HALIDES AND NITROGEN DERIVATIVES OF PHOSPHORUS

1+ 2+ 3+ 5+

References

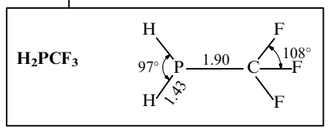
HPF$_2$, g., colrl., m.p. −124, b.p. −65, μ = 1.32, mol.: pyramid, P—H 1.41, P—F 1.58, ∠FPF 99, ∠HPF 96; $+H_2O \longrightarrow H_2 + HPOF_2 + HF + H_3PO_2$

H$_2$PF$_3$, m.p. −47, b.p. +1, dec. 20°

HF

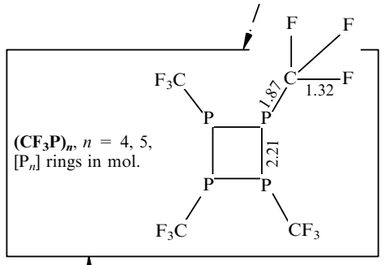
H_3PO_2

H$_2$PCF$_3$



t

(CF$_3$P)$_n$, *n* = 4, 5, [P$_n$] rings in mol.



Hg (−Hg$_2$I$_2$)

P

P_2O_3

I_2 (P)

HI (−PH_4I); I_2(−CS_2)

Hal_2; HHal(BrF)

Hal_2

H_2 (discharge)

Hg

HF

	m.p.	b.p.	μ
P$_2$F$_4$, g., colrl., unstab.	−86	−6	—
P$_2$Cl$_4$, liq., colrl.	−28	180	—
P$_2$I$_4$, cr., orange	126	dec.	0.45

mol. − $Hal_2P—PHal_2$, P—P 2.2–2.3, P—Hal 1.59 (F), 2.48 (I), ∠HalPHal 99 (F), 102 (I), ∠HalPP 94 [18]

[P$_2$I$_5$]$^+$[AlI$_4$]$^-$, cation − $[I_3P—PI_2]^+$, P—P 2.22, P—I 2.41 [24]

P(NCS)$_3$, liq.

NH$_3$ liq. (ex.)

P$_2$(NH)$_3$, imide

t (−H_2)

t

HPOF$_2$, mol.: distort. tetrahedron, P—H 1.39, P—F 1.54, P—O 1.44, ∠HPO = ∠FPO 117, ∠HPF = ∠FPF 101

HPF$_4$, m.p. −89, b.p. −36, unstab., mol.: trig. bipyr., P—F 1.55 (equ.), 1.59 (ax.), P—H 1.36, ∠HPF 90 (ax.), 124 (equ.) **[R$_4$N]$^+$[HPF$_5$]$^-$** [24]

H_3PO_3

HF

PN

$[NH_4]H_2PO_4$ (927°)

	m.p.	b.p.	Δ*H*	μ	P—Hal (g.)	∠HalPHal
PF$_3$, g., colrl., toxic	−151	−101	−959	1.03	1.55	97
PF$_2$Cl, g., colrl., toxic	−165	−47	—	—	1.57; 2.03	—
PF$_2$Br, g., colrl., toxic	−134	−16	—	—	—	—
PF$_2$I, g., colrl., toxic	—	—	—	—	—	—
PFCl$_2$, g., colrl., toxic	−144	+14	—	—	1.55 (F) 2.02 (Cl)	—
PFBr$_2$, g., colrl., toxic	−115	78	—	—	—	—
PCl$_3$, liq., colrl.	−90	75	−314	0.78	2.04	100
PBr$_3$, liq., colrl.	−40	173	−175	0.52	2.23	101
PI$_3$, cr., red [25]	+61	dec.	−46	0.34	2.46	102

hyg. substs., sol. in CS_2, CCl_4, eth., bz.; + $H_2O \longrightarrow H_3PO_3 + HHal$; mol. [:$PHal_3$] − ψ-tetrahedron, donor of 2 el., forms dative bond P:←M (by $d\pi$-orbitals of P), stabilises M^0

[Cr(PF$_3$)$_6$]; KRe(PF$_3$)$_5$; [Pt(PF$_3$)$_4$]; [Ni(PCl$_3$)$_4$]

PCl$_3$ · *n* L, L = Br_2 (*n* = 2, 9); NH_3 (*n* = 5); Me_3N

PI$_2$CF$_3$

P≡N, cr., yel.-brn.; 800° → $P_4 + N_2$; insol. in ac., alk.; PN mol. exists in g., P—N 1.49, μ = 2.75

P$_4$N$_6$, cr., colrl., insol. in ac., alk., infl. in air

> 700° (−N_2)

700° (−N_2)

Cl_2; Br_2 (vigorously)

P_2O_3

SO_2Cl_2; O_2(Pt, *t*)

P

BrF_3

Hal_2

t (−Hal_2)

Hal = Cl (100°); Br (35°)

PO(NCS)$_3$, liq.

Oxohalides [7]	m.p.	b.p.	Δ*H*	μ	P−Hal
POF$_3$, g., colrl.	−39 (*p*)	−40 (subl.)	−1218	1.77	1.52
POF$_2$Cl, g., colrl.	—	—	—	—	—
POFCl$_2$, g., colrl.	—	—	—	—	—
POCl$_3$ liq., colrl.	+1	107	−602	2.40	1.99
POCl$_2$Br, liq., colrl.	—	79	—	—	—
POBr$_3$, cr., colrl.	56	192	−460	—	2.17
POI$_3$, cr., viol.	50	—	—	—	—

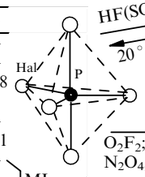
$POHal_3$, hyg., sol. in org. solv.; $+H_2O \longrightarrow H_3PO_4 + HHal$; $POBr_3$ and POI_3 dec. in light; $POCl_3$ (ε = 14) − $MHal_n$ solv., mol.: distort. tetrahedron (sp^3), P=O 1.45, ∠HalPHal ~ 103, ∠OPHal 114

P_2O_5

	m.p	b.p.	Δ*H*	μ
PF$_5$, g., colrl.	−94	−85	−1594	—
PF$_4$Cl, g., colrl.	−132	−43	—	—
PF$_3$Cl$_2$, g., colrl.	−125	+7	—	0.68
PF$_2$Cl$_3$, g., colrl.	—	—	—	0
PF$_3$Br$_2$, liq.	−20	dec. 15	—	—
PCl$_4$F, liq., colrl.	−63	67	—	0.21
PCl$_5$, cr., colrl.	160, subl.	159 (*p*)	−433 [13]	—
PBr$_5$, cr., orange	106 with dec.	—	−231	—
PI$_5$, cr., blk.	40 [27]	—	—	—

$PHal_5$ − v. hyg. subst., sol. in CCl_4, CS_2, bz.; mol. PF_5, PF_nCl_{5-n}, PCl_5 (.): trig. bipyr. (sp^3d), P—Hal (equ.) 1.54 (F), 2.02 (Cl), P—Hal (ax.) 1.58 (F), 2.14 (Cl). $[PCl_4]^+[PCl_6]^-$, $[PBr_4]^+Br^-$ form CsCl type structs.

PCl$_5$ · *n* L, L = NH_3, N_2O_4, $SeCl_4$, $MoCl_4$



HF(liq.); 20° (slowly)

O_2F_2; NOCl; N_2O_4; XeF_6

MI

[PF$_4$]$^+$[Sb$_3$F$_{16}$]$^-$ [9]

[PCl$_4$]$^+$X$^-$, X = F, $[PCl_6]$, $[PF_6]$, $[BCl_4]$, $[ICl_2]$

P$_2$Cl$_9$Br = $[PCl_4]_3^+[PCl_3Br]^+Br_2^-[PCl_6]_2^-$ [8]

[PBr$_4$]$^+$X$^-$, X = F−Br, $[Cl_3]$, $[Br_3]$ (= PBr_7), $[PF_6]$, cations: tetrahedra (sp^3), P—Hal 1.98 (Cl), 2.15 (Br)

[PI$_4$]$^+$[AlI$_4$]$^-$, cation: distort. tetrahedron, P—I ≈ 2.4 [24]

I_2 + AlI_3 (CS_2)

PI_3

PO(NH$_2$)$_3$, cr., colrl., slowly hydrol., mol.: distort. tetrahedron, P—O 1.51, P—N 1.66; **PO(N$_2$H$_3$)$_3$**

[PO(NH$_2$)(NH)]$_4$, oxoamidoimide

↓ *t* (−NH_3)

(PON)$_n$, oxonitride, powder, wh., amorph. or cr., insol., nonvolatile, 1000°(vac.) → P_2O_5 + PN; + $NH_3 \longrightarrow$ **P$_4$ON$_6$** [26]

NH_3 (liq.)

N≡P(NH$_2$)$_2$, amidonitride, m.p. 162; **[N≡PX$_2$]$_n$,** X = NCS (*n* = 3, 4), CF_3; **N≡P(N$_3$)$_2$** = PN_7, azidonitride

N≡P=NH, imidonitride (phospham), powder, wh., insol. in ac., alk.

125°, vac. (−NH_3)

↓ 400°, vac. (−NH_3)

P$_3$N$_5$, nitride

$LiNH_2$

Li[PN$_2$], cr., colrl., stab. up to 1000°, insol. in ac., alk.

Mg$_2$[PN$_3$], anion: of tetrahedra chains, P—N 1.76, Mg—N 2.09 [28]

(NPX$_2$)$_n$, X = F, Cl, Br, SCN, NH_2, R, *n* > 3, **phophonitrile halides, thiocyanates, amides, -alkyls,** etc. (**phosphazenes**)

(NPCl$_2$)$_n$, cr., colrl., nonwettable with water, stab. to ac., alk., sol. in eth., μ = 0.5

n	m.p.	b.p.
3	114	256
4	123	328
5	41	224
6	90	262
7	−18	—
∞	—	> 250

at *n* = 3 − planar rings, P—Hal 1.52 (F), 1.98 (Cl); at *n* = 4 nonplanar rings

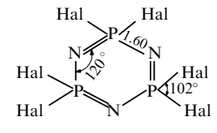
↓ 250° (polymerization)

transparent rubber-like mass (linear polymers)

↓ 350° (depolymerization)

oligomers

(NPCl$_2$)$_n$ · *m* L, L = SO_3 (*m* = 3); $HClO_4$ (*m* = 1, 2)



In mol.: 3 conjugated double bonds (nonaromatic system)

	m.p.	b.p.		m.p.
(NPF$_2$)$_3$	28	52	**(NPBr$_2$)$_3$**	192
(NPF$_2$)$_4$	30	120	**(NPBr$_2$)$_4$**	202

N$_4$P$_4$F$_n$Cl$_{8-n}$, m.p. 63 (*n* = 1), −5 (*n* = 7), b.p. 301 (*n* = 1), 117 (*n* = 7)

PCl$_5$

NH_4Cl (*t*, *p*) (−HCl)

(PO$_2$F)$_n$, cr., colrl.
PO$_2$Cl, oil, colrl.
(PO$_2$CF$_3$)$_n$

	m.p.	b.p.
(POF$_2$)$_2$O, liq.	0	72
(POCl$_2$)$_2$O, liq.	−16	65

4+
(PF$_3$)$_2$O
g., colrl., b.p. −18;
20° → PF_3 + **(POF$_x$)**

H_2O (0°)

LiI

MI

P_2O_5

NH_4F; HF (40%)

H$_2$[PO$_3$F], liq., colrl., *d* = 1.8, $K_1 \approx K_2 \approx 10^{-5}$; $+H_2O \rightarrow HF + H_3PO_4$
M$_2$[PO$_3$F], M = M^1, NH_4, Ca/2, stab. to H_2O, anion: distort. tetrahedron, P—O 1.51, P—F 1.59 [6]

HSO_3F

KH_2PO_4

H[PO$_2$F$_2$], liq., colrl., *d* = 1.6, strong ac.; $+H_2O \longrightarrow HF + H_3PO_4$ [30]
M[PO$_2$F$_2$], anion: distort. tetrahedron, P—O 1.47, P—F 1.58, ∠OPO 122, ∠FPF 97
H[PO$_2$Cl$_2$], liq., colrl., m.p. −28, stab. at 20°; $+H_2O \longrightarrow HCl + H_3PO_4$
M[PO$_2$Cl$_2$]
M[PO$_2$Br$_2$]

PF$_2$(O)OOCF$_3$ [14]

MPO$_3$

BF_3

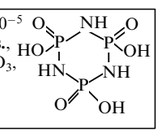
HPF$_6$, oil, colrl., · **6 H$_2$O**, m.p. 32, strong ac., **M$^+$[PF$_6$]$^-$**, M = Na(·H_2O), K−Cs, Tl, Ag (sol. as $MClO_4$), $[O_2]$, $[NO]$, $[NO_2]$, $[PCl_4]$, $[PBr_4]$, $[Ir(O_2)(PR_3)_4]$, $[Xe_2F_{11}]$
[ECl$_4$]$^+$[PCl$_6$]$^-$, E = P, As, anions: octahedron (sp^3d^2), P—Hal 1.59 (equ.), 1.73 (ax.) (F), 2.07 (Cl), $[PF_6]^-$ stab. at pH > 7

PI_3

I_2 + AlI_3 (CS_2)

H$_2$[PO$_3$(NH$_2$)], cr., colrl., $K_1 = 10^{-3}$, $K_2 = 10^{-8}$, 100° → NH_4PO_3
Ag$_2$[PO$_3$(NH$_2$)]↓
Na$_2$[PO$_3$(NH$_2$)] 210°, −H_2O → **Na$_4$[(PO$_3$)$_2$NH]** 450°, −H_2O → **Na$_6$[(PO$_3$)$_3$N]**
amidophosphate — imidodiphosphate — nitridotriphosphate

H[PO$_2$(NH$_2$)$_2$], cr., colrl., pentabasic. a., $K_1 = 10^{-5}$
H$_n$[— PO$_2$(NH)]$_n$, *n* = 3−6, **metaphosphimic acs.**, cr., colrl., sol. in H_2O, slowly hydrol. → NH_4PO_3, mol.: rings, most stab. at *n* = 4



M$_n$[− PO$_2$(NH)]$_n$ M (liq. NH_3) → **M$_2n$[PO$_2$N]$_n$**

M[P(N$_3$)$_6$], azidophosphates, M = [R_4N], Cs

[P$_2$I$_5$]$^+$[AlI$_4$]$^-$, cation − $[I_3P—PI_2]^+$, P—P 2.22, P—I 2.41 [24]

P(NCS)$_3$, liq.