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Nomenclature of Phosphorus Compounds*

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Aside from carbon, probably a greater number and variety of compounds have been described for phosphorus than for any other element. Furthermore, the study of phosphorus compounds is a very active branch of present-day chemistry, and our knowledge of phosphorus chemistry is ever-widening. Although the chemistry of phosphorus has been reasonably well systematized,¹ the present-day nomenclature is most inadequate and often confusing. Indeed, when one is writing about any organic phosphorus compound except a few of the more common

ones, it is wise to have a structural formula accompany the name when it is first stated. Furthermore, phosphorus chemistry during the past decade or so has been extended to include whole families² of compounds in which phosphorus atoms appear repeatedly in the molecular backbone, and there must be names not only for individual compounds but also for families.

NOMENCLATURE HERITAGE IN PHOSPHORUS CHEMISTRY

Peculiarities in Inorganic Naming.—In the early days of chemistry, study of phosphorus compounds was very

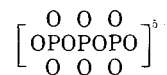
* Adapted from the paper presented before the Divisions of Inorganic Chemistry and Chemical Literature, 136th National Meeting of the American Chemical Society, Atlantic City, N. J., September 18, 1959.

popular. There was then a lull in activity in this field from the latter part of the 19th century through the first quarter of the 20th century. This means that some of the nomenclature dealing with phosphorus compounds was established during the period in which chemistry was first being developed. For example, phosphorus pentoxide was discovered before the acceptance of Avogadro's hypothesis, during the time when water was written as HO. Consequently, the structure of phosphorus was given as PO_5 instead of P_2O_5 —hence the name phosphorus pentoxide instead of diphosphorus pentaoxide (see rule 2.26 in ref. 22). A similar situation is found in the case of P_2O_3 , which is called phosphorus trioxide; P_4S_{10} , phosphorus pentasulfide; and P_4S_3 , phosphorus sesquisulfide (*i.e.*, $\text{PS}_{1.5}$). However, the other phosphorus sulfides, P_4S_7 and P_4S_5 , are generally called tetraphosphorus heptasulfide and tetraphosphorus pentasulfide, on the basis of the presently accepted atomic weight of oxygen as 16 rather than the outmoded value of 8 on the standard scale in which hydrogen is assigned a molecular weight near unity.

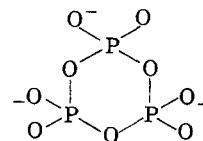
Phosphorus pentoxide points up another interesting problem of nomenclature in phosphorus chemistry. This concerns differences in molecular structure (isomerism, polymorphism, allotropy, etc.) to be found after various thermal or other treatments of an inorganic material having a given empirical formula. Thus, phosphorus pentoxide may exist in the form of the bird-cage molecule, P_4O_{10} , which is known to be present in the vapor and in one of the crystalline species. Two other crystalline species consist of infinite sheet polymers—one based on 12-atom, the other on 20-atom rings fused together—and there are at least two amorphous solids which apparently also have different molecular structures. One of these, vitreous P_2O_5 , is thought to consist of random, three-dimensional-network macromolecules. In addition, there are two liquid forms—one quite limpid (presumably having a high content of P_4O_{10} bird-cage molecules) and the other viscous (network structures), the latter having a more than tenfold lower vapor pressure than the former. Yet they are all called simply phosphorus pentoxide. This situation, which is repeated for many phosphorus compounds as well as for elemental phosphorus, points up the fact that not only are generic names—such as phosphorus pentoxide—needed, but that a good system of nomenclature for inorganic compounds should in addition be able to differentiate between various isomers and polymers and allow for the fact that there may be several kinds of macromolecular polymers corresponding to the same stoichiometry.

Another interesting curio in simple, inorganic phosphorus chemistry is found in the nomenclature of calcium orthophosphates. In this case, the salt with the formula $\text{CaH}_4\text{P}_2\text{O}_8$ is commonly known as monocalcium phosphate, CaHPO_4 as dicalcium phosphate, and $\text{Ca}_3\text{P}_2\text{O}_8$ as tricalcium phosphate. Of course, what is meant is calcium phosphate monobasic, dibasic, and tribasic, respectively. This is clearly seen when the empirical formulas are written as $\text{Ca}(\text{H}_2\text{PO}_4)_2$, $\text{Ca}(\text{HPO}_4)$, and $\text{Ca}_3(\text{PO}_4)_2$.

A nomenclature peculiarity in common use by industrial chemists is found in the name sodium tripolyphosphate for the completely substituted sodium salt of the acid having the following anion.



Some people prefer to call this salt sodium triphosphate since they object to the juxtaposition of the Greek prefixes for three and for many. On the other hand, others reserve the term triphosphate for describing a more general class of compounds including the salts based on the anion shown above and those based on the ring anion



the sodium salt of which is generally known as sodium trimetaphosphate. In this case, "poly" is taken to mean a straight chain. This usage is exemplified by the sentence: "Pyrophosphoric acid is one member of a series of polyphosphoric acids which range in size up to macromolecules containing as many as a million phosphorus atoms."

A number of materials prepared by the early inorganic chemists have been named after their discoverer, *e.g.*, Graham's, Maddrell's, and Kurrol's salts. These terms refer to a particular crystalline or amorphous solid solution and are as meaningful as the trivial names of organic chemistry, *e.g.*, formic and oxalic acids.

In discussing nomenclature of inorganic compounds, the minerals should not be forgotten. Extensive ranges of solid solution (berthollides, see rule 4 in ref. 22) are commonly found in naturally occurring salts, oxides, sulfides, etc., but *chemical* nomenclature has never been extended to the point where it could adequately cope with this problem. Therefore, mineralogists have been content with adding the suffix -ite to a long list of trivial names—often the names of their friends or mentors. Thus, for example, the orthophosphate salts exhibiting a particular set of "fingerprints" in their X-ray diffraction powder patterns are called apatites (from the Greek word "to deceive"). These "fingerprints" correspond to a particular arrangement of ions—including the PO_4^{3-} and/or HPO_4^{2-} molecule-ions—in the crystal lattice. Because a whole host of ions may substitute for each other in the crystal structure, the apatites are subdivided into more than a dozen more-or-less overlapping and only vaguely distinguishable groups, *e.g.*, fluorapatite, francolite, svabite.¹ The formula for francolite, for example, is often given as $(\text{Ca}, \text{H}_2\text{O})_{10}(\text{F}, \text{OH})_2(\text{PO}_4, \text{CO}_3)_6$, but mineral compositions included in this class may have tucked away into the crystal lattice small amounts of many other elements than those given in the "simple" formula above. Fluorapatite and svabite are often formulated as $\text{Ca}_{10}\text{F}_2(\text{PO}_4)_6$ and $(\text{Ca}, \text{Pb})_{10}(\text{F}, \text{Cl}, \text{OH})_2(\text{AsO}_4, \text{PO}_4)_6$, respectively. Chemists generally use a few reasonable pure substances as reagents in stewing up a compound but Nature puts practically everything in her stew pot. Isomorphism and its attendant nomenclature problems would be more significant to preparative chemists if they were to throw more things together in exploratory preparations.

An interesting aberration in inorganic phosphorus nomenclature is found in the case of the soluble glass

having an empirical formula (in the Berzelius notation) near $\text{Na}_2\text{O} \cdot \text{H}_2\text{O} \cdot 2\text{P}_2\text{O}_5$. This material is an analytical reagent which is called "metaphosphoric acid" and is generally given the formula HPO_3 on the label of commercial C.P. preparations. A famous analytical chemist once told me that the sodium in these glasses is no different from water in, say, HCl or NH_4OH and hence is unworthy of being included in the name or empirical formula. However, a suitable name for the glass would seem to be "a sodium acid (or hydrogen) metaphosphate" and a correct empirical formula "*ca.* $\text{NaH}(\text{PO}_3)_2$."

Problems in Organic Nomenclature.—Probably the greatest confusion of terminology in phosphorus chemistry occurs in the simple organophosphorus acids and their derivatives. For example, the compound $\text{R}_2\text{PO}(\text{OH})$ is called dialkylphosphinic acid in *Chemical Abstracts* (this is the general usage today), dialkylphosphonic acid in the key American reference to the descriptive chemistry³ of organic phosphorus compounds, dialkylphosphonous acid according to British usage before 1952, and dialkylphosphinous acid in Beilstein. Furthermore, it can logically be thought of as a derivative of hypophosphorus acid, $\text{H}_2\text{PO}(\text{OH})$, in which the two hydrogens are substituted by alkyl groups, and hence might be called dialkylhypophosphorous acid.

The problems in the naming of inorganic phosphorus compounds have generally come from a devil-may-care attitude concerning precise terminology. However, in the case of the organophosphorus acids, the trouble has arisen from too assiduous attention to nomenclature. Each name for $\text{R}_2\text{PO}(\text{OH})$ has a rational explanation! Since for this and the other organic monophosphorus acids different people have used different names for the same compound and the same name for different compounds, it is impossible to understand the literature without seeing formulas or knowing beforehand to which school of nomenclature the author subscribed. A detailed listing of these various names has been assembled.⁴ Because of the great confusion attending the use of the endings -inic, -onic, -inous, and -onous, it would be desirable to drop these suffixes completely and replace them by other notation. This was not done in the 1952 ACS Committee report⁵ dealing with the nomenclature of organic phosphorus compounds.

NOMENCLATURE OBJECTIVES AND PROBLEMS

Highlights of Phosphorus Chemistry.—In order to have an adequate system of chemical nomenclature, one must understand the chemistry involved. It now appears that the general principles of phosphorus chemistry are reasonably clearly elucidated⁷ so that the key points of importance to nomenclature may be given below.

1. Phosphorus is always covalently bonded to its neighboring atoms, in the same sense as is carbon. (This means that the various allotropic forms of elemental phosphorus are all molecular in nature and that anions or cations containing phosphorus are molecule-ions.)

2. There are four well-known arrangements of the neighboring atoms around phosphorus. Employing only s- and p-orbitals in the σ -bond base structure, phosphorus may either have three atoms bonded to it with an unshared

pair of electrons so as to exhibit the gross atomic geometry of p^3 -hybridization, or it may have four bonded atoms arranged in an approximately tetrahedral manner about it as expected for sp^3 -hybridization. Phosphorus is also known to use one or two d-orbitals in its σ -bond base structure. Using one d-orbital, the phosphorus is bonded to five neighboring atoms arranged at the apexes of a trigonal bipyramid (sp^3 -hybridization); or, using two d-orbitals, there are six bonded neighbors at the apexes of a hexagonal bipyramid (sp^3d^2 -hybridization). In addition, there is a single reasonably acceptable literature report⁹ of the bonding of a phosphorus atom (in a compound which is stable at room temperature) to only two neighboring atoms with two unshared pairs of electrons (presumably exhibiting a geometry approximating p^2 -hybridization). At very high temperatures, the so-called spectrographic molecules, such as CP , P_2 , and PN , have a structure in which the phosphorus has only one atom bonded to it.

To recapitulate, phosphorus may have from one to six other atoms bonded to it (it is thought unlikely that there will be more than six in any stable molecule), with the majority of the known compounds being based on phosphorus with three or four bonded atoms and a growing literature on phosphorus bonded to five atoms.

3. Multiple bonds to phosphorus do exist but the exact resonance structures and the bond order is still questionable for any and all compounds. It seems that such multiple (or π -) bonding which involves d-orbitals is generally found when the phosphorus is bonded to four other atoms and is absent or at a minimum when the phosphorus is bonded to three or five other atoms.⁷ Few chemists relate the chemical and physical properties of a phosphorus compound to the presence or absence (much less the exact distribution) of π -character in the bonds to phosphorus.

4. Polyphosphorus compounds are readily prepared and entire families of molecules, ranging from the simplest monophosphorus compound to polyphosphorus macromolecules of infinite size, are known.

5. Phosphorus compounds are generally more labile than are the compounds of carbon so that rearrangements and scrambling reactions are not uncommon.⁸

6. Because of 5 above, much of present-day phosphorus chemistry is equilibrium chemistry in which reaction products are not determined by the reaction mechanism but by the relative proportions of exchangeable groups and free-energy differences. In particular, polyphosphorus compounds are generally produced as mixtures.

General Principles of Nomenclature.—In an interesting note, Nutting⁹ has presented ten factors which chemists would like to include in naming covalently bonded compounds. In slightly modified form, these are presented below.

Each name should:

1. Be as simple as possible (easy to recognize, spell, and pronounce).
2. Be unique and capable of distinguishing any given compound from all others.
3. Tell the kinds of atoms in the molecule.
4. Tell the number of each kind of atom in the molecule.
5. Show the relationship of one atom to another in the molecule.

6. Be derived easily from the structural formula.
7. Lead immediately to the structural formula from the name.
8. Give broad clues as to the structural relationships of one compound to another.
9. Contain clues as to chemical reactivity.
10. Lead to groupings of like compounds together in an index.

The first objective listed above is easier said than done. No systematic nomenclature system which fulfills the requirements of factors 4-9 will result in a truly simple name for complicated molecular structures. In organic chemistry, the need for simplicity has led to special names for common atomic groupings, such as are found in the "Ring Index,"¹⁰ and to the use of common (generic and trade-marked) names for complicated chemical structures such as pharmaceuticals.

For phosphorus chemistry, there are two other factors which should also be considered¹¹:

11. The system of nomenclature for monophosphorus compounds should be applicable to polyphosphorus compounds either directly or by simple extension. In particular, it should provide names of maximum possible simplicity for the polyphosphoric acids.
12. The names used for phosphorus compounds should be equally applicable to the elements near phosphorus in the Periodic Table, lest there arise a jungle of individual nomenclatures for each element.

These twelve factors seem to enunciate adequately the principles on which a systematic nomenclature for phosphorus must be based. However, the application of factor 12 to the relationship between the nomenclature appropriate for phosphorus and that used for its diagonal neighbor, carbon, will be treated in the next section since this may be the source of much difficulty.

Problems in the Extension of Organic Nomenclature Usages.—The general approach^{5,11} in attempting to set up a systematic naming system for phosphorus compounds has been to model the proposed system on the present-day nomenclature used in organic chemistry. This organic nomenclature, however, is difficult to generalize since carbon, being a first-row element, has a number of peculiarities not shared by other elements, particularly those in the second row and below of the Periodic Table. First-row elements have somewhat unique chemistries because the energy levels of their various electronic orbitals are rather widely spaced and the d-orbitals have such high energies that they are simply unavailable.

A feature of classical organic chemistry which is unknown for elements other than carbon is that, at least formally, the sum of the σ - and the π -bonds to a given carbon may be set equal to four. Because of this, the bond order is a basic part of organic chemical nomenclature. When this nomenclature was first developed about a century ago, valence was most satisfyingly conceived as the number of "hooks" by which an atom could hold onto neighboring atoms, and it was aesthetically very satisfying to think of carbon as having a fixed number of such hooks. One could probably develop a very good argument that it was precisely this type of thinking which caused inorganic chemistry (including work on phosphorus) to stagnate for many years. The present-day renaissance in inorganic chemistry is attributable in great part to the realization that the bonding considerations developed in classical organic chemistry are

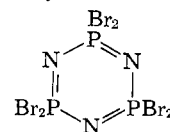
generally not applicable to compounds other than those of carbon and nitrogen with hydrogen, oxygen, and halogens.

In addition to the twelve principles of nomenclature set out in the preceding section, it is also important that the naming system not be misleading, and this is bound to be the case when a nomenclature system which makes precise statements about bond orders (single, double, triple bonds, etc.) is applied to elements other than carbon and perhaps nitrogen.

Another undesirable feature of the nomenclature of organic chemistry from the point of view of general chemistry is the tacit assumption that certain atoms always have a fixed functionality. Thus, it is generally considered that fluorine and oxygen, for example, are always monofunctional and bifunctional, respectively. Nothing could be further from the truth, as evidenced by the bifunctional bridging fluorine atoms in such structures as the antimony pentafluoride polymer¹² and the presence of $>O<$ as well as $-O-$ in the heteropoly acids (see Fig. 1). Related features of general chemistry not found in classical organic chemistry are hydrogen bridges of the type found in the boron hydrides¹³ and bridging methyl groups, as in the aluminum alkyls.¹³

In short, the emphasis on bond order in organic nomenclature introduces specious problems into general chemistry where nonclassical valence appears to be more the rule than the exception. The theory of chemical bonding has been recently described as "a dynamic, interesting, and elusive thing, still to be captured, not dogma."¹⁴ Instead of basing a nomenclature system on the shifting sands of bond order, it would be better to have the names give only the *number* of neighboring atoms about each constituent atom in a molecule.

A similar approach should also be used in writing structural formulas. Thus, in the book "Phosphorus and Its Compounds," I employed¹⁵ a single line to indicate a bond, regardless of the bond order and whether or not the electrons in the bond came primarily from one atom or the other. Use of a double bond or arrow to denote a coordinate-covalent or dative bond adds little or nothing to the structural formula of a compound as given in descriptive chemical writings. In most cases the use of this double-bond or arrow notation is inadvisable since it implies that a given neighboring atom bears all of the difference in charge between phosphorus and its four neighboring atoms; whereas, in reality, the charge difference indicated by the coordinate-covalent bond is probably smeared around more or less evenly between the neighboring atoms. For example, trimeric phosphonitrile bromide is generally written as



However, there is no evidence that whatever π -bonding is present between a given phosphorus atom and its four adjoining atoms is confined to or even predominates in the bonds to the bridging nitrogens of the ring. An unprejudiced system of nomenclature and of drawing structural formulas would make no such *a priori* implication.

Table I
Examples of the Greatly Extended Oxa-Aza Nomenclature as Applied to Known Phosphorus Compounds

Structure	Common name	Liberalized oxa-aza name
$\begin{array}{c} \text{O} \quad \text{O} \quad \text{O} \\ \quad \quad \\ \text{HOPOPOPOH} \\ \quad \quad \\ \text{H} \quad \text{H} \quad \text{H} \end{array}$	Tripolyphosphoric acid	1,1,1,3,3,5,5,5-Octoxo-2,4,1,3,5-dioxatriphosphapentanic(5) acid
$\begin{array}{c} \text{Cl}_2 \\ \\ \text{N} \text{---} \text{P} \text{---} \text{N} \\ \quad \quad \\ \text{Cl}_2 \text{---} \text{P} \text{---} \text{N} \text{---} \text{P} \text{---} \text{Cl}_2 \\ \quad \\ \text{Cl}_2 \end{array}$	Trimeric phosphonitrilic chloride	2,2,4,4,6,6-Hexachloro-1,3,5,2,4,6-triazatriphosphacyclohexane
$\begin{array}{c} \text{CH}_3\text{C} \quad \text{O} \\ \quad / \quad \backslash \\ \text{CH}_3\text{C} \quad \text{P}(\text{OCH}_3)_3 \end{array}$	1:1 adduct of trimethyl phosphite with biacetyl	2,2,2-Trimethoxy-4,5-dimethyl-1,3,2-dioxaphospha-4-cyclopentene
$(\text{C}_2\text{H}_5)_2\text{P} \text{---} \text{P}(\text{S})(\text{C}_2\text{H}_5)_2$	Tetraethyldiphosphine monosulfide	As a phosphorus compound: 1,1,2,2-tetraethyl-1-thiodiphosphaethane As a carbon-phosphorus chain: 3,4-diethyl-3-thio-3,4-diphosphahexane
$(\text{Cl}_2\text{P} \text{---} \text{N} \text{---} \text{PCl}_2)^+ (\text{PCl}_6)^-$	Hexachlorodiphosphonitrilium hexachlorophosphate or 2:1 adduct of phosphorus pentachloride with monomeric phosphonitrilic chloride	As a phosphorus compound: 1,1,1,3,3,3-hexachloro-2,1,3-azadiphosphapropanium(1) hexachlorophosphamethanate(1)

long names containing extended sequences of numbers can be eliminated for many inorganic compounds. It is important that the names for the cage structures and other fused-ring systems do not imply that any particular elements are involved in the structure. For example, the cage structure based on ten atoms exhibited by P_4O_6 occurs in a number of other instances both within and without phosphorus chemistry.

The Real Need in Phosphorus Nomenclature.—In addition to the need for simple names describing the various cage and other extended fused-ring systems which are so common in general chemistry and receive such little attention in organic circles, it is also desirable for general chemical nomenclature (a) to have generic or family names, (b) to be able to describe simply collections of molecules in which some or all of the atoms or groups are randomly arranged, (c) to have terminology of maximum simplicity for chains or rings of alternating atoms or groups, and (d) to be able to describe infinite or extremely large macromolecules in terms of the repeating parts of their structure. In Table II are listed a number of Anglicized Greek roots which may be used as either adjectives, suffixes, or prefixes.

It is entirely possible to set up a nomenclature system which would supply the needs of present-day inorganic chemistry and would result in simple, reasonably clear names for at least the more important compounds of phosphorus.²⁰ (Since the polyphosphate anions play the same role in phosphorus chemistry as do the hydrocarbons in carbon chemistry, one might conclude that the key system of compounds for phosphorus nomenclature should be these anions instead of the hydrides, as is the usual practice of those patterning nomenclature after organic usage.) Thus, the indication of bond order in a general chemical name could be avoided by designating with a prefix the number of neighboring atoms bonded to a given central atom, such as phosphorus. In order to achieve the simplest possible names, it would be desirable to omit such an enumerative prefix for the commonest coordination number of an element (*e.g.*, 4 for phosphorus).

Table II
Useful Word-Roots for General Chemical and Mineral Nomenclature^a

Root	Meaning
geno	family (series)
neso	smallest molecule of a family
oligo	small or medium sized
macro	large
apeiro	infinite
ino ^b	chain
cyclo	ring (preferably a simple ring)
clovo	bird-cage
phyllo	sheet
diktyo	network
ampho	simultaneously anionic and cationic
zeugo	branched
zeugotato	most branched
amoebo	alternating
mikto	scrambled or mixed up (random scrambling implied)

^a Other roots used by silicate chemists are "tecto" for a continuous framework and "soro" for a group. ^b In the IUPAC Inorganic Nomenclature Rules,²² "catena" is used in place of "ino" to indicate a chain. However, the word catenation is generally used to describe a chain of like atoms, as a C-C chain. Thus, it is thought that *catena* should be reserved for this restricted usage and hence be included as a special case under *ino*, just as *allotropism* refers to like atoms and is thus a subgrouping under *polymorphism*.

The "siloxane" type of nomenclature is particularly advantageous for chains of alternating atoms or groups and may be incorporated into a wide range of nomenclature systems through modification in such a way that the repeating units in the chains or rings of a molecular structure could be designated by the use within parentheses of the word-stems for the two elements or groups immediately beside each other.

Suffixes denoting ring sizes could be based on a modification and extension of those already accepted for heterocyclic rings, as "ole" and "in" for five- and six-membered

rings, respectively. Such suffixes might be employed in the description of infinite network structures or other complex molecules based on fused rings of a given size.

Although it represents a splendid treatment of the available material, the most recent formulation²¹ of general rules for the nomenclature and indexing of inorganic compounds bears evidence that the time is now ripe for some radical departures from tradition aimed at achieving an entirely new system of nomenclature which will meet all requirements (see Nutting's ten factors above). Were this to be done, it would probably be desirable to introduce new suffixes which would not be confused with existing ones such as "-ate," "-ium," "-ane," and "-ene." It seems reasonable to devise suffixes indicating that substances are either anionic or cationic, with no suffix for neutral substances. The charge of an anion or cation could then be given by an Arabic number in parentheses at the end of the name, as proposed by Ewens and Bassett for complex anions (rule 2.252, comment in ref. 22).

Innovations along these lines might lead to an approach which could solve the problem of obtaining simple names for a large number of compounds in general chemistry—especially the common compounds of phosphorus and those of the elements close to it in the Periodic Table and, in particular, chain structures based on repeating units.

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