Kirk-Othmer Encyclopedia of Chemical Technology.

FLUORINE COMPOUNDS, INORGANIC, PHOSPHORUS

The majority of the fluorine in the earth's crust is present in the form of the phosphorus fluoride fluoroapatite [1306-05-4], $Ca_5(PO_4)_3F$. Phosphate rock deposits contain an average concentration of 3.5 wt % fluorine. During phosphate processing these fluorine values are partially recovered as by-product fluorosilicic acid. The amount of fluorosilicic acid recovered has grown steadily, in part because of environmental requirements (see Phosphoric acid and the phosphates).

The compounds phosphorus trifluoride [7783-55-3], PF_3; phosphorus pentafluoride [7647-19-0], PF_5; phosphorus oxyfluoride [13478-20-1], POF_3; and phosphorus thiofluoride [2404-52-6], PSF_3, were prepared prior to 1900. The most widely studied of these are PF_5 and PF_3. Physical properties are given in Table 1. The mixed chlorofluorides PCl_xF_y where $x + y = 3$ and 5 have also been studied. Diphosphorus tetrafluoride [13537-32-1], P_2F_4, was first reported in 1966 (1–3).

1. Phosphorus Pentafluoride

Phosphorus pentafluoride was first prepared in 1876 through fluorination of phosphorus pentachloride using arsenic trifluoride (1). Other routes to PF_5 have included fluorination of PCl_5 by HF, AgF, benzoyl fluoride, SbF_3, PbF_2, or CaF_2 (10). It can also be made by the reaction of PF_3 and fluorine, chlorine (11), or chlorine in contact with calcium fluoride (12); by the reaction of FSO_3H on fluoride and phosphate-containing rocks (13); by the reaction of SF_6 and PF_3 at high ($\sim 400°C$) temperature (14); VF_5 and POF_3 (15), and Ca_3P_2 and NF_3 (16); by the reaction of alkali or alkaline-earth metal fluorides or fluorosulfonate fluorides with P_2O_5 or H_3PO_4 at 180–200°C (17); by the reaction of POF_3 and HF at 60–80°C (18); $HPF_6{\cdot}XH_2O$ and SO_3 or HSO_3F (19); by reaction of $POF_3{\cdot}SO_3$ adduct with HF (20); and by the reaction of carbonyl fluoride with POF_3 (21). From 1968–1973 a series of patents (22–25) reported the production of PF_5, PF_3, POF_3, and the hexa-, di-, and monofluorophosphoric acids by fluorination of phosphoric and phosphorus acids using calcium fluorosulfate fluoride, $CaFSO_3F$, produced by reaction of CaF_2 and SO_3 (22–25). Based on these patents a pilot plant was established to produce fluorine–phosphorus chemicals, but the activity was not commercially successful and was terminated in 1972.

Phosphorus pentafluoride is a colorless gas which fumes in contact with moist air and reacts immediately with water to hydrolyze, first to POF_3 and then to the fluorophosphoric acids. Although PF_5 is probably stable in completely dry glass, glass (qv) is not recommended for storage as even a trace of moisture generates HF which regenerates moisture converting the glass to SiF_4 and PF_5 to POF_3.

Phosphorus pentafluoride behaves as a Lewis acid showing electron-accepting properties. It forms complexes, generally in a ratio of 1:1 with Lewis bases, with amines, ethers, nitriles, sulfoxides, and other bases. These complexes are frequently less stable than the similar BF_3 complexes, probably owing to stearic factors. Because it is a strong acceptor, PF_5 is an excellent catalyst especially in ionic polymerizations. Phosphorus pentafluoride is also used as a source of phosphorus for ion implantation (qv) in semiconductors (qv) (26).

Table 1. Properties of Phosphorus Fluorides[a]

Property	PF_5	POF_3	PF_3	PSF_3
melting point, °C	−91.6	−39.1	−151.5	0.15
boiling point, °C	−84.8	−39.7	−101.8	−0.5
density, liquid, at bp, g/mL			1.6	
critical temperature, °C	>25	73.3	−2.05	−0.73
critical pressure, MPa[b]		4.23	4.33	
heat of fusion, kJ/mol[c]	12.1	14.9		
heat of vaporization, kJ/mol[c]	16.7	23.2[d]	16.5	
heat of formation, $-\Delta H_f$, kJ/mol[c]	1210[e]		946[f]	

[a] Refs. (4–6) unless otherwise noted.
[b] To convert MPa to atm, divide by 0.101.
[c] To convert kJ to kcal, divide by 4.184.
[d] Ref. 7.
[e] Ref. 8.
[f] Ref. 9.

2. Phosphorus Trifluoride

Phosphorus trifluoride was prepared by Moissan in 1884 by reaction of copper phosphide and lead fluoride [7783-55-3]. It is usually prepared by fluorination of PCl_3 with CaF_2 (11), AsF_3, SbF_3, AgF, PbF_2, ZnF_2, or NaF; reaction of fluorosulfonate, $CaF(FSO_3)$, using molten H_3PO_3 (27); by the reaction of phosphorus oxide and F_2 or NF_3 gas (28) or reaction of PH_3 and NF_3 (29); by the reaction of KHF_2 and PCl_3 or PBr_3 (30). PF_3 can be purified for semiconductor devices by contacting it with nickel silicide (31) or with Cu arsenide, phosphide, or silicide (32). Laboratory-scale syntheses have been published (33, 34) and PF_3 is commercially available.

Phosphorus trifluoride is an almost odorless gas that does not fume in air and reacts slowly with water but rapidly with base. It may be very toxic, and great care should be taken in handling it. It reacts with ferrohemoglobin to form an unstable complex (35). Because the action may be similar to carbon monoxide poisoning, oxygen may be helpful in treatment. Phosphorus trifluoride acts as a Lewis base and forms many complexes by donating the lone electron pair on the phosphorus atom. Complexes similar to those of CO (see Carbonyls) are $Ni(PF_3)_4$ [13859-65-9] (36), $Fe(PF_3)_5$ [13815-34-4] (37), $(PF_3)_2PtCl_2$ [15977-33-0] (38), $Mo(PF_3)_6$ [15339-46-5] (39), and $Cr(PF_3)_6$ [26117-61-3] (39). Although AsF_3 and SbF_3 have acceptor properties and function as Lewis acids, no evidence has been found for molecular complex formation by PF_3 as a Lewis acid nor for stable fluorophosphites ($PF^-{}_4$).

3. Phosphorus Oxyfluoride

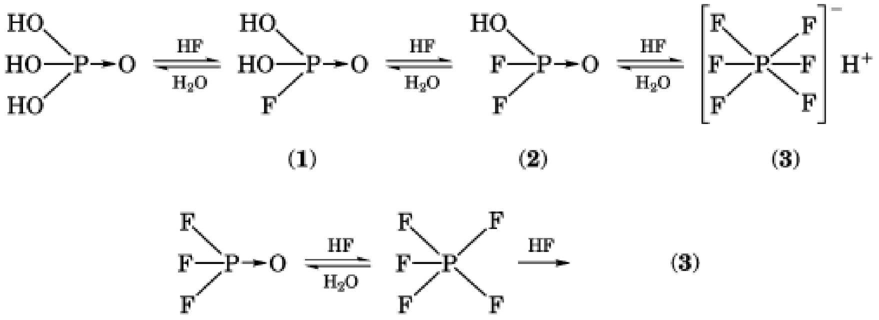
Phosphorus oxyfluoride is a colorless gas which is susceptible to hydrolysis. It can be formed by the reaction of PF_5 with water, and it can undergo further hydrolysis to form a mixture of fluorophosphoric acids. It reacts with HF to form PF_5. It can be prepared by fluorination of phosphorus oxytrichloride using HF, AsF_3, or SbF_3. It can also be prepared by the reaction of calcium phosphate and ammonium fluoride (40), by the oxidization of PF_3 with NO_2Cl (41) and NOCl (42); in the presence of ozone (43); by the thermal decomposition of strontium fluorophosphate hydrate (44); by thermal decomposition of $CaPO_3F{\cdot}2H_2O$ (45); and reaction of SiF_4 and P_2O_5 (46).

4. Phosphorus Thiofluoride

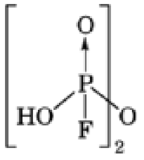
Phosphorus thiofluoride can be prepared at a low temperature by uv radiation of OCS and PF_3 (47); by the reaction of PF_5 and $(C_2H_5)_4NSH$ in acetonitrile (48); by the reaction of PF_3 and SF_6 at elevated temperature (49), or with H_2S (50); by the reaction of $PSCl_3$ and NaF (51); and by the high temperature reaction of PF_3 and S (52).

5. Fluorophosphoric Acids and the Fluorophosphates

The three primary fluorophosphoric acids, monofluorophosphoric acid [13537-32-1], H_2O_3PF **(1)**, difluorophosphoric acid [13779-41-4], HO_2PF_2 **(2)**, and hexafluorophosphoric acid [16940-811], HPF_6 **(3)**, were discovered in 1927 (53). In 1963 *sym*-difluorodiphosphoric acid [44801-72-1] **(4)** was reported (54). The three primary acids can be prepared by reaction of phosphoric acid or phosphoric anhydride (55) using varying amounts of HF or phosphorus oxyfluoride (23–26) and HF or water, or both. The reaction of anhydrous hydrogen fluoride and phosphoric anhydride is extremely violent. These acids are in equilibrium with each other, HF, and phosphoric acid. The interrelationships of the acids are



(1) **(2)** **(3)** **(3)**



(4)

All three fluorophosphoric acids are commercially available. The mono- and difluoro acids can be made as anhydrous or hydrated liquids. Commercial hexafluorophosphoric acid is an aqueous solution. Anhydrous hexafluorophosphoric acid may be prepared at reduced temperatures and pressures but it dissociates rapidly into PF_5 and HF at 25°C (56). When diluted with water all the fluorophosphoric acids hydrolyze producing orthophosphoric acid. The hexafluoro acid is the most stable of the three fluorophosphoric acids.

A number of salts of the monofluoro- and hexafluorophosphoric acids are known and some are commercially important. The salts of difluorophosphoric acid are typically less stable toward hydrolysis and are less well characterized. Sodium monofluorophosphate [7631-97-2], the most widely used dentifrice additive for the reduction of tooth decay, is best known (see Dentifrices). Several hexafluorophosphates can be prepared by neutralization of the appropriate base using hexafluorophosphoric acid. The monofluorophosphates are usually prepared by other methods (57) because neutralization of the acid usually results in extensive hydrolysis.

Because HF is present in the aqueous acids and can be generated by hydrolysis of the anhydrous acids, glass should be avoided in handling or processing. Teflon or other plastics can generally be used for laboratory work although there is evidence for migration of the acids through both thin plastic and plastic bottle closures. The acids are generally shipped and stored in United Nations (UN) 6HA1 heavy plastic drums with steel overpacks. Aluminum is also satisfactory for storage and use of concentrated solutions of the difluoro acid and hexafluoro acid.

Experimentation with test animals and laboratory and plant experience indicate that the fluorophosphoric acids are less toxic and dangerous than hydrogen fluoride (58). However, they contain, or can hydrolyze to, hydrofluoric acid and must be treated with the same care as hydrofluoric acid. Rubber gloves and face shields are essential for all work with these acids, and full rubber dress is necessary for handling larger quantities. The fumes from these acids contain HF.

5.1. Monofluorophosphoric Acid

Monofluorophosphoric acid **(1)** is a colorless, nonvolatile, viscous liquid having practically no odor. On cooling it does not crystallize but sets to a rigid glass at −78°C. It has a density of d_{25} = 1.818 g/mL. Little decomposition occurs up to 185°C under vacuum but it cannot be distilled. An aqueous solution shows the normal behavior of a dibasic acid; the first neutralization point in 0.05 *N* solution is at pH 3.5 and the second at pH 8.5. Conductance measurements, however, indicate H_2PO_3F behaves as a monobasic acid in aqueous solution (59). The permanent end point shows the stability of PO_3F^{2-} ions at this pH. Slow hydrolysis occurs at low pH to give orthophosphoric and hydrofluoric acids. These kinetics have been studied (60, 61). Equilibrium concentrations of H_2PO_3F at varying acid strengths have been determined by nmr studies (62). The anhydrous acid causes rapid swelling of cellulose, and acts as a polymerization catalyst. It has no oxidizing character.

Monofluorophosphoric acid is one of the hydrolysis products of POF_3. It is the primary product of reaction between theoretical amounts of phosphoric anhydride and aqueous hydrogen fluoride. However, the product of this reaction usually contains up to 20% each of orthophosphoric and difluorophosphoric acids. Reaction of P_2O_5 and 40% aqueous hydrogen fluoride gives more complete conversion to monofluorophosphoric acid. Although difluorophosphoric acid is formed initially, it hydrolyzes to give an aqueous solution of primarily monofluorophosphoric acid, some orthophosphoric acid, and HF.

5.2. Difluorophosphoric Acid

Difluorophosphoric acid **(2)** is a mobile, colorless liquid. It fumes on contact with air, probably owing to HF aerosol formation. The mp of anhydrous difluorophosphoric acid has been reported to be -96.5 ± 1°C (63) and -91.3 ± 1°C (64). The density at 25°C is 1.583 g/mL. It partially decomposes on heating above 80–100°C. An extrapolated normal boiling point is 116°C (63) although it boils at 107–111°C (64, 65) with decomposition. Vapor pressure data are available (65, 66), however, the data above ca 80°C may be unreliable.

A freshly made solution behaves as a strong monobasic acid. Neutralized solutions slowly become acidic because of hydrolysis to monofluorophosphoric acid and hydrofluoric acid. The anhydrous acid undergoes slow decomposition on distillation at atmospheric pressure, reacts with alcohols to give monofluorophosphoric acid esters, and is an alkylation (qv) and a polymerization catalyst.

The commercially available difluorophosphoric acid has a formula approximating 2 $HPO_2F_2 \cdot H_2O$ and contains some monofluorophosphoric acid **(1)** and some hexafluorophosphoric acid **(3)** as well as HF. It is primarily used in catalytic applications.

5.3. Hexafluorophosphoric Acid

Hexafluorophosphoric acid **(3)** is present under ambient conditions only as an aqueous solution because the anhydrous acid dissociates rapidly to HF and PF at 25°C (56). The commercially available HPF_6 is approximately 60% HPF_6 based on PF_5^- analysis with HF, HPO_2F_2, HPO_3F, and H_3PO_4 in equilibrium equivalent to about 11% additional HPF_6. The acid is a colorless liquid which fumes considerably owing to formation of an HF aerosol. Frequently, the commercially available acid has a dark honey color which is thought to be reduced phosphate species. This color can be removed by oxidation with a small amount of nitric acid. When the hexafluorophosphoric acid is diluted, it slowly hydrolyzes to the other fluorophosphoric acids and finally phosphoric acid. In concentrated solutions, the hexafluorophosphoric acid establishes equilibrium with its hydrolysis products in relatively low concentration. Hexafluorophosphoric acid hexahydrate [40209-76-5], $HPF_6 \cdot 6H_2O$, mp ca 31.5°C, also forms (66). This compound has been isolated in good yield when a concentrated acid solution is cooled rapidly to prevent renewed equilibration. The hexahydrate forms hard, coarse crystals having a cubic structure (67) which are very hygroscopic. However, upon melting, an equilibrium is again established. Liquid $HPF_6 \cdot (C_2H_5)_2O$ [4590-57-2], boiling at 114°C and melting at −35°C, has been reported (68). Hexafluorophosphoric acid is used catalytically, as a fluorinating reagent, as a fungicide, and extensively in preparation of numerous hexafluorophosphates (see Fungicides, agricultural).

The PF_6 ion can be determined by precipitation with nitron or tetraphenyl-arsonium chloride (69).

5.4. Monofluorophosphates

Monofluorophosphates are probably the best characterized series of fluoroxy salts. The PO_3F^{2-} ion is stable in neutral or slightly alkaline solution. The alkali metal and ammonium monofluorophosphates are soluble in water but the alkaline-earth salts are only slightly soluble, eg, $CaPO_3F$ is not water-soluble and precipitates as the dihydrate.

Monofluorophosphates of ammonium, lithium, sodium, potassium, silver, calcium, strontium, barium, mercury, lead, and benzidine have been described (70) as have the nickel, cobalt, and zinc salts (71), and the cadmium, manganese, chromium, and iron monofluorophosphates (72). Many of the monofluorophosphates are similar to the corresponding sulfates (73).

The monofluorophosphates can be prepared by neutralization of monofluorophosphoric acid **(1)**. Sodium monofluorophosphate [7631-97-2] is prepared commercially (57) by fusion of sodium fluoride and sodium metaphosphate, and the potassium monofluorophosphate [14104-28-0] can be prepared similarly. Insoluble monofluorophosphates can be readily prepared from reaction of nitrate or chloride solutions with sodium monofluorophosphate. Some salts are prepared by metathetical reactions between silver monofluorophosphate [66904-72-1] and metal chlorides.

Molten alkali metal monofluorophosphates are reactive and corrosive, hydrolyzing to generate HF and reacting with many metals and ceramics. They readily dissolve metal oxides and are effective metal surface cleaners and fluxes (see Metal surface treatments). They also have bactericidal and fungicidal properties (74). However, the main commercial application among monofluorophosphates is of sodium monofluorophosphate in dentifrices.

Sodium monofluorophosphate, mp 625°C, is soluble in water to the extent of 42 g/100 g solution. The pH of a 2% solution is between 6.5 and 8.0. Dilute solutions are stable indefinitely in the absence of acid or cations that form insoluble fluorides.

Sodium monofluorophosphate is used in most dentifrices at a concentration of 0.76 wt % which produces the desired fluoride level of 1000 ppm although one extra strength dentifrice has 1.14 wt % and 1500 ppm F. Although the mechanism of its efficacy in reducing dental decay is not completely understood (75), it almost certainly reacts with the apatite of the tooth converting it to fluoroapatite which is less soluble in mouth acids (see Dentifrices).

The *United States Pharmacopeia* (76) specifications for sodium monofluorophosphate require a minimum of 12.1% fluoride as PO_3F^{2-} (theoretical 13.2%) and a maximum of 1.2% fluoride ion reflecting unreacted sodium fluoride. Analysis for PO_3F^{2-} is by difference between total fluoride in the product less fluoride ion as determined by a specific ion electrode. The oral LD_{50} of sodium monofluorophosphate in rats is 888 mg/kg.

Sodium monofluorophosphate decahydrate [7727-73-3], $Na_2PO_3F{\cdot}10H_2O$, melts at 9°C. Commercial sodium monofluorophosphate can be purified using this salt. The commercial salt is dissolved in about 10% more than the theoretical water and filtered. The filtrate is cooled to 0°C and allowed to stand. If crystals do not form, the solution may be seeded with $Na_2PO_3F{\cdot}10H_2O$ or $Na_2SO_4{\cdot}10H_2O$. The resulting crystals are filtered cold and washed with small quantities of ice water. Attempts to remove the water of hydration by heating lead to hydrolysis of the sodium monofluorophosphate. The water can be extracted by multiple extractions with ethyl alcohol (77).

Calcium, strontium, and barium monofluorophosphates can be precipitated from aqueous solutions using sodium monofluorophosphate. The salts obtained are $CaPO_3F{\cdot}2H_2O$ [37809-19-1], $SrPO_3F{\cdot}H_2O$ [72152-36-4], and $BaPO_3F{\cdot}xH_2O$ [58882-62-5] where $x < 1$. The solubility of $CaPO_3F{\cdot}2H_2O$ is 0.417 g/100 mL solution at 27°C (78). It can be partially dehydrated to the hemihydrate [72152-38-6] but further attempts cause hydrolysis to CaF_2 and phosphate. Heating $SrPO_3F{\cdot}H_2O$ to 450°C gives anhydrous $SrPO_3F$ [66546-46-1] but $BaPO_3F{\cdot}xH_2O$ retains water even at 500°C (79).

5.5. Difluorophosphates

Difluorophosphates have limited applications largely because of hydrolytic instability of the $PO_3F^{-}{}_2$ ion. The ammonium salt can be prepared from ammonium fluoride and phosphoric anhydride.

$$3\ NH_4F + P_2O_5 \longrightarrow NH_4PO_2F_2 + (NH_4)_2\ PO_3F$$

The $NH_4PO_2F_2$ can be extracted from the solid reaction product with boiling methanol (80). Alkali metal difluorophosphates are prepared from the hexafluorophosphates by one of the following fusion reactions (81):

$$KPF_6 + 2\ KPO_3 \longrightarrow 3\ KPO_2F_2$$

$$3\ KPF_6 + 2\ B_2O_3 \longrightarrow 3\ KPO_2F_2 + 4\ BF_3$$

Even though the $PO_2F^{-}{}_2$ is considered to be hydrolytically unstable, hydrolysis is slow in a neutral solution. However, in a solution initially 0.1 *N* in NaOH, at 70°C, $NaPO_2F_2$ is quantitatively hydrolyzed to give the PO_3F^{2-} and F^- ions within 10 min (82).

A number of organic nitrogen-containing basic compounds give insoluble difluorophosphates. Among these is nitron which can be used for the gravimetric determination of $PO_2F^{-}{}_2$ (83). Potassium and other metal difluorophosphates have been reported as stabilizing agents in chloroethylene polymers (84).

5.6. Hexafluorophosphates

There is a great deal of interest in the hexafluorophosphate anion [1691-18-8], mostly as organic hexafluorophosphates for catalysis in photopolymerization. A number of the compounds are diazonium compounds (see Photoreactive polymers).

The hexafluorophosphates are among the most stable halogen complexes known. The highly symmetrical $PF^{-}{}_6$ ion is stable to boiling aqueous alkali and is decomposed only slowly in acidic solutions at ambient temperatures. It does hydrolyze rapidly at elevated temperatures in acid (85). The stability of the $PF^{-}{}_{6}$ ion can be compared to the isoelectronic SF_6. The hexafluorophosphates can be decomposed yielding PF_5 although in many cases only at temperatures where the PF_5 reacts with the metal containers. Benzenediazonium hexafluorophosphate can be decomposed to PF_5, N_2, and fluorobenzene at 120°C (86) and is a convenient source for laboratory amounts of PF_5 as well as a frequently used catalyst.

Many of the organic and inorganic hexafluorophosphates can be prepared by reaction of hexafluorophosphoric acid and the appropriate base. Another method involves reaction of the appropriate chloride and PCl_5 with anhydrous HF (87).

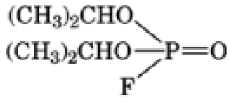
Potassium hexafluorophosphate [17084-13-8], KPF_6 and ammonium hexafluorophosphate [16941-11-0], NH_4PF_6, are the most readily available PF_6 salts. The KPF_6 salt melts with slow decomposition to PF_5 and KF at ca 565°C. The density of KPF_6 is 2.55 g/mL, and its solubility in water is 3.56 g/100 g solution at 0°C, 8.35 g/100 g solution at 25°C and 38.3 g/100 g solution at 100°C (88). A solution of KPF_6 is neutral and stable against hydrolysis unless the pH is reduced to about 3. The salt has a minimum intraperitoneal lethal dose of 1120 mg/kg for female albino mice (89). Potassium hexafluorophosphate is a soluble neutral salt which can be used in syntheses of other $PF^{-}{}_{6}$ salts as a substitute for HPF_6 **(3)**. Ammonium hexafluorophosphate has a water solubility of 60.4 g/100 g solution at 25°C (90).

Anhydrous silver hexafluorophosphate [26042-63-7], $AgPF_6$, as well as other silver fluorosalts, is unusual in that it is soluble in benzene, toluene, and *m*-xylene and forms 1:2 molecular crystalline complexes with these solvents (91). Olefins form complexes with $AgPF_6$ and this characteristic has been used in the separation of olefins from paraffins (92). $AgPF_6$ also is used as a catalyst. Lithium hexafluorophosphate [21324-40-3], $LiPF_6$, as well as KPF_6 and other $PF^{-}{}_{6}$ salts, is used as electrolytes in lithium anode batteries (qv).

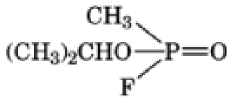
Substituted ammonium hexafluorophosphates are of decreasing water solubility corresponding to the greater number of hydrogens on the ammonium group replaced by the organic radicals. Unusual thermal stability is found in the quaternary compounds when the R groups are the low alkyl radicals. For example, tetramethylammonium hexafluorophosphate [558-32-7], $(CH_3)_4NPF_6$, is stable up to about 400°C.

6. Fluorophosphate Esters

The esters of monofluorophosphoric acid are of great interest because of their cholinesterase inhibiting activity which causes them to be highly toxic nerve gases and also gives them medical activity (see Enzyme inhibitors). The most studied is the bis(1-methylethyl)ester of phosphorofluoridic acid also known as diisopropyl phosphorofluoridate [155-91-4], DFP (**5**), and as the ophthalmic ointment or solution Isoflurophate USP. It is used as a parasympathomimetic agent, and as a miotic in glaucoma and convergent strabismus. Developed during World War II as a nerve gas, (93) it is prepared by reaction of PCl_3 and isopropanol, followed by chlorination and conversion to the desired product using NaF (94).



(**5**)



(**6**)

In the nerve gas known as Sarin [107-44-8] or GB**(6)**, one of the isopropoxy groups of DFP is replaced by a methyl group. Sarin is more toxic than DFP; oral LD_{50} in rats are 550 μg/kg and 6 mg/kg (95), respectively (see Chemicals in war).

The esters of monochloro- and dichlorophosphoric acids having polyfluoroalkyl groups Rf, eg, $Rf = (CF_3)_2CH_3C$—, $CF_3(CH_3)_2C$—, CF_3CH_2—, $CH_2(CF_2CH_2\!\!\rightharpoondown_{n}$, $n = 2, 4$, have been synthesized by the reaction of PCl_3 and the lithium salt of the respective polyfluoroalkyl alcohols followed by oxidation with N_2O_4 (96, 97). Toxicity data of these compounds are not available. The esters have been hydrolyzed to acid phosphates. These acids have potential as fuel cell electrolytes (see Fuel cells).

$$RfOLi + PCl_3 \longrightarrow RfOPCl_2 + LiCl$$

$$2\ RfOPCl_2 + N_2O_4 \longrightarrow 2\ RfOP\,(O)\,Cl_2 + 2\ NO$$

$$RfP\,(O)\,Cl_2 \xrightarrow[2\ HCl]{H_2O} RfOP\,(O)\,OH_2$$

The perfluoroalkylphosphorus(V) acids and bis(perfluoroalkyl)phosphorus(V) acids, $RfPO(OH)_2$ and $(Rf)_2P(O)(OH)$, where $Rf = CF_3$, C_2F_5, C_3F_7, and C_4F_9 have also been reported (98).

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