The manufacture and properties of phosphonic (phosphorous) acid

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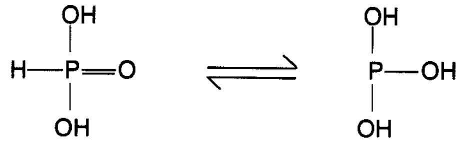
Abstract

Formulations containing salts of phosphonic acid are registered in Australia as systemic fungicides for the control of certain fungal diseases of plants. A brief summary of the chemistry, manufacture and properties of phosphonic acid is presented.

Introduction

Phosphonic acid (H_3PO_3) exists in aqueous solution in equilibrium with its tautomeric form which is known as phosphorous acid.



$$\mathrm{H{-}P({=}O)(OH)_2} \rightleftharpoons \mathrm{P(OH)_3}$$

phosphonic acid phosphorous acid

An aqueous solution of the acid has been shown to be effective for treatment of certain fungal diseases of plants, but the use of a partially neutralised solution is preferred in order to minimise phytotoxic effects. Formulations based on potassium neutralised acid have been registered in Australia by UIM Agrochemicals (Aust.) Pty Ltd.

The registered active ingredient is pure phosphorous acid flake manufactured by Albright & Wilson Ltd.

Phosphonic acid is also believed to be the effective agent in fungicides based on the aluminium salt of ethyl hydrogen phosphonate. It is postulated that the product is degraded in the plant to yield a mixture of phosponic acid, ethyl alcohol and aluminium salts.

Manufacture of phosphorous acid flake

Pure phosphorous acid is a white, crystalline, hygroscopic solid which is produced from phosphorus trichloride (PCl_3) by hydrolysis.

$$PCl_3 + 3H_2O \rightarrow H_3PO_3 + 3HCl$$

The hydrochloric acid is removed by stripping under reduced pressure and the resultant crystalline flake H_3PO_3 is of very high purity.

A technical grade of H_3PO_3 can be produced as a by-product of the manufacture of acid chlorides from carboxylic acids and phosphorous trichloride.

$$3RCOOH + PCl_3 \rightarrow 3RCOCl + H_3PO_3$$

where R represents a fatty alkyl group.

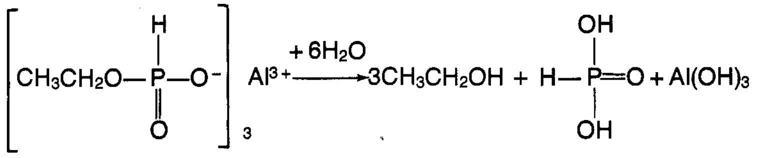
This material is, however, unsuitable for fungicidal formulations as it contains a high level of impurities. Table 1 compares typical specification data for the pure flake and technical grades.

Table 1 Specifications of pure flake and technical grade H_3PO_3

	Pure flake	Technical
Assay (% minimum)	98.5	69
Arsenic (ppm maximum)	Negligible	1
Heavy metals (ppm maximum)	Negligible	300
Iron (ppm maximum)	20	250
Chloride (ppm maximum)	20	100

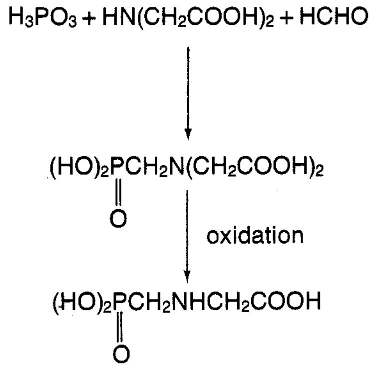
Non-fungicide uses of phosphonic acid

Phosphonic acid is mainly used as an intermediate in the manufacture of other chemicals. Of most interest to agriculturalists will be its use in the



$$\left[\mathrm{CH_3CH_2O{-}PH({=}O){-}O^-}\right]_3 \mathrm{Al^{3+}} \xrightarrow{+6H_2O} \mathrm{3CH_3CH_2OH + H{-}P({=}O)(OH)_2 + Al(OH)_3}$$

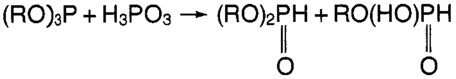
production of the post-emergence, non-selective herbicide, glyphosate, (N-phosphonomethyl glycine) from iminodiacetic acid.



$$\begin{array}{c} H_3PO_3 + HN(CH_2COOH)_2 + HCHO \\ \downarrow \\ (HO)_2\underset{\overset{\|}{O}}{P}CH_2N(CH_2COOH)_2 \\ \Big\downarrow \text{ oxidation} \\ (HO)_2\underset{\overset{\|}{O}}{P}CH_2NHCH_2COOH \end{array}$$

glyphosate

It is also used to convert trialkyl phosphites into dialkyl phosphites which are important intermediates in the manufacture of insecticides.



$$(RO)_3P + H_3PO_3 \rightarrow (RO)_2\underset{\overset{\|}{O}}{P}H + RO(HO)\underset{\overset{\|}{O}}{P}H$$

where R represents an alkyl group.

Hazards

Phosphonic (phosphorous) acid is a corrosive material, but is generally regarded as having low hazard potential. Tests on rabbits show that 10% solutions in water are non-corrosive to skin, but more concentrated solutions can lead to tissue damage.

Acute oral toxicity studies (rat) show that the pure flake grade of phosphorous acid, when tested as a 10% aqueous solution in order to avoid corrosivity effects, is regarded as only slightly toxic. To put this into perspective, in terms of the LD_{50}, it has similar low toxicity to phosphoric acid, which is a permitted food additive under the Food Chemicals Codex, and it is slightly less toxic than aspirin.

The formulated fungicide, being less concentrated and partially neutralised, is even less hazardous than the acid itself.

Environmental impact

In light of the current trend towards minimisation of the environmental impact of agricultural and other chemicals, there is much to recommend phosphonic acid. Not only does it have low toxicity, providing benefits for both the applicator and the end consumer of produce, but it is also readily degraded in the soil, through biological oxidation, to yield phosphates which provide valuable nutrients for plant growth. It is unlikely that there will ever be many fungicides which can match phosphonic acid and its salts in terms of safety and environmental acceptability.

Rapid, quantitative detection of phosphonate by simple ion-exchange chromatography using post-separation suppression

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Abstract

Previous methods of quantifying the phosphonate ion in plants were difficult, time consuming and costly. A cheaper ion chromatography separation method using conductivity detection of ions in solution after eluent suppression, proved simple, rapid and effective. The procedure was used to investigate control of *Plasmopara viticola* by Foli-R-Fos 200 (phosphonic acid). Limits of detecting phosphonate in leaves of *Vitis vinifera* were 0.5–1.0 ppm. Mean efficiency of recovery was 98.2% total phosphonate.

The short-term efficacy of phosphonic acid (H_3PO_3) for the pre-infection control of downy mildew (caused by *Plasmopara viticola* (Berk. & Curt.) Berl. & de Toni) of grapevine (*Vitis vinifera* L.) was being studied (Magarey *et al.* 1990). This investigation required determination of levels of phosphonate (HPO_3^{-2}), the anionic hydrolysis product of H_3PO_3 in grapevine leaves.

Previous methods of detecting phosphonate (e.g. Saindrenan *et al.* 1985) were costly and tedious, so a relatively cheap and simple, yet reproducible, method was required. Development of a procedure to quantify phosphonate residues following foliar sprays of phosphonic acid (as Foli-R-Fos 200, UIM Agrochemicals (Aust.) Pty Ltd) began in 1987.

A Dionex AutoIon System 12 ion chromatograph (Dionex Corp., Sunnyvale, CA), with conductivity detector linked to a chart recorder, was used with a model AMMS-1 anion micromembrane suppressor connected in-line with a HPIC-AG4A guard column and an Ionpac AS4A separator column.