SULFUR DERIVATIVES OF PHOSPHORUS [29)]

References

Polysulfides
$(PS)_n$; $(P_2S_{11})_n$; $(P_2S_{14})_n$, yel. subst, insol. in H_2O and org. solvents, sol. in alk., dec. 200

$SCl_2 + S_2Cl_2$

P_{red} — $S(t)$

Sulfides [17)]
cr., yel., volatile, sol. in CS_2, bz., naphthalene (melt), infl. in air (t), hyg. (except P_4S_3)

P_4S_2	P_4S_3	P_4S_4 $(PS)_n$	P_4S_5	P_4S_n $n = 5.5-6.7$	P_4S_7	P_4S_9	P_4S_{10} (2 forms)
m.p. 46	174	—	162 with dec.	232 with dec.	308	250 with dec.	288
b.p. —	408 most stab.	—	—	—	523	—	514

$[P_4]$ tetrahedron in all P_4S_n mol., P—P 2.2, S (br.) at tetrahedron edges, at $n > 6$ S – termnl., P—S 2.1 (br.), 1.9 (termnl.); P_4S_6 and P_4S_{10} – struct. analogues of P_4O_6 and P_4O_{10}

P_4Se_3, cr., orange, m.p. 247 [33)]

Thiohalides [20)]

	m.p.	b.p.	μ
5+			
PSF_3, g., colrl., infl.	−149	−52	0.63
$PSCl_3$, liq.	−36	125	1.41
$PSBr_3$, cr.	37	206	—
PSFClBr	—	98	—
PSI_3, cr.	47	—	—

$[P_4]$ tetrahedron in tetrameric mols., P—P 2.20, P—S 1.86–2.19, P—Hal 2.19 (Br), 2.48 (I), $PSHal_3$ monomers in g. are distort. tetrahedra
$P_4S_3I_2$, cr., orange, m.p. 121, S-br. of 3 ats. along edges, 2 at. I termnl.
$PS(NCS)_3$, liq.

$PS(NH_2)_3$, cr., colrl., slowly hydrol.

$(SPN)_n$

Thiophosphates [23)]

3+	4+		5+
$M_3[PS_3]$ **$M_4[P_4S_8]$**, stab. to hydrol., $[P_4]$ square in anion	**$[R_4N]_2[H_2P_2S_6]$** **$M^{II}_2[P_2S_6]$**, M = Cd, Hg, Sn, Fe, anion: 2 crossing tetrahedra	**$Zn_4[P_2S_6]_3 = Zn_4[P^{IV}_2S_6] \cdot [P^{V}_2S_6]_2$**	**$H_3[PS_4]$** **$M_3[PS_4]$**, $+H_2O \longrightarrow H_2S + M_3[PS_nO_{4-n}]$, $n = 0-3$, anion: tetrahedron **$Ag_7[PS_6]$** **$Ag_4[P_2S_7]$**, anion: isostruct. to $[P_2O_7]^{4-}$

In all anions P—S 1.99–2.12, P—P 2.28

Oxosulfides
3.5+ **$P_4O_4S_3$**; 4+ **P_4O_7S** [36)]; 5+ **$P_4O_4S_6$**, **$P_4O_6S_4$**, m.p. 102, b.p. 295, **$P_4O_7S_3$**

Oxothiophosphoric acs. and oxothiophosphates

S_nHal_2 (eth., −20°)

$H_3[PO_3S]$, $K_2 = 10^{-6}$, $K_3 = 10^{-11}$
$Na_3[PO_nS_{4-n}] \cdot x\,H_2O$, $n = 1, 2, 3$
$M_3[P_3O_3S_6]$, M = Na, Tl, $[P_3O_3]$ rings in anion

$[(HO)_2OP]_2S_n$, $n = 3, 10$, rapidly hydrol.
$Ba_4[P_2O_6]S_n$, stab.

$I_2(HCl)$

$H_4P_2S_2O_6$, dithioperoxodiphosphoric, strong ac., exists in soln.; $+OH^- \rightarrow S^{2-} + S + PO_4^{3-}$, struct. analogue of $H_4P_2O_8$
$\uparrow HClO_4$
$K_2H_2P_2S_2O_6\downarrow$

Na_2HPO_4 — $NaHSO_4$

$HOSO_2OPO(OH)_2$, pyrosulfophosphoric ac., $+H_2O \longrightarrow H_2SO_4 + H_3PO_4$
$Na_3[PSO_7]$
$Ba_3[PSO_7]_2$, readily sol., stab.

PHOSPHORUS IONS IN AQUEOUS SOLUTIONS

3− 0 1+ 3+ 4+ 5+

HNO_3 (30%); $HClO_4$

HAl_2; Ag^+; Hg^{2+}; O_2 (I_2); H_2O ($-H_2$, t)

$[H\uparrow]$

$[PH_4]^+$, v. strong Red agent, ion: tetrahedron

P, wh.↓ — $H^+ \uparrow\downarrow H_2O\ (OH^-)$

$I_2 + H_2O$

$H^+ \uparrow\downarrow OH^-$

OH^-

$PH_3\uparrow$, v. strong Red agent, trig. pyramid

$[H_2PO_2]^-$ stab. to Ox and Red; $+ OH^- \longrightarrow H_2 + HPO_3^{2-} + PO_4^{3-}$

H_2O_2 (OH^-)

$[H\uparrow]$

$H_3PO_2 = H[H_2PO_2]$, $K = 10^{-1}$, v. strong Red agent (in conc. solns., t); $\xrightarrow{t} PH_3 + H_3PO_4 + P\downarrow + H_2 + \cdots$

Ag^+; Hg^{2+} / Cu^{2+} ($-CuH\downarrow$)

H_2SO_4

$H_3PO_3 = H_2[HPO_3]$, $K_1 = 10^{-2}$, $K_2 = 10^{-7}$, strong Red agent, slowly reacts, not Red by HNO_3

$H^+ \uparrow\downarrow OH^-$

$[HPO_3]^{2-}$ $\underset{H_2O}{\overset{H^+}{\rightleftharpoons}}$ **$[H_2P_2O_5]^{2-}$**
distort. tetrahedron

$[H_2PO_3]^-$
$H^+ \uparrow\downarrow OH^-$

$[P_2O_6]^{4-}$ (hypophosphate), stab. to Ox and Red, 2 crossing tetrahedra

$[H_2P_2O_6]^{2-}$
$H^+ \uparrow\downarrow OH^-$

$H_4P_2O_6$ (hypophosphate ac.), $K_1 > 10^{-2}$, $K_2 = 10^{-3}$, $K_3 = 10^{-8}$, $K_4 = 10^{-10}$, weak Red agent ($< H_3PO_3$), reacts with HNO_3 only in the presence of NO_2

H^+, t

KMnO₄

H_2O_2; MnO_4^-

H_3PO_4, $K_1 = 10^{-2}$, not Ox

$H^+ \uparrow\downarrow OH^-$

$[H_2PO_4]^-$, $K_2 = 10^{-7}$, pH 4.6*

$H^+ \uparrow\downarrow OH^-$

$[HPO_4]^{2-}$, $K_3 = 10^{-13}$, pH 8.9

$H^+ \uparrow\downarrow OH^-$

$[PO_4]^{3-}$, tetrahedron (sp^3), pH 12.1

H_2O ($-H_2PO_4$)

H_2O (H^+, t)

$H_4P_2O_7$, $K_1 = 10^{-2}$, $K_2 = 10^{-3}$

H_2O

$H^+ \uparrow\downarrow OH^-$

$[H_2P_2O_7]^{2-}$, $K_3 = 10^{-7}$, $K_4 = 10^{-10}$, pH 4.2

$H^+ \uparrow\downarrow OH^-$

H_2O_2

H_2O (H^+, t)

Hypothetic **polyphosphoric ac.**, strong (for **$H_5P_3O_{10}$** $K_3 = 10^{-3}$, $K_4 = 10^{-7}$, $K_5 = 10^{-9}$, for **$H_6P_4O_{13}$** $K_3 = 10^{-2}$, $K_4 = 10^{-3}$, $K_5 = 10^{-7}$, $K_6 = 10^{-9}$), therefore at pH < 7 equilibrium is shifted towards weaker ac.: H_3PO_4 and $H_4P_2O_7$ (oligomerization)

H^+

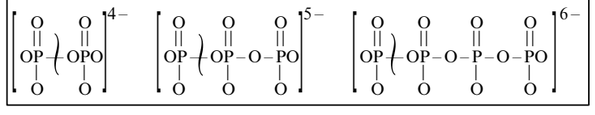
$[H_2P_nO_{3n+1}]^{n-}$, pH ≈ 7, helices of tetrahedra

H^+

OH^- ($-H_2O$, 40°) ring opening

$[P_2O_7]^{4-}$ pH 10.2 $\xleftarrow[-H_2PO_4^-]{H_2O}$ **$[P_3O_{10}]^{5-}$** pH 10 $\xleftarrow[-H_2PO_4^-]{H_2O}$ **$[P_4O_{13}]^{6-}$**

Chains of tetrahedra

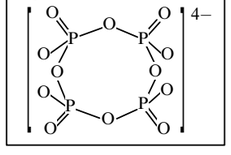


$[HPO_3]_n$, $n = 3, 4, 6$, strong ac., $K_3 = 10^{-2}$, $K_4 = 10^{-3}$, coagulates proteins

$H^+ \rightleftarrows OH^-$

H_2O (t)

$[PO_3]^{n-}_n$, at pH 6.5 ($n = 4$), rings of tetrahedra.



H_2O

$H_4P_2O_8$, $K_1 = 2$, $K_2 = 10^{-1}$, $K_3 = 10^{-5}$, $K_4 = 10^{-8}$, not reacts with KI

$H^+ \uparrow\downarrow OH^-$

$[H_2P_2O_8]^{2-}$
$H^+ \uparrow\downarrow OH^-$

anod. Ox

$[P_2O_8]^{4-}$, weak Ox, 2 $[PO_4]$ tetrahedra

H_3PO_5, $K_1 = 10^{-1}$, $K_2 = 10^{-6}$, $K_3 = 10^{-13}$, v. strong Ox. agent ($+Mn^{2+} \rightarrow HMnO_4$; $+I^- \rightarrow I_2$)

* pH data are given for 1% solutions

PHOSPHATES