouraged)

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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 aerial 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

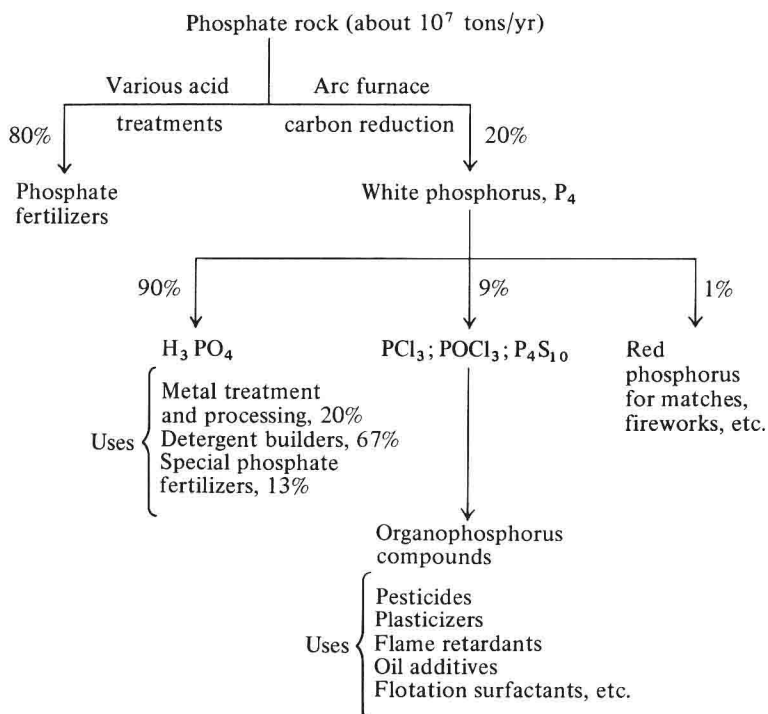


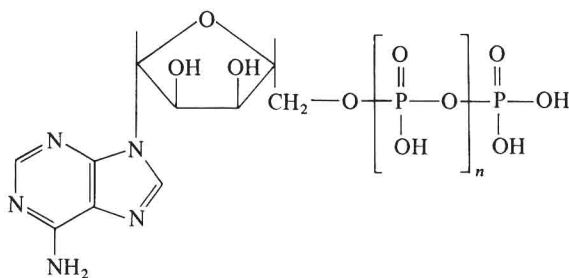
Chart 1. Phosphorus in the economy (figures for U.S. production, early 1970s).

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.

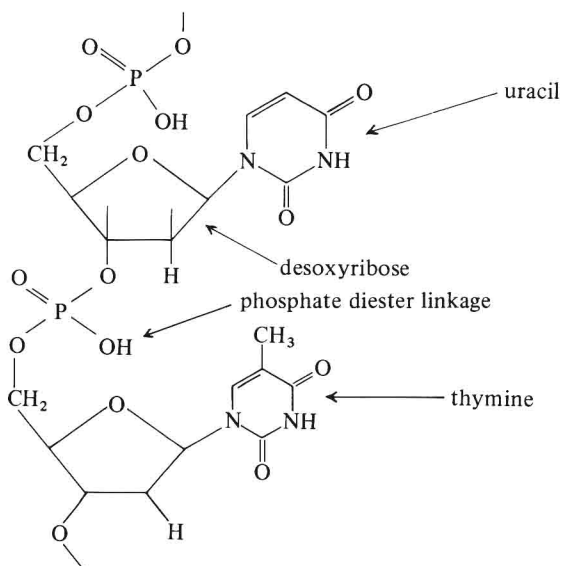
In the second type, phosphate esters provide linkages in biologically important systems. Thus the major energy-storage and -transfer mechanisms in all living systems involve the synthesis and breakdown of phosphate ester linkages such as those present in adenosine diphosphate, ADP, and adenosine triphosphate, 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



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

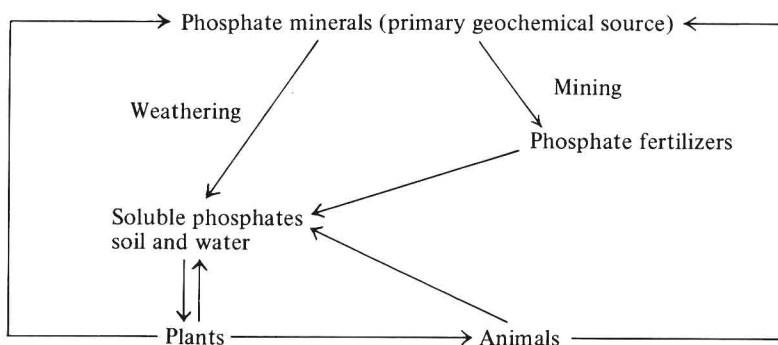


Chart 2. The phosphorus cycle in nature.

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.