Electron Spin Resonance Studies on γ-Irradiated Tetraphosphorus Decaoxide, Decasulphide, and Decaselenide †

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γ-Irradiation of P_4O_{10}, P_4S_{10}, and P_4Se_{10} produces the following radicals: $[P_4O_{10}]^+$, $[P_4S_{10}]^+$, and $[P_4Se_{10}]^+$ in which the unpaired electron is based on one PX_4 unit and thus related to $[PO_4]^{2-}$; $[P_4O_{10}]^-$ and $[P_4S_{10}]^-$ related to $[PO_4]^{4-}$; and $[P_4S_9]^+$ and $[P_4Se_9]^+$ related to $[PO_3]^{2-}$. In the case of $[P_4S_{10}]^-$, further hyperfine coupling (21.6 G) to the other three phosphorus atoms is seen. A mechanism for the radiation damage is proposed.

A CONSIDERABLE number of oxy-radicals of phosphorus have now been identified by e.s.r. spectroscopy as having structures based on the 25- and 27-electron $[PO_3]^{n-}$ unit and the 31- and 33-electron $[PO_4]^{n-\cdot}$ unit (*e.g.* refs. 1—7). Radicals derived from the dimeric pyrophosphate unit $[P_2O_7]^{4-}$ have recently been characterised[8] where, in the case of $H_4P_2O_7$, a hyperfine coupling of 68 G ‡ to the second phosphorus atom was observed. A logical extension to this is the investigation of radicals based on the tetrameric unit P_4O_{10} and the related P_4S_{10} and P_4Se_{10}. This paper describes such studies.

The crystal structure of P_4O_{10} shows it to consist of descrete P_4O_{10} tetrahedral units with each phosphorus bonded to the others *via* oxygen bridges, and a fourth oxygen on the C_3 axis.[9] The structure of P_4S_{10} is similar[10] and that of P_4Se_{10} is presumed similar also; P_4S_{10} differs only in the much larger bridging S–P–S bond angles.

EXPERIMENTAL

All the chemicals were handled in a nitrogen-filled dry-box. Samples were irradiated at 77 K in a ^{60}Co Vickrad source and spectra were recorded on a Varian E3 spectrometer at 77 K and room temperature. Spectral parameters were derived from the experimental spectrum by simulating the spectrum using a computer program correct to second order in perturbation theory.

RESULTS

γ-Irradiation of a powder sample of phosphorus pentaoxide at 77 K yielded a spectrum which consisted of well defined signals from two different paramagnetic species, (1) and (2). No colour changes were observed in the sample after irradiation or subsequent annealing. Species (1) gives an intense nearly isotropic doublet with $A_{\parallel} = 55.3$ and $A_{\perp} = 52.0$ G (Figure 1) and is stable when annealed to room temperature. Species (2) gave a very weak intensity anisotropic doublet whose parameters, after correction, are

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† No reprints available.

‡ Thoughout this paper: $1 \text{ G} = 10^{-4}$ T.

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

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

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$A_{\parallel}$ = 1 400 ± 15 and $A_{\perp}$ = 1 300 ± 15 G. This spectrum irreversibly disappeared on annealing to room temperature.

γ-Irradiation of phosphorus pentasulphide yielded a spectrum having three well defined features (Figure 2).

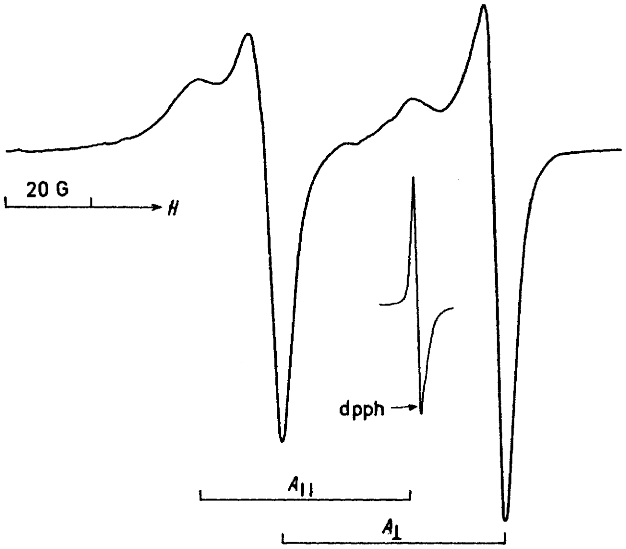

FIGURE 1 Central position of the spectrum of γ-irradiated P_4O_{10} showing the doublet attributed to $[P_4O_{10}]^+$ [species (1)]. dpph = Diphenylpicrylhydrazyl

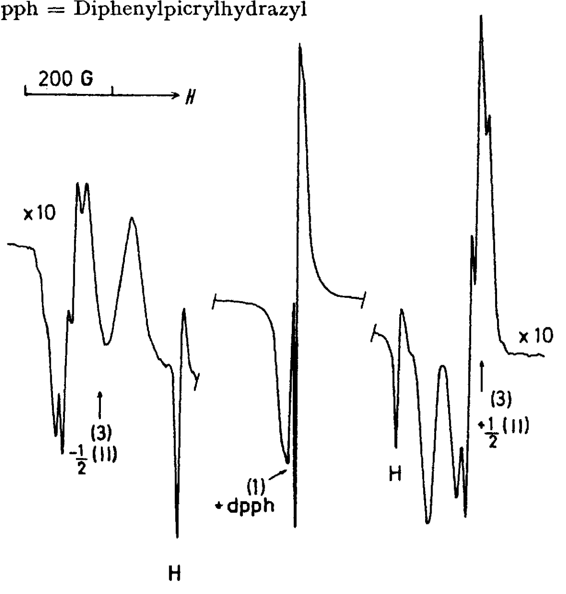

FIGURE 2 Spectrum of γ-rradiated P_4S_{10} showing (poorly resolved) doublets [species (1)] attributed to $[P_4S_{10}]^+$, two quartets [species (2)] attributed to $[P_4S_{10}]^-$, and the perpendicular features of $[P_4S_9]^+$ [species (3)]. Lines labelled H are from free hydrogen atoms

The central doublet [species (1)] was very strong and had $A_{\parallel}$ = 38.0 and $A_{\perp}$ = 37.0 G and is stable when annealed to room temperature. The doublet arising from species (2) had a much larger hyperfine coupling and its spectrum was isotropic. Each line was split into a well resolved quartet of lines with spacing 21.6 G attributed to further coupling to three equivalent phosphorus atoms. A third species showed a weak but well resolved pair of perpendicular features ($A_{\perp}$ 690 G) whose corresponding parallel features were lost under the lines of species (2) but whose position may be inferred from the line shape of species (2) and by the corresponding spectrum of P_4Se_{10}.

In the case of γ-irradiated phosphorus pentaselenide, only two species were seen. The first was an anisotropic doublet [species (1)] and on either side of it there were several weak broad lines extending up to 150 G which are attributed to ^{77}Se (7.5%, $I = \frac{1}{2}$). A second anisotropic doublet, species (3), with $A_{\parallel}$ = 880 and $A_{\perp}$ = 701 G was seen (Figure 3), but was much weaker in intensity than the other signal, so weak that coupling to ^{77}Se could not be detected. The results are summarised in the Table.

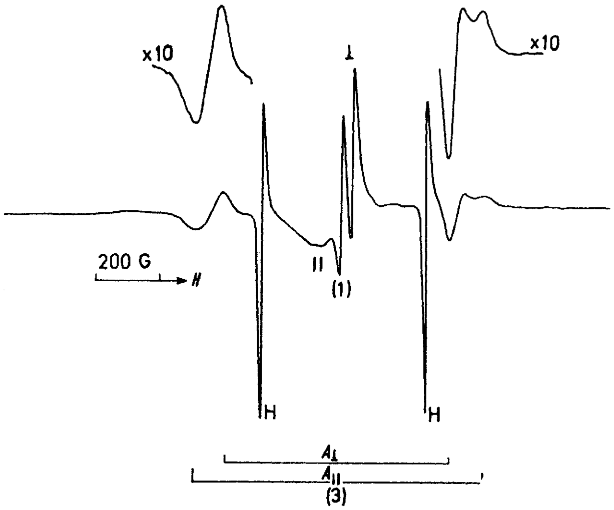

FIGURE 3 Spectrum of γ-rradiated P_4Se_{10} showing the doublets [species (1)] attributed to $[P_4Se_{10}]^+$ and the features of species (3), $[P_4Se_9]^+$. Lines labelled H are from free hydrogen atoms

In each sample, a sharp doublet with a separation of *ca.* 500 G was seen and is attributed to free hydrogen atoms from damaged trace quantities of water or hydrolysis products.

DISCUSSION

$[P_4O_{10}]^+$.—From the form of the g and A tensors the radical [species (1)] associated with the small weakly anisotropic doublet with hyperfine splitting due to ^{31}P must be related to the $[PO_4]^{2-}$ radical (31-electron MO_4 species). We believe the radical to be $[P_4O_{10}]^+$. One electron has been removed from the a_2 orbital which is based mainly on three bridging oxygens and with some interaction with the terminal oxygen atom, and is nonbonding with respect to the phosphorus (Figure 4). It is not possible with certainty to tell if any of the P–O–P bonds are broken, but the detection of coupling to only one phosphorus atom suggests that the unpaired electron is localised in one of the PO_4 units. The spectrum showed unmistakable axial symmetry suggesting maintenance of the dominant C_{3v} local symmetry.

Comparison of our e.s.r. data with those of related radicals (Table) shows that this radical has a surprisingly high coupling to phosphorus. Since coupling to ^{31}P is expected to occur *via* spin polarisation of the O–P σ electrons, it would put negative spin density into the phosphorus 3s and 3p orbitals. The anisotropy is very small (−2.2 G) and arises from a combination of indirect dipolar coupling from spin on oxygen and spin polarisation

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

Radical	Matrix	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel}$	$A_{\perp}$	$A_{iso.}$	$A_{aniso.}$	s Character (%) [a]	p Character (%) [a]	p : s	Ref.
				G							
31-Electron $[PO_4]^{2-}$-type radicals											
PCl_2O_2	PCl_3O	2.052	2.000	43	45	44.4	−1.4				1
PF_2O_2	$PF_2(O)(OH)$	2.010 0		43.8		43.8	0				3
$[PFO_3]^-$	$K[PF_2O_2]$	2.027 4	2 008 5	39.1	39.1	39.1	0				3
$[PO_4]^{2-}$	$CaCO_3$	2.012 0	2.005 5	18.65	19.41	19.2	−0.5				2
$[P_4O_{10}]^+$	P_4O_{10}	2.007	2.004	55.3	52.0	53.1	2.2				b
$[P_4S_{10}]^+$	P_4S_{10}	2.010	2.004	38.0	37.0	37.3	0.7				b
$[P_4Se_{10}]^+$	P_4Se_{10}	2.032	2.004	30.0	ca. 30	ca. 30	ca. 0				b
33-Electron $[PO_4]^{4-}$ type radicals											
$[PO_4]^{4-}$	Be_2SiO_4	2.010 3	2.001 6 2.010 0	1 242	1 120	1 105, 1 156	86	32	42	1.3	6
$[P_2O_7]^{5-}$	$H_4P_2O_7$			1 368		1 169, 1 264	100	34	50	1.5	8
$[P_4O_{10}]^-$	P_4O_{10}	2.017	1.977	1 400		1 300, 1 333	67	36	33	0.9	b
$[P_4S_{10}]^-$	P_4S_{10}	1.994			934	934		26			b
25-Electron $[PO_3]^{2-}$ type radicals											
$[PO_3]^{2-}$	$Na_2[HPO_3]{\cdot}5H_2O$	1.994	2.001 1	703		541, 595	108	16.0	52	3.3	5
	$Mg[HPO_3]{\cdot}6H_2O$	1 998	1.999	790		618, 675	115	18.6	56	3.0	4
$[P_4S_9]^+$	P_4S_{10}		1.998	ca. 860		690, 747	113	20.6	55	2.7	b
$[P_4Se_9]^+$	P_4Se_{10}	1.987	1.990	880		701, 761	119	20.9	58	2.8	b

[a] Calculated using the data in B. A. Goodman and J. B. Raynor, *Adv. Inorg. Radiochem.*, 1970, **13**, 135. [b] Present work.

in the σ bonds. By use of the method of McConnell and Strathdee,[11] the indirect dipolar coupling should give a parallel value of *ca.* +3 G using an O–P bond distance [9] of 1.6×10^{-10} m. The spin polarisation based on the arguments detailed by Symons and his co-workers,[2,12] would contribute *ca.* −5 G along the terminal O–P bond direction, giving a net coupling of −2 G if the electron were localised on this one oxygen. The greater the degree of delocalisation of the electron (or hole) over the other oxygen atoms the smaller will be the anisotropy and it may be either positive or negative. From our results, the principal value of $A_{aniso.}$ is −2.2 G which is entirely reasonable and compares with, for example, +0.3 for $[PO_4]^{2-}$ in $CaWO_4$, +0.45 G for $[PO_4]^{2-}$ in $CaCO_3$, and −2 G for $PO_2(OH)_2$ in concentrated aqueous phosphoric acid.[2]

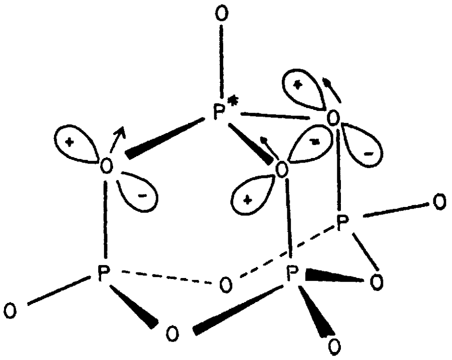

FIGURE 4 The species $[P_4O_{10}]^+$, showing the a_2 orbital containing the unpaired electron in $2p$ orbitals on three oxygens. The P* atom is the one with hyperfine coupling. The arrows show the probable direction of movement of the oxygens from the equilibrium positions in P_4O_{10}

Our value for $A_{iso.}$ (52.3 G) is much larger than that found in any other PX_4 31-electron system, which range from 19.1 G for $[PO_4]^{2-}$ in $CaCO_3$ to 43.8 G for PF_2O_2.[2] The increased electronegativity of those oxygen atoms from which the electron has been removed causes the P–O σ bonds involved to be more *p*-like and makes the O–P–O bond angle decrease. The smaller 3*s*(P) character in the P–O σ bonds results in a reduction of $A_{iso.}$ from the value normal for sp^3. Many $[PO_4]^{2-}$ species have $A_{iso.} = 29.4$—30 G with the more distorted radicals having values of $A_{iso.}$ down to 19.1 G.[2] Larger values are attributed to the effect of different (more electronegative) groups or atoms, *e.g.* F or OH bonded to the phosphorus. Our much larger $A_{iso.}$ can only arise from more polarisation of the P–O σ bond and must be due to either (*i*) the bond having much larger 3*s*(P) character with consequent increase in the bridging O–P–O bond angle, or (*ii*) the P–O(br) bond distance is considerably shortened so that more polarisation of the phosphorus *s* electrons takes place.

Possibly (*i*) can occur if the P atom is drawn down towards the centre of the P_4O_{10} unit so as to increase the bridging O–P–O angle from 101° to something significantly in excess of the tetrahedral angle. The disadvantage of this argument is that polarisation of the three σ bonds to the basal P atoms in P_4O_{10} would be expected to yield an appreciable secondary hyperfine coupling to these three equivalent phosphorus atoms. Possibility (*ii*) is more likely in that movement of the three bridging oxygens upwards and towards one phosphorus (say, the apical) will increase the bridging O–P–O bond angle and shorten the P–O bond distance, both effects resulting in a larger $A_{iso.}$. At the same time, coupling to the three basal phosphorus atoms will be considerably reduced to the extent of not being resolved. Symmetry reasons preclude the possibility of the hole being on the terminal oxygen.

The values of $g_{\parallel}$ and $g_{\perp}$ are both rather smaller than typically found for $[PO_4]^{2-}$ species. This may arise because the bonding a_1 and e energy levels are stabilised by the better σ and π overlap resulting from bringing

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[11] H. M. McConnell and J. Strathdee, *Mol. Phys.*, 1959, **2**, 129.

[12] T. F. Hunter and M. C. R. Symons, *J. Chem. Soc.* (*A*), 1967, 1770.

the three bridging oxygen atoms closer to the phosphorus. Figure 5 shows schematically the changes that would take place in the energy levels on going from $[PO_4]^{2-}$ to $[P_4O_{10}]^+$. The values of $g_\parallel$ and $g_\perp$ are given to first order by expressions (1) and (2), and as

$$g_\parallel = g_0 + \frac{2\lambda}{\Delta E(a_2 - 1a_1)} - \frac{2\lambda}{\Delta E(2a_1{}^* - a_2)} \quad (1)$$

$$g_\perp = g_0 + \frac{2\lambda}{\Delta E(a_2 - 2e)} - \frac{2\lambda}{\Delta E(3e^* - a_2)} \quad (2)$$

$\Delta E(a_2 - 1a_1)$ and $\Delta E(a_2 - 2e)$ are larger in $[P_4O_{10}]^+$ then $g_\parallel$ and $g_\perp$ become smaller.

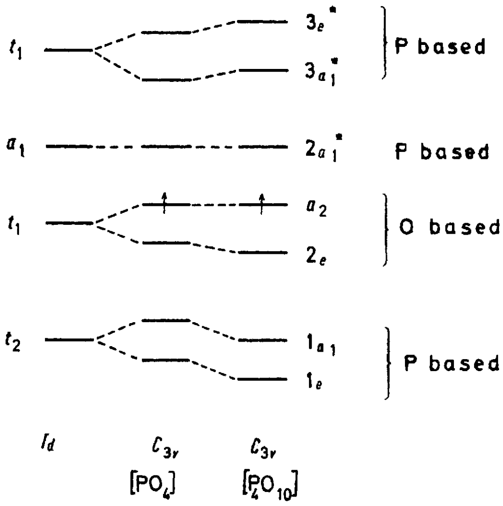

FIGURE 5 Relative energies (not to scale) of some of the molecular-orbital energy levels of $[PO_4]^{2-}$ and $[P_4O_{10}]^+$. The arrow shows the orbital of the unpaired electron

$[P_4S_{10}]^+$ *and* $[P_4Se_{10}]^+$.—By analogy with $[P_4O_{10}]^+$, the radical species (1) in P_4S_{10} and in P_4Se_{10} are $[P_4S_{10}]^+$ and $[P_4Se_{10}]^+$ respectively. The hyperfine coupling to phosphorus is much smaller than that in $[P_4O_{10}]^+$ and reflects the reduced polarisation of σ electrons in the P–S (or P–Se) bonds because of the much longer bond distances :[10] P–O(br) $= 1.60 \times 10^{-10}$ and P–S(br) $= 2.09 \times 10^{-10}$ m. The decrease in the anisotropy (to zero in the case of $[P_4Se_{10}]^+$) is consistent with the lengthening of the bonds and the reduced indirect dipolar coupling and polarisation of $3p$ orbitals. The value of $g_\parallel$ also increases and is a result of larger spin–orbit coupling to S and Se and also destabilisation of the a_1 orbital energy level.

Since the unpaired electron is localised mainly on the sulphur and selenium atoms, then analysis of the ^{33}S or ^{77}Se hyperfine tensor would provide valuable information. No lines attributable to ^{33}S were seen, but in the selenide several low-intensity broad lines were observed extending up to 150 G from the main features which we attribute to ^{77}Se. We cannot analyse them properly since the direction of the hyperfine tensor for ^{77}Se is not collinear with that for ^{31}P and the turning points in the powder spectrum will be at an intermediate angle. Our apparent large coupling to ^{77}Se is the right order of magnitude for an electron in an a_2 molecular orbital which is effectively spread over p orbitals on three selenium atoms and polarising the electrons in selenium s orbitals. A single-crystal study would solve this, but single crystals cannot be grown, nor has the crystal structure been reported.

$[P_4O_{10}]^-$ *and* $[P_4S_{10}]^-$.—The pair of anisotropic lines with a large separation in γ-irradiated P_4O_{10} arise from a radical [species (2)] which from the form of its g and A tensors must be related to the 33-electron $[PO_4]^{4-}$ radical. We believe it to be $[P_4O_{10}]^-$ with one electron added to the $2a_1{}^*$ orbital which is largely based on one phosphorus atom. Since no further coupling to other phosphorus atoms was detected, there must be distortions to permit the electron to be largely localised on one phosphorus atom only. Signals were weak and broader than for $[P_4O_{10}]^+$, and so possible coupling to other phosphorus atoms was not detected. Molecular-orbital energy levels have been calculated[13] for D_{2d} distorted $[AsO_4]^{4-}$, but it is probable that our radical is C_{3v} distorted because of the dominant three-fold axis in P_4O_{10}. The electron would thus be in the $2a_1{}^*$ orbital which is mainly a mixture of $3s$, $3p_z$, $3d_{z^2}$, and appropriate oxygen orbitals (Figure 5). The derived unpaired electron p and s characters are similar to those for $[PO_4]^{4-}$, although the p character is now smaller and brings the $p:s$ ratio to $<1:1$ (Table). The bridging O–P–O bond angle is thus less than the corresponding angle in $[PO_4]^{4-}$ and correlates well with the bond angles in the parent molecule (101.6°) and ion (109.5°). With the unpaired electron in the $2a_1{}^*$ orbital, the g tensors will be given by expressions (3) and (4). Thus $g_\parallel > 2$

$$g_\parallel = 2 + \frac{2\lambda}{\Delta E(2a_1{}^* - a_2)} \quad (3)$$

$$g_\perp = 2 + \frac{2\lambda}{\Delta E(2a_1{}^* - 2e)} - \frac{2\lambda}{\Delta E(3e^* - 2a_1{}^*)} \quad (4)$$

and, because the third term dominates in the expression for $g_\perp$, $g_\perp \leqslant 2$. Our values correlate well with these predictions.

The corresponding radical in P_4S_{10} shows a small coupling to the other three phosphorus atoms (21.6 G). The larger overlap between the phosphorus and sulphur orbitals will permit transfer of some spin density to the other phosphorus atoms (up to 0.5%). The only other related radical which shows this type of behaviour is $[P_2O_7]^{5-}$ where there is a 68 G coupling to the second phosphorus atom.[8] The $[P_4S_{10}]^-$ radical is isotropic in contrast to $[P_4O_{10}]^-$. The larger bridging S–P–S angle (109°)[10] would lead us to expect a larger $p:s$ ratio for $[P_4S_{10}]^-$ than for $[P_4O_{10}]^-$. We suggest that the increased participation of both phosphorus and sulphur $3d$ orbitals could considerably alter the make-up of the $a_1{}^*$ orbital. The value of g compares well with that found for $[P_4O_{10}]^-$.

We found no evidence for $[P_4Se_{10}]^-$ in γ-irradiated P_4Se_{10}. Reasons for this are given in the mechanism section.

$[P_4S_9]^+$ *and* $[P_4Se_9]^+$.—Species (3) in γ-irradiated P_4S_{10} and P_4Se_{10} has e.s.r. g and A tensors very close to the 25-electron $[PO_3]^{2-}$ radical[7] which is a phosphorus-(IV) species having the unpaired electron in an antibonding a_1 orbital (C_{3v} symmetry) made up mainly of phosphorus $3s$, $3p_z$, and possibly $3d_{z^2}$ character plus appropriate orbitals on the oxygens. We postulate that the radicals formed are $[P_4S_9]^+$ and $[P_4Se_9]^+$ having an unpaired electron added to the apical phosphorus of the parent molecule but without an axial S or Se bonded to it. The slightly larger $3s$(P) character of the unpaired electron probably arises from the larger bridging S–P–S and Se–P–Se bond angles caused by the larger and less electronegative atoms rather than possible effects from involvement of *d* orbitals on the phosphorus, sulphur, and selenium. The reason for this is the electronegativity difference between P and O, S, or Se.[7] As the electronegativity difference increases, so the spin density on the central atom increases since the unpaired electron is in an antibonding orbital. There is a corresponding decrease in the $p:s$ ratio of the unpaired electron as the outer atoms attract p-electron density from the σ-bonding orbitals. The $p:s$ ratio and total central-atom ($s+p$) unpaired electron density for ClO_3, $[SO_3]^-$, $[PO_3]^{2-}$, $[PS_3]^{2-}$, and $[PSe_3]^{2-}$ fit this pattern well, which was pointed out by Symons for $[MO_3]^{2-}$ radicals.[7]

Mechanism of Radiation Damage.—The radicals formed arise from processes which may be described by equations (5)—(7). The radical cations are readily formed and

$$P_4X_{10} \longrightarrow [P_4X_{10}]^+ + e^- \qquad (5)$$

$$e^- + P_4X_{10} \longrightarrow [P_4X_{10}]^- \qquad (6)$$

$$[P_4X_{10}]^- \longrightarrow [P_4X_9]^+ + X^{2-} \qquad (7)$$

have strong signals. The released electron may be trapped by the host or be lost, and the resulting radical anion is formed in small abundance. Because the terminal P–S and P–Se bonds are much weaker than the terminal P–O bond, as reflected in the following bond lengths for P–O(t), P–O(br), P–S(t), and P–S(br) which are 1.40, 1.60, 1.96, and 2.09 × 10^{-10} m respectively [the P–Se bond lengths are not known but P–Se(t) is not expected to be much shorter than P–Se(br)], there is ready loss of S^{2-} or Se^{2-} to form $[P_4X_9]^+$ radicals. Indeed, the weakness of the P–Se bond means that $[P_4Se_{10}]^-$ is particularly unstable and dissociates immediately. This contrasts with the strength of the P–O(t) bond which is less likely to break with the formation of $[P_4O_9]^+$; such a radical was not detected.

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