Phosphorous acid

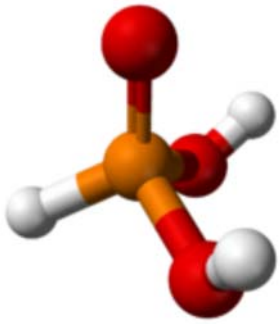
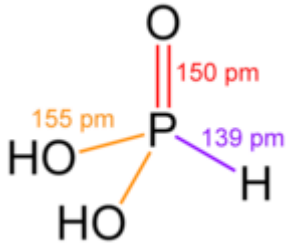
From Wikipedia, the free encyclopedia

Phosphorous acid is the compound described by the formula H_3PO_3. It can be formulated as $HP(O)(OH)_2$ and therefore contains phosphorus in oxidation state +3. It is one of the oxoacids of phosphorus, other important members being phosphoric acid (H_3PO_4) and hypophosphorous acid (H_3PO_2). Note that only the reduced phosphorus compounds are spelled with an "ous" ending. Other names for this acid are orthophosphorous acid and dihydroxyphosphine oxide.

$HP(O)(OH)_2$ is the product of the hydrolysis of its acid anhydride, P_4O_6:

$$P_4O_6 + 6\ H_2O \rightarrow 4\ HP(O)(OH)_2$$

An analogous relationship connects H_3PO_4 and P_4O_{10}.

Phosphorous acid	
	
	
IUPAC name	phosphonic acid
Other names	phosphonic acid
Identifiers	
CAS number	[13598-36-2 (http://www.commonchemistry.org/ChemicalDetail.aspx?ref=13598-36-2)]
RTECS number	SZ6400000
Properties	
Molecular formula	H_3PO_3
Molar mass	82.00 g/mol
Appearance	white solid deliquescent
Density	1.651 g/cm^3 (21 °C)
Melting point	73.6 °C
Boiling point	200 °C (decomp)
Solubility in water	310 g/100 mL

Contents

Tautomerization

H_3PO_3 is better described with the structural formula $HP(O)(OH)_2$. This species exists in equilibrium with a minor tautomer $P(OH)_3$. (IUPAC recommendations, 2005, are that the latter is called phosphorous acid, whereas the dihydroxy form is called phosphonic acid. [1]) The $P(OH)_3$ tautomer has recently,(2004), been stabilised as a ligand bonded to molybdenum.[2][3] Many of the reduced phosphorus acids are subject to similarly complicated equilibria involving

shifts of H between O and P.

Structure

In the solid state, $HP(O)(OH)_2$ is tetrahedral with one shorter P=O bond of 148 pm and two longer P-O(H) bonds of 154 pm.

Preparation

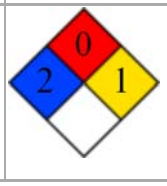
Although commercially available, the acid is most commonly prepared by hydrolysis of phosphorus trichloride with water or steam:

$$PCl_3 + 3\ H_2O \rightarrow HP(O)(OH)_2 + 3\ HCl$$

Potassium phosphite is a convenient precursor to phosphorous acid:

$$K_2HPO_3 + 2\ HCl \rightarrow 2\ KCl + H_3PO_3$$

In practice aqueous potassium phosphite is treated with excess hydrochloric acid. By concentrating the solution and precipitations with alcohols, the pure acid can be separated from the salt.

Solubility	soluble in alcohol
Structure	
Molecular shape	tetrahedral
Hazards	
R-phrases	22-35
S-phrases	26-36/37/39-45
NFPA 704	
Related compounds	
Related compounds	H_3PO_4 (i.e., $PO(OH)_3$) H_3PO_2 (i.e., $H_2PO(OH)$)
Except where noted otherwise, data are given for materials in their standard state (at 25 °C, 100 kPa) Infobox references	

Acid-base properties

Phosphorous acid is a diprotic acid, since the hydrogen bonded directly to the central phosphorus atom is not readily ionizable. Chemistry examinations often test students' appreciation of the fact that all three hydrogen atoms are *not* acidic under aqueous conditions, in contrast with phosphoric acid. $HP(O)_2(OH)^-$ is a moderately strong acid.

$$HP(O)(OH)_2 \rightarrow HP(O)_2(OH)^- + H^+ \quad pK_a = 1.3^{[4]}$$
$$HP(O)_2(OH)^- \rightarrow HPO_3^{2-} + H^+ \quad pK_a = 6.7$$

The $HP(O)_2(OH)^-$ species is called the hydrogenphosphite ion, and the HPO_3^{2-} the phosphite ion.[5](Note that the IUPAC recommendations are dihydrogenphosphite and hydrogenphosphite respectively)

The IUPAC (mostly organic) name is **phosphonic acid**. This nomenclature is commonly reserved for substituted derivatives, that is, organic group bonded to phosphorus, not simply an ester. For example, $(CH_3)PO(OH)_2$ is "methylphosphonic acid", which may of course form "methylphosphonate" esters.

Both phosphorous acid and its deprotonated forms are good reducing agents, although not necessarily quick to react. They are oxidized to phosphoric acid or its salts. It reduces solutions of noble metal cations to the metals.

Uses

Conversion to phosphine

Phosphine PH_3, being a flammable and toxic gas, is inconvenient to store. Fortunately this useful species is readily prepared by thermal decomposition of phosphorous acid, at 205 - 210 °C:[5]

$$4\ HP(O)(OH)_2 \rightarrow PH_3 + 3\ H_3PO_4$$

In agriculture

A large quantity of phosphorous acid is used as phosphatic fertilizer. [6] Pure phosphorous acid is also used for preparing phosphite salts, such as monopotassium phosphite or aluminum phosphonite. These salts, as well as aqueous solutions of pure phosphorous acid, have shown effectiveness in controlling a variety of microbial plant diseases—in particular, treatment using either trunk injection or foliar containing phosphorous acid salts is indicated in response to infections by *phytophthora* and *pythium*-type plant pathogens (both within class *oomycetes*, known as water molds), such as dieback/root rot and downy mildew.[7] Anti-microbial products containing salts of phosphorous acid are marketed in Australia as 'Yates Anti-Rot'; and in the United States of America, for example, aluminum salts of phosphorous acid (known generically as 'Fosetyl-Al') are sold under the trade name 'Aliette'. Phosphorus acid and its salts, unlike phosphoric acid, are highly toxic and should be handled carefully. Only about 1 g of phosphorus acid are lethal to an adult human.[8][9]

As a chemical reagent

Phosphorous acid is used in chemical reactions as a reducing agent that is somewhat less vigorous than the related hypophosphorous acid.[10]

References

1. ^ NOMENCLATURE OF INORGANIC CHEMISTRY IUPAC Recommendations 2005 ed. N. G. Connelly et al. RSC Publishing http://www.chem.qmul.ac.uk/iupac/bioinorg/
2. ^ Chanjuan Xi , Yuzhou Liu, Chunbo Lai , Lishan Zhou (2004). "Synthesis of molybdenum complex with novel $P(OH)_3$ ligand based on the one-pot reaction of $Mo(CO)_6$ with $HP(O)(OEt)_2$ and water". *Inorganic Chemistry Communications* **7**: 1202. doi:10.1016/j.inoche.2004.09.012.
3. ^ M. N. Sokolov, E. V. Chubarova, K. A. Kovalenko, I. V. Mironov, A. V. Virovets1, E. V. Peresypkina,V. P. Fedin (2005). "Stabilization of tautomeric forms $P(OH)_3$ and $HP(OH)_2$ and their derivatives by coordination to palladium and nickel atoms in heterometallic clusters with the $Mo_3MQ_4^{4+}$ core (M = Ni, Pd; Q = S, Se)". *Russian Chemical Bulletin* **54**: 615. doi:10.1007/s11172-005-0296-1.
4. ^ CRC Handbook of Chemistry and Physics, 87th Ed. 8-42
5. ^ ***a b*** Josef Novosad, 1994, Encyclopedia of Inorganc Chemistry, John Wiley and Sons, ISBN 0471936200
6. ^ Allison E. McDonald; Bruce R. Grant; William C. Plaxton (2001). "Phosphite (Phosphorous acid): Its Relevance in the Environment and Agriculture and Influence on Plant Phosphate Starvation Respose". *Journal of Plant Nutrition* **24** (10): 1505–1519. doi:10.1081/PLN-100106017.
7. ^ Organic Labs. Product label for 'Exel LG,' Retrieved April 9, 2007. (http://organiclabs.com/images/logos /110_EXEL%20LG%20Back%20NEW.doc)
8. ^ Yates, a Division of Orica Australia Pty Ltd. “MSDS ('Yates Anti Rot Phosacid Systemic Fungicide').” Version 1. SH&E Shared Services, Orica. Homebush, NSW (Australia): April 4, 2005 (retrieved from www.orica.com April 9, 2007). (http://msds.orica.com/pdf/shess-en-cds-010-000000020540.pdf)
9. ^ US EPA. “Fosetyl-Al (Aliette): Reregistration Eligibility Decision (RED) Fact Sheet.” Office of Pesticide Programs, US EPA. Washington, DC (USA): 1994 *(retrieved from www.epa.gov April 9, 2007).*
10. ^ “Phosphorous acid.” The American Heritage Dictionary of the English Language, 4th ed. Boston: Houghton Mifflin, 2000 (retrieved from www.bartleby.com April 9, 2007). (http://www.bartleby.com/61/93/P0259300.html)

Other references

- Holleman, A. F.; Wiberg, E. “Inorganic Chemistry.” Academic Press: San Diego, 2001. ISBN 0-12-352651-5.
- D. E. C. Corbridge. “Phosphorus: An Outline of its Chemistry, Biochemistry, and Technology.” 5th ed. Elsevier: Amsterdam. ISBN 0-444-89307-5.