Electron Spin Resonance Studies of γ-Irradiated Thiophosphates †

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γ-Irradiation of the powdered sodium salts of $[PO_3S]^{3-}$, $[PO_2S_2]^{3-}$, $[POS_3]^{3-}$, and $[PS_4]^{3-}$ yield the following newly characterised radicals: $[PO_3S]^{2-}$, $[PO_2S_2]^{2-}$, $[POS_3]^{2-}$, $[PS_4]^{2-}$, $[PO_2S_2]^{4-}$, $[POS_3]^{4-}$, $[PS_4]^{4-}$, $[PO_2S]^{2-}$, $[POS_2]^{2-}$, $[PS_3]^{2-}$, and $[PS_2]^{2-}$. The g and ^{31}P hyperfine tensors of each species are reported and compared with the related $[PO_4]^{2-}$, $[PO_4]^{4-}$, $[PO_3]^{2-}$, and $[PO_2]^{2-}$ radicals.

THERE have been many reports of the effects of radiation damage in alkali-metal phosphates and in phosphoric acid, as well as phosphate substituted in various host lattices and minerals. The usual radical species formed is $[PO_4]^{2-}$ (31 electrons) which is sometimes protonated as in the case of irradiated H_3PO_4. Only in one case has the 33-electron radical $[PO_4]^{4-}$ been detected, namely in $[PO_4]^{3-}$-substituted phenacite,[1] Be_2SiO_4.

In order to determine factors which may cause the radical $[PO_4]^{4-}$ to be stabilised, we have studied the effect of γ-irradiation on a series of thiosubstituted orthophosphates, namely the sodium salts of $[PO_3S]^{3-}$, $[PO_2S_2]^{3-}$, $[POS_3]^{3-}$, and $[PS_4]^{3-}$. This paper describes the radicals so formed and throws light on the radiation mechanisms involved. There have been a number of studies where the oxygens have been replaced by more electronegative groups, but less frequently are radicals studied where a more electropositive substituent is formed. In no case have a full series $[PO_nX_{4-n}]^{m-}$ ($n = 0$—4) been studied.

EXPERIMENTAL

The thiophosphate salts listed in Table 1 were prepared and purified by standard procedures.[2] The purity of the salts was monitored by i.r. and Raman spectroscopy.[3] Samples were irradiated in a ^{60}Co Vickrad radiation source at room temperature and 77 K. Electron spin resonance spectra were recorded on a Varian E3 spectrometer at room temperature and 77 K using diphenylpicrylhydrazyl (dpph) as an internal standard. The spectral parameters were determined by computer simulation using a program which solves the spin Hamiltonian to second order in perturbation theory.

TABLE 1

Summary of radical species formed in various matrices

Matrix	Radicals formed			
$Na_3[PO_4]\cdot12H_2O$	$[PO_4]^{2-}$ *			
$Na_3[PO_3S]\cdot12H_2O$	$[PO_3S]^{2-}$		$[PO_3]^{2-}$	
$Na_3[PO_2S_2]\cdot11H_2O$	$[PO_2S_2]^{2-}$	$[PO_2S_2]^{4-}$	$[PO_2S]^{2-}$	
$Na_3[POS_3]\cdot11H_2O$	$[POS_3]^{2-}$	$[POS_3]^{4-}$	$[POS_2]^{2-}$	
$Na_3[PS_4]\cdot8H_2O$	$[PS_4]^{2-}$	$[PS_4]^{4-}$	$[PS_3]^{2-}$	$[PS_2]^{2-}$

* Reported in ref. 4.

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† No reprints available.

[1] H. Lozykowski, R. G. Wilson, and F. Holuj, *J. Chem. Phys.*, 1969, **51**, 2309; M. C. R. Symons, *ibid.*, 1970, **53**, 857.

[2] G. Brauer, 'Handbook of Preparative Inorganic Chemistry,' Academic Press, New York, 1963, vol. 1.

[3] M. J. F. Leroy, G. Kaufmann, A. Muller, and H. W. Roesky, *Compt. rend.*, 1968, **C267**, 563; M. J. F. Leroy, personal communication.

[4] S. Subramanian, M. C. R. Symons, and H. W. Wardale, *J. Chem. Soc.* (*A*), 1970, 1239.

RESULTS

γ-Irradiation at 77 K of all the salts except the monothiophosphate caused them to become purple; this colour faded irreversibly on annealing to room temperature. In each case, there was a well resolved intense anisotropic doublet having hyperfine coupling *ca.* 20 G * and $g_{\parallel} > g_{\perp} \sim 2$. Figure 1 shows a typical spectrum of the radical species responsible for this signal. The radical shows axial symmetry in each case except in $Na_3[PO_2S_2]\cdot 11H_2O$ where the spectrum indicates rhombic symmetry for the radical (Figure 2). At room temperature, the signal remained, although broadening to a single line in most cases, in contrast to most orthophosphates other than $Na_2[HPO_4]$, where the species is lost irreversibly at *ca.* 150 K. In addition to this signal, a pair of isotropic lines of lower intensity centred at *ca.* $g = 2$ with spacing *ca.* 1 000 G was seen in the di-, tri-, and tetra-thiophosphates (Figure 3). These signals disappeared irreversibly on annealing to room temperature. Further lines at field positions between those for the first two species were seen for all the compounds. These lines were strongly anisotropic and (except for $Na_3[PO_3S]\cdot 12H_2O$) showed rhombic symmetry with hyperfine couplings in the 400—700 G region (Figure 4). The hyperfine couplings and g values were temperature dependent and changed by as much as 33 G between liquid-nitrogen and room temperatures. The spectra of irradiated $Na_3[PO_3S]\cdot 12H_2O$ showed axial symmetry at room temperature and rhombic symmetry at 77 K and is identical to that of irradiated $Na_2[HPO_3]\cdot 5H_2O$ at room temperature.

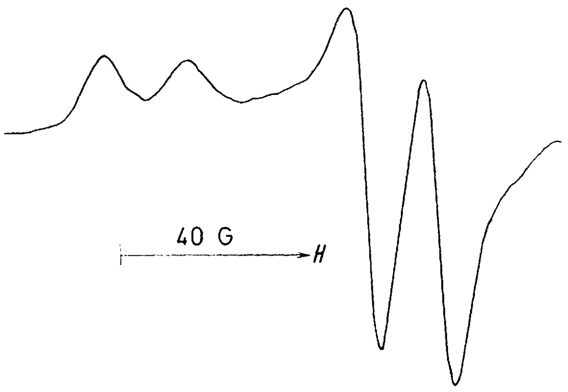

FIGURE 1 Portion of the spectrum of γ-irradiated $Na_3[PS_4]\cdot 8H_2O$ showing the signal due to the axially symmetric $[PS_4]^{2-}$ radical at 77 K

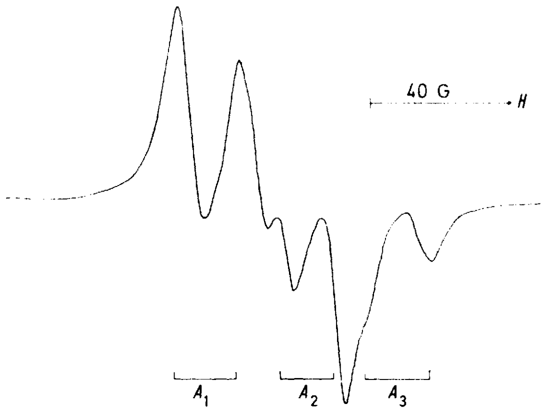

FIGURE 2 Portion of the spectrum of γ-irradiated $Na_3[PO_2S_2]\cdot 11H_2O$ showing the signal due to the $[PO_2S_2]^{2-}$ radical at 77 K

For $Na_3[PS_4]\cdot 8H_2O$, lines attributed to a fourth radical (D) were detected. Only the parallel features were seen (Figure 3), with a hyperfine coupling of 232 G. The perpendicular features were lost under the intense central lines. This radical was only seen when the salt was irradiated and the spectrum run at 77 K without warming up.

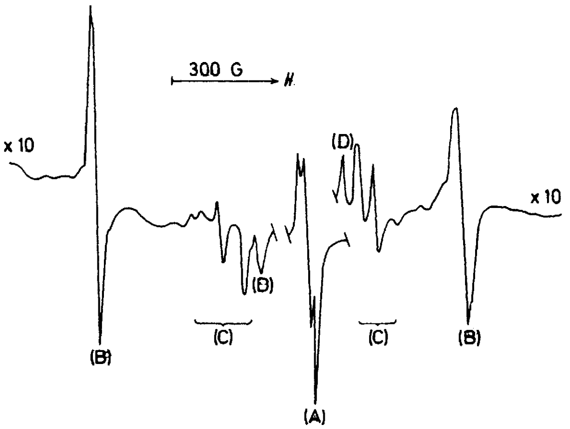

FIGURE 3 Spectrum of γ-irradiated $Na_3[PS_4]\cdot 8H_2O$ showing (A) the $[PS_4]^{2-}$ radical, (B) lines due to the $[PS_4]^{4-}$ radical, (C) lines due to the $[PS_3]^{2-}$ radical, and (D) the perpendicular feature of the $[PS_2]^{2-}$ radical

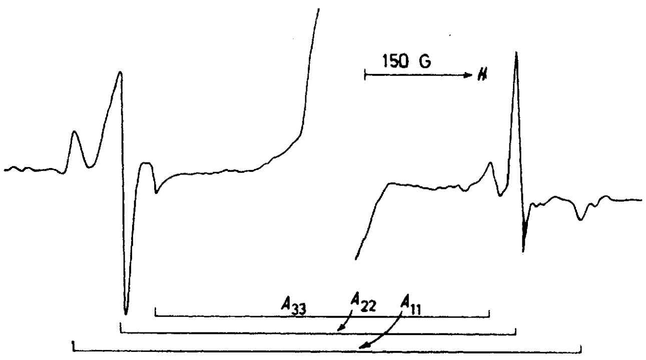

FIGURE 4 Spectrum of γ-irradiated $Na_3[PO_3S]\cdot 12H_2O$ showing the lines attributed to $[PO_3]^{2-}$ at 77 K

DISCUSSION

31-Electron $[PX_4]^{2-}$*-type Radicals.*—The group of radicals formed whose spectra are characterised by strong signals having hyperfine coupling ($A_{\parallel}$ and $A_{\perp}$) to ^{31}P in the 10—30 G region may readily be attributed to radicals related to $[PO_4]^{2-}$ (Table 2). We have detected the full family of radicals $[PO_xS_{4-x}]^{2-}$ ($x = 0$—3) which may be compared with $[PO_4]^{2-}$.[4] In these radicals one electron has been removed from the a_2 orbital of the host anion which is based on the oxygen and sulphur atoms. Coupling to phosphorus is expected to occur *via* spin polarisation of the O–P or S–P σ electrons which would put negative spin density into the phosphorus 3*s* and 3*p* orbitals.

Our values of $A_{iso.}$ (^{31}P) are in general much lower than those found in other PX_4 31-electron systems. These range from a maximum of 53.1 G in the related

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* Throughout this paper: 1 G = 10^{-4} T.

TABLE 2

E.s.r. parameters for the phosphorus species in γ-irradiated thiophosphates and related species

Radical	Matrix	$g_{\parallel}$	$g_{\perp}^{j}$	$A_{\parallel}$	$A_{\perp}^{j}$	$A_{iso.}$	$A_{aniso.}$	s Character (%)[a]	p Character (%)[a]	p : s	T/K	Ref.
				G								
31-Electron$[PX_4]^{2-}$-type radicals												
$PO_4]^{2-}$	$Na_3[PO_4]\cdot 12H_2O$	2.014 7	2 006 8	28.7	30.0	29.6					77	7
$[PO_2S_2]^{2-}$	$Na_3[PO_2S_2]\cdot 11H_2O$	2.026 6,	1 992 9 2 006 7	18.0,	17.5 15.0	16.8					77	b
$[POS_3]^{2-}$	$Na_3[POS_3]\cdot 11H_2O$	2.015 5	2.005 0	15.0	12.7	13.5					77	b
$[PS_4]^{2-}$	$Na_3[PS_4]\cdot 8H_2O$	2.024 9	2.004 2	15.5	13.2	14.0					77	b
PCl_2O_2	PCl_3O	2.052	2.000	43.0	45.0	44.3					77	6
PF_2O_2	PF_3O	2.010 0	2.010 0	43.8	43.8	43.8					77	7
$PO_2(OH)_2$	$CaH_4[PO_4]_2$	2.051	2.003 5	35.3	35.5	35.4					77	7
$[PCl_3S]^+$	PCl_3S	2.00	2.04		ca. 30						77	8
$[PO_4]^{2-}$	$Ca[CO_3]$	2.012 2,	2 007 2 2.003 3	18.61,	18.76 20.06	19.1					77	7
$[PFO_3]^-$	$K[PF_2O_2]$			39.1	39.1	39.1					77	7
33-Electron $[PX_4]^{4-}$-type phosphoranyl radicals												
$[PO_4]^{4-}$	Be_2SiO_4	2.010 0,	2.010 3 2.011 6	1 105,	1 242 1 120	1 156		31.4	ca. 42	1.3	r.t.[c]	1
$[PO_2S_2]^{4-}$	$Na_3[PO_2S_2]\cdot 11H_2O$	2.009		997		997		27.1			77	b
$[POS_3]^{4-}$	$Na_3[POS_3]\cdot 11H_2O$	2.011		1 025		1 025		27.9			77	b
$[PS_4]^{4-}$	$Na_3[PS_4]\cdot 8H_2O$	2.008		1 056		1 056		28.7			77	b
$[PCl_3O]^-$	PCl_3O			1 371	1 371	1 371		37.6			77	d
$PCl_2(OEt)(OBu^t)$	C_5H_{10}	2.011		1 145		1 145		31.1			223	e
PF_4	PF_3	2.000 9		1 322		1 322		36.0			73	f
PH_4	$PH_3–C_5H_{10}$	2.003		519.3		519.3		14			103	g
PPh_3Cl	$PPh_3\cdot BCl_3$	2.010,	2.001 2.009	720,	540 552	604	116	16	56	3.5	77	h
$[PBr(OMe)_2S]^-$	$PBr(OMe)_2S$			780	600	660	120	18	59	3.3	77	11
25-Electron $[PX_3]^{2-}$-type radicals												
$[PO_3]^{2-}$	$Na_2[HPO_3]\cdot 5H_2O$	1.992	2.007	706.5	540.2	596	ca. 110	16.2	ca. 54	ca. 3.3	77	12
	$Na_3[PO_3S]\cdot 12H_2O$	2.001,	1.994 2.000	718,	465 555	579	ca. 139	15.7	ca. 69	ca. 4.4	77	b
		2.000	2.000	692	536	558	ca. 104	16.0	ca. 51	ca. 3.2	r.t.	b
$[PO_2S]^{2-}$	$Na_3[PO_2S_2]\cdot 11H_2O$	2.012,	1.996 2.006	681,	402 498	527	ca. 154	14.3	ca. 76	ca. 5.3	77	b
		2.002,	2.001 2.003	648,	391 476	505	ca. 143	13.7	ca. 71	ca. 5.2	r.t.	b
$[POS_2]^{2-}$	$Na_3[POS_3]\cdot 11H_2O$	1.998,	2.006 2.013	638,	321 442	467	ca. 171	12.7	ca. 85	ca. 6.7	77	b
		2.008,	2.014 2.017	617,	325 445	462	ca. 155	12.6	ca. 77	ca. 6.1	r.t.	b
$[PS_3]^{2-}$	$Na_3[PS_4]\cdot 8H_2O$	2.000,	2.012 2.017	608,	327 431	445	ca. 152	12.4	ca. 76	ca. 61.	77	b
		2.004,	2.010 2.018	585,	337 420	447	ca. 137	12.2	ca. 68	ca. 5.6	r.t.	b
$[PFO_2]^-$	$K[PF_2O_2]$	1.992,	2.006 2.009	807	630 620	690	117	19	57	3.0	77	13
$[HPO_2]^-$	$[NH_4][H_2PO_2]$	2.001 9,	2.003 7 2.003 5	607	439	495	112	15	61	4.07	77	i
19-Electron $[PX_2]^{2-}$-type phosphinyl radicals												
$[PS_2]^{2-}$	$Na_3[PS_4]\cdot 8H_2O$	2.021		232							77	b
PF_2	PF_3	2.002 7	2.001 6	308.1	−27.2	84.6	223.5	2.3	110	48	77	15
PCl_2	PCl_3	1.995	2.018 7	272.5	−22.5	75.8	196.7	2.1	9.7	46	77	17
PH_2	PH_3	2.002		275		80	195	2.2	96	44	77	17
$[PO_2]^{2-}$	$PhPH(O)OH$			270	ca. 0	ca. 90	ca. 180	2.4	89	37	323	16
$P(SMe)_2$	$P(SMe)_3$	2.002		237.6							77	17

[a] Using the data of B. A. Goodman and J. B. Raynor, *Adv. Inorg. Radiochem.*, 1970, **13**, 135. [b] Present work. [c] r.t. = Room temperature. [d] T. Gillbro and F. Williams, *J. Amer. Chem. Soc.*, 1974, **96**, 5032. [e] D. Griller and B. P. Roberts, *J.C.S. Perkin II*, 1973, 1339. [f] A. Hasegawa, K. Ohnishi, K. Sogabe, and M. Miura, *Mol. Phys.*, 1975, **30**, 1367. [g] A. J. Colussi, J. R. Morton, and K. F. Preston, *J. Chem. Phys.*, 1975, **62**, 2004. [h] T. Berclaz, M. Geoffroy, and E. A. C. Lucken, *Chem. Phys. Letters*, 1975, **36**, 677. [i] J. R. Morton, *Mol. Phys.*, 1962, **5**, 217. [j] Where two figures are bracketed together in the $g_{\perp}$ and $A_{\perp}$ columns, it represents systems with 3 *g*-values or 3 *A*-values.

$[P_4O_{10}]^+$,[5] through 44.3 G for PCl_2O_2,[6] 43.8 G for PF_2O_2,[7] 39.1 G for $[PFO_3]^-$,[7] *ca.* 35 G for $PO_2(OH)_2$,[4] 30 G ($A_{\perp}$) for $[PCl_3S]^+$,[8] 29.6 G for $[PO_4]^{2-}$ in $Na_3[PO_4]\cdot 12H_2O$,[4] to 18.76 G for $[PO_4]^{2-}$ in $Ca[CO_3]$.[4] The increased electronegativity of those oxygen (or sulphur) atoms from which the electron has been removed causes the P–O (or P–S) σ bonds involved to become more *p*-like. The smaller 3*s* (P) character in the σ bonds results in a reduction of $A_{iso.}$ from the value normal for sp^3. Many $[PO_4]^{2-}$ species have $A_{iso.}$ *ca.* 29 G:[4] values of $A_{iso.}$ which are larger are attributed to the effect of more electronegative groups or atoms, *e.g.* F or OH, bonded to the phosphorus. Our much smaller $A_{iso.}$ can only arise

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[5] R. F. Picone and J. B. Raynor, preceding paper.

[6] A. Begum and M. C. R. Symons, *J. Chem. Soc.* (*A*), 1971, 2065.

[7] A. Begum, S. Subramanian, and M. C. R. Symons, *J. Chem. Soc.* (*A*), 1970, 1323.

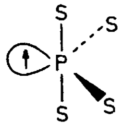
[8] S. P. Mishra, K. V. S. Rao, and M. C. R. Symons, *J. Phys. Chem.*, 1974, **78**, 576.

from less polarisation of the σ bonds and must be due to the presence of the more electropositive sulphurs at a greater distance from the phosphorus than the oxygen. The general decrease in $A_{\text{iso.}}$ to 13.5 and 14.0 G in $[POS_3]^{2-}$ and $[PS_4]^{2-}$ supports this argument. The trend is not smooth throughout the series because of the different detailed symmetry of each ion. Each spectrum shows unmistakable axial symmetry, except for $[PO_2S_2]^{2-}$ which is clearly rhombic. In this case, such a lower symmetry fits well with expectation for the radical. The degree of axial distortion in $[PS_4]^{2-}$ (and $[PO_4]^{2-}$) is likely to be much less than in $[PO_3S]^{2-}$ and $[POS_3]^{2-}$. We feel a more useful correlation is within the families of like symmetry: *e.g.* PF_2O_2, PCl_2O_2, $PO_2(OH)_2$, $[PO_2S_2]^{2-}$; $[PO_4]^{2-}$, $[PS_4]^{2-}$; $[PO_3S]^{2-}$, $[PCl_3S]^+$; $[PFO_3]^-$, $[PO_3S]^{2-}$ (see Table 2). It is difficult to be very precise about the cause of the trends since several factors are involved. For example, electronegativity[6] clearly could be an important factor in the relative values of $A_{\text{iso.}}$ in the pairs PF_2O_2 and $[PO_2S_2]^{2-}$, and $[PO_4]^{2-}$ and $[PS_4]^{2-}$, but does not explain the large value of $A_{\text{iso.}}$ (^{31}P) in PCl_2O_2 (close to that for PF_2O_2), nor the relative values of $A_{\text{iso.}}$ in $[PO_3S]^{2-}$ and $[PCl_3S]^+$. Other factors are bond lengths (especially for $[PO_4]^{2-}$ and $[PS_4]^{2-}$) and bond angles which are indeterminate in the radicals but which play a major part in determining the amount of σ polarisation because of their effect on the *p* character of the bonds. Since detailed crystal structures[9] are not known for any of the thiophosphates, we cannot make useful comments about bond angles as has been done for the family $[PO_4]^{3-}$, $[PFO_3]^{2-}$, and $[PF_2O_2]^-$.[7] For this reason, also, single-crystal e.s.r. studies were not undertaken.

The anisotropic hyperfine tensors are very similar to those already recorded for $[PO_4]^{2-}$ and related species and do not yield any further useful information.[4] It is interesting that, for $[PO_3S]^{2-}$, $A_{\parallel} < A_{\perp}$ like that found for $[PO_4]^{2-}$ in various hosts,[4] but the anisotropy in our case is rather larger. In each case, $g_{\parallel} > g_{\perp}$ and is in accord with most other data. There is no evidence for tumbling or significant libration at 77 K, but in most cases the signal collapses to a broad single line which was sometimes anisotropic on warming to room temperature.

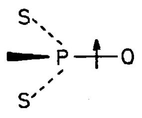
33-*Electron* $[PX_4]^{4-}$-*type Phosphoranyl Radicals*.—In irradiated salts of $[PO_2S_2]^{3-}$, $[POS_3]^{3-}$, and $[PS_4]^{3-}$, the spectra exhibited isotropic lines with large hyperfine coupling to ^{31}P of *ca.* 1 000 G. These are readily attributed to the radicals $[PO_2S_2]^{4-}$, $[POS_3]^{4-}$, and $[PS_4]^{4-}$, and their parameters may be compared with that for $[PO_4]^{4-}$ in phenacite[1] (see Table 2). The species $[PO_4]^{4-}$ has only been found to be stabilised in this mineral and has not been formed in irradiated $Na_3[PO_4]\cdot12H_2O$. The corresponding radical was found in irradiated $Na_3[PO_3S]\cdot12H_2O$. In these radicals an electron is added to the $a_1{}^*$ orbital which is largely based on the phosphorus atom and has p_z and *s* character. The spectra are isotropic at 77 K and disappear irreversibly on annealing to room temperature. They differ from the phenacite spectrum which is both anisotropic and stable at room temperature. We believe the radicals must be tumbling under our experimental conditions.

Molecular-orbital energy-level diagrams have been calculated[10] for D_{2d} distorted $[AsO_4]^{4-}$, but, since our radicals may have different symmetries, comparisons may not be fruitful. However, because the similarity in $g_{\text{av.}}$ and $A_{\text{iso.}}$ are so good, we are led to believe that the orbital of the unpaired electron must be very similar in each case. The lack of detectable anisotropy prevents us from making estimates of the phosphorus $3p_z$ population of the $a_1{}^*$ orbital. In phenacite, this is large (42%) and it also has a 3*s* population of 32%. Our 3*s* populations range from 26.1% in $[PO_2S_2]^{4-}$ to 28.8% in $[PS_4]^{4-}$ and the similarity with phenacite suggests comparable 3*p* characters. There is probably more overall unpaired electron delocalisation in the thiophosphates because of the more electropositive character of the sulphur. Phosphoranyl radicals are usually C_{2v} distorted (1) and are structurally related to a trigonal bipyramid with the unpaired electron in an equatorial position. This is likely for $[PO_4]^{4-}$, $[PS_4]^{4-}$, and $[PO_2S_2]^{4-}$, but for $[POS_3]^{4-}$, using the arguments presented by Symons,[11] a C_{3v} distorted tetrahedron (2) would be expected. The species $[PO_3S]^{4-}$, had it been detected, would have been C_{2v} distorted. Unfortunately proof of structure relies on detecting superhyperfine splittings and this is not possible in our systems unless enriched ^{33}S is used.



C_{2v}

(1)



C_{3v}

(2)

25-*Electron* $[PX_3]^{2-}$-*type Radicals*.—A third group of radicals detected in γ-irradiated thiophosphates has hyperfine coupling intermediate between those hitherto mentioned. In each case, the spectrum shows rhombic symmetry. Couplings typically in the 400—700 G region are attributed to radicals related to $[PO_3]^{2-}$ (Table 2). We have detected the full family $[PO_3]^{2-}$, $[PO_2S]^{2-}$, $[POS_2]^{2-}$, and $[PS_3]^{2-}$ which we will compare with the already known $[PO_3]^{2-}$, $[PFO_2]^-$, and $[HPO_2]^-$. These radicals may be best considered as derived from an appropriate phosphoranyl radical by loss of S^{2-}. The mechanism for this will be considered later. These ions all show temperature-dependent e.s.r. spectra with marked changes in hyperfine coupling between 77 K and room temperature. Changes in *g* are less marked, but nevertheless are present. In each case, the average hyperfine couplings for both temperatures are similar. Absolute values of *p* : *s* ratios and orbital populations are open to error because the cause of the temperature

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[9] D. P. Elias, *Acta Cryst.*, 1957, **10**, 600; H. Schafer, G. Schafer, and A. Weiss, *Z. Naturforsch.*, 1965, **B20**, 811.

[10] M. Hampton, F. G. Herring, W. C. Lin, and C. A. McDowell, *Mol. Phys.*, 1966, **10**, 565.

[11] M. C. R. Symons, *Chem. Phys. Letters*, 1976, **40**, 226.

effect is probably libration of the radicals in the cavity of the solid, and this can seriously reduce the observed coupling. The presence of such temperature effects supports our assignment of these species, since related radicals, *e.g.* $[PO_3]^{2-}$ and $[NO_3]^{2-}$, are noted for this behaviour.[12]

Ions of this class are pyramidal with the unpaired electron in an sp^n hybrid orbital whose axis is lined up along the C_3 axis. Analyses of the $p:s$ ratios show that they all range between 3.2 and 4.6, similar to, but slightly larger than, those for $[PO_3]^{2-}$ (3.2), $[PFO_2]^-$ (3.0), and $[HPO_2]^-$ (3.9). Our values for the $p:s$ ratio show a distinct increase from 3.2 for $[PO_3]^{2-}$ (which has e.s.r. parameters identical to $[PO_3]^{2-}$ in $Na_2[HPO_3].5H_2O$) [12] to *ca.* 6 for $[PS_3]^{2-}$. This increase in p character of the a_1 orbital causes a flattening of the $[PX_3]^{2-}$ pyramid as the bonding becomes more covalent and may be qualitatively related to electronegativity changes as sulphur atoms replace oxygen.[13] Thus sulphur, because it is more electropositive, will have a higher unpaired electron spin density than oxygen and favours a reduction in the $3p$ character of the P–S bond and hence the ^{31}P s character of the unpaired electron is reduced. These changes parallel those seen in the $[PO_3]^{2-}$–$[HPO_2]^-$ pair and even more dramatically in the CF_3–$[CO_3]^{3-}$ pair where substituting the more electropositive oxygen for fluorine causes an unambiguous flattening of the molecule.[14] Because of the considerable temperature effects, and not being able to place too much emphasis on absolute values of p and s character, and also because of the reduced symmetry from C_{3v}, a detailed analysis of the trend cannot be attempted.

19-*Electron* $[PX_2]^{2-}$ *Phosphinyl-type Radicals.*—The radical in $Na_3[PS_4]{\cdot}8H_2O$ whose spectra is characterised by $A_z = 232$ G, and with very small A_x and A_y values, may be attributed to a radical related to $[PO_2]^{2-}$. Radicals of this type are not seen in any of the other thiophosphates. We believe the radical is $[PS_2]^{2-}$. Since the more sulphur atoms the anion has the more likely one sulphur may be lost, the best chance of finding such a radical is from the $[PS_4]^{3-}$ salt. In these phosphinyl radicals, the unpaired electron is in the $2b_1^*$ orbital whose lobes are perpendicular to the plane (yz) of the bent PX_2 arrangement of atoms (Figure 5). The unpaired electron is almost totally localised in the p_x orbital of the phosphorus.

Analysis of the spectra in the g_x and g_y region is difficult because of overlap with other stronger lines and also because of the doubt in its sign of the hyperfine coupling. In the related radicals PF_2 [15] and PCl_2,[6] the sign is taken as negative because it gives more reasonable results, and it may well be the same in our radical. The radical $[PO_2]^{2-}$ has been postulated in γ-irradiated $PhPO(OH)_2$,[16] and others reported include PR_2, PPh_2, $P(OR)_2$, and $P(SR)_2$ (R = Me, Et, or Pr^i).[17] In all cases, $A_{aniso.}$ (^{31}P) is *ca.* 200 G and represents *ca.* 100% $3p$(P) character for the unpaired electron. Our value of $A_z = 232$ G is very similar to that for $P(SMe)_2$ and lower than that for PF_2, PCl_2, PH_2, and $[PO_2]^{2-}$.[15-17] This is probably because there is more unpaired electron delocalisation in the $P(SR)_2$ or $[PS_2]^{2-}$ radicals compared with the others, due to the more efficient overlap between P($3p$) and S($3p$) orbitals compared with the P($3p$)–O($2p$) overlap whose sizes and energies match less well.

The value of g_z (2.021) is much larger than that of the other PX_2 radicals. This arises through a combination of increased spin–orbit interaction with the sulphur atoms because of the larger spin–orbit coupling constant of sulphur, and the greater delocalisation on to the sulphurs. The order of the nearby molecular-orbital energy levels for C_{2v} symmetry is $3b_2^* > 4a_1^* > 2b_1^* > 2b_2 > 1a_2 > 1b_2 > 2a_1$.[18] From this, g_z is dependent on the separation $2b_1^* - 2b_2$ (Δg large and positive), g_x on the separation $2b_1^* - 1a_2$ (Δg small and negative), and g_y on the separation $4a_1^* - 2b_1^*$ (Δg small and negative).

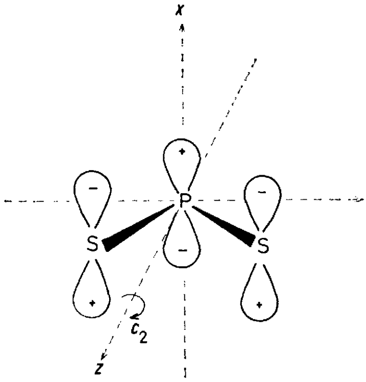

FIGURE 5 Axis notation for $[PS_2]^{2-}$ showing the $2b_1^*$ orbital containing the unpaired electron

We also prepared the radical $[AsS_2]^{2-}$ and this has the following ^{75}As hyperfine coupling: 193, 36, and 24 G. The similarity with $[PS_2]^{2-}$ is striking and will be discussed in a subsequent paper.

Mechanism of Radical Formation.—The radicals arise from processes which may be described by the following equations. Phosphate, in all cases except in phenacite, loses an electron, and so its reactions are (1) and (2).

$$[PO_4]^{3-} \longrightarrow [PO_4]^{2-} + e^- \quad \text{(usual process)} \quad (1)$$

$$e^- + [PO_4]^{3-} \longrightarrow [PO_4]^{4-} \quad \text{(phenacite)} \quad (2)$$

Reaction types (1) and (2) both occur for most of the thiophosphates. For $[PO_2S_2]^{3-}$, $[POS_3]^{3-}$, and $[PS_4]^{3-}$, the 4− ion is formed but irreversibly disappears on annealing to room temperature. The relative abundances of the radical species $[PX_4]^{2-}$ and $[PX_4]^{4-}$ formed at 77 K (the former always being very much more

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intense) suggest sequence (2) follows (1). We believe the reason why the phosphorus(IV) thio-salts are relatively more stable than $[PO_4]^{4-}$ is because of the overall greater electron delocalisation in orbitals on the sulphur which are larger and can accommodate the excess of charge more easily. Nevertheless, such ions are only stable at low temperatures, and readily decay by loss of a sulphide according to (3). A sulphur is lost

$$[PX_4]^{4-} \longrightarrow [PX_3]^{2-} + X^{2-} \qquad (3)$$

in preference to an oxygen because of the lower bond strengths to phosphorus. This is clearly shown in the detection of $[PO_3]^{2-}$ as the sole radical of this type in irradiated $Na_3[PO_3S]\cdot 12H_2O$. The loss of a further sulphur in $Na_3[PS_4]\cdot 8H_2O$ to form the $[PS_2]^{2-}$ radical may be caused by the overall reaction (4). Even $[PS_3]^{2-}$ is likely to lose a sulphur, and since the product detected is $[PS_2]^{2-}$, we suggest that the breakdown products are strong electron traps and that the final

$$[PS_3]^{2-} \xrightarrow{+\,2e^-} [PS_2]^{2-} + S^{2-} \qquad (4)$$

products are $[PS_2]^{2-}$ and S^{2-}. This may occur *via one* or more of processes (5)—(7) where the species marked

$$[PS_3]^{2-} \longrightarrow [PS_2]^{2-} + S\,* \qquad (5)$$

$$[PS_3]^{2-} \longrightarrow PS_2\,* + S^{2-} \qquad (6)$$

$$[PS_3]^{2-} \longrightarrow [PS_2]^{-}\,* + S^{-}\,* \qquad (7)$$

with an asterisk would readily absorb electrons to form $[PS_2]^2$ and S^{2-}.

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