Unstable Intermediates. Part CXXXI.[1] An Electron Spin Resonance Study of a Range of Radicals in Irradiated Phenylphosphonic Dichloride and Phenylphosphonothionic Dichloride

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Exposure of the title compounds [$PhP(O)Cl_2$ and $PhP(S)Cl_2$] to ^{60}Co γ-rays at 77 K gave initially e.s.r. spectra characteristic of the corresponding radical anions. Doublets of lower intensity were assigned to $PhP(O)Cl$ and $PhP(S)Cl$ radicals, the latter being clearly derived from the parent anions. Alone or in various solvents, the oxy-compound gave Cl_2^- on annealing, whereas the sulphur analogue gave $Ph\dot{P}(S)Cl$ radicals. The electronic structures of these four phosphorus radicals are discussed in the light of the e.s.r. data. In both cases, the pure compounds gave, on annealing, a species characterised by doublets separated by *ca.* 1400 G. For dilute solutions in a range of solvents, these species were not formed, and for this and other reasons we conclude that they are radical dimers containing two equivalent or nearly equivalent phosphorus atoms. Possible structures are discussed.

CONTINUING our studies of radicals that can be thought of as derivatives of the phosphorus oxy-radicals PO_3^{2-},[2] and PO_4^{4-},[3] (see, for example, refs. 4—6) we have compared the title compounds [$PhP(O)Cl_2$ and $PhP(S)Cl_2$] with respect to their reactivity towards ^{60}Co γ-rays and to the electronic structures of the resulting oxy- and thio-radicals. As expected, both three and four-co-ordinated radicals were formed, but several other unexpected results were obtained which add considerably to the interest of these studies. Thus the radical anions, $PhP(S)Cl_2^-$ reacted in various solvents to give $PhP(S)Cl$, presumably by loss of Cl^-, whilst $PhP(O)Cl_2^-$ gave, predominantly, Cl_2^- radicals. Kerr and Williams[7] recently showed that $SO_2Cl_2^-$ radicals gave Cl_2^- on annealing in various solvents, and came to the conclusion that the structure of the parent anion was a novel one which strongly favoured such an elimination. Our results for this system largely confirm those of Kerr and Williams, although features assigned to $^{33}SO_2Cl_2^-$ radicals were normal for this class of radicals.[8]

The other unexpected result was that on annealing, new doublets to high- and low-field of the doublets assigned to the parent anions were obtained. In previous work on irradiated phosphines and arsines, we observed similar behaviour, and concluded that these outer lines were the $M_I = \pm 1$ lines of dimers, $R_3P-PR_3^+$.[9] This was not perhaps very surprising for R_3P compounds, but is far more surprising for the four-co-ordinated phosphorus compounds used in the present study. So far as we are aware, none of the radicals reported in this work have been previously detected.

EXPERIMENTAL

Phenylphosphonothionic dichloride (Emanuel), phenylphosphonic dichloride (Emanuel), methyl cyanide (Koch-Light), [$^2H_3$]methyl cyanide (N.M.R. Limited, U.K.), [$^2H_4$]methyl alcohol (N.M.R. Limited, U.K.), methylcyclohexane (Hopkin and Williams) and carbon disulphide (May and Baker) were used without further purification. Glassy beads of phenylphosphonothionic dichloride and phenylphosphonic dichloride and their solutions were obtained by pipetting directly into liquid nitrogen. These were irradiated at 77 K in a ^{60}Co Vickrad source for up to 2 h, at a nominal dose rate of 4 Mrad h^{-1}. All glassy beads after exposure to γ-radiation were rose-pink in colour.

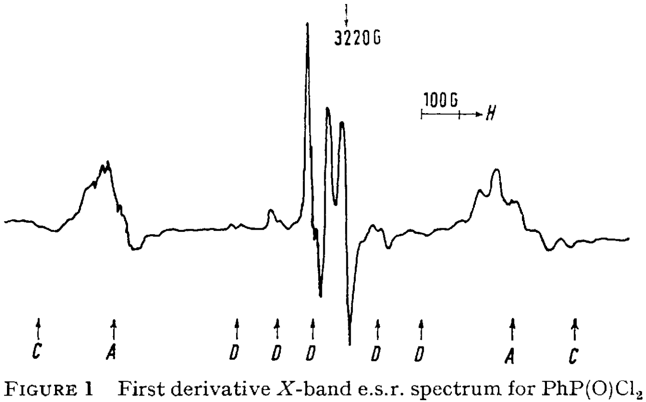

FIGURE 1 First derivative *X*-band e.s.r. spectrum for $PhP(O)Cl_2$ after exposure to ^{60}Co γ-rays at 77 K and partial annealing. Features (*A*), assigned to $PhP(O)Cl_2^-$ radicals, have decayed, and features (*C*), assigned to 'dimers,' and (*D*), assigned to Cl_2^- radicals, have grown during the annealing process

E.s.r. spectra were recorded at *X*-band frequencies on a Varian E3 spectrometer at 77 K and above. *Q*-Band spectra were recorded on a spectrometer constructed in these laboratories.[10]

RESULTS AND DISCUSSION

Typical results are shown in the Figures and the resulting data, suitably corrected, are summarised in the Table.

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[5] A. Begum and M. C. R. Symons, *J.C.S. Faraday II.*, 1973, **69**, 43.

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[7] C. M. L. Kerr and F. Williams, *J. Amer. Chem. Soc.*, 1972, **94**, 5212.

[8] K. V. S. Rao and M. C. R. Symons, *J.C.S. Dalton*, 1973, 9.

[9] A. R. Lyons and M. C. R. Symons, *J.C.S. Faraday II*, 1972, **68**, 1589.

[10] J. A. Brivati, J. M. Gross, M. C. R. Symons, and D. J. A. Tinling, *J. Chem. Soc.*, 1965, 6504.

Species A *and* A′.—In all solvents these species have spectra comprising a doublet splitting of *ca.* 1000 G split further into septets. The low field line was always relatively poorly resolved, and there was clear anisotropy in some solvents. This anisotropy has three origins, namely the *g*-tensor, and the ^{31}P and $^{35/37}Cl$ hyperfine tensors, and since the nett effect is small, we have made no attempt to estimate the different components. The values given in the Table are based on the arbitrary assumption that the chlorine coupling is nearly isotropic.

The most likely assignments for *A* and *A′* are the molecular cations or anions of the parent molecules. The cations are isostructural with species such as PO_4^{2-}, and are expected to have their unpaired electrons located primarily in non-bonding orbitals on the ligands.[11] The large hyperfine coupling to ^{31}P therefore rules out such species.

The anions, however, are expected to exhibit very large hyperfine coupling to ^{31}P since, unless it were to be accommodated in the benzene ring, the unpaired electron should be placed in an orbital primarily on phosphorus and having considerable 3*s*-character.[11] Radicals of this class are usually distorted from the near tetrahedral structure of the parent molecules in a manner that places the most electronegative ligands into a near *trans*-axial position and the remaining two together with the unpaired electron into equatorial positions. This results in considerable hyperfine interaction with the axial ligands but only minor interaction with the equatorial ligands.[12] The strong hyperfine couplings to chlorine in *A* and *A′* are certainly reasonable for the anions $PhP(O)Cl_2^-$ and $PhP(S)Cl_2^-$, by comparison with values for the related radicals PCl_4, $POCl_3^-$, and $SO_2Cl_2^-$, as indicated in the Table, and these assignments will be accepted in the remaining discussion.

Magnetic data for various phosphorus radicals obtained by exposing $PhP(O)Cl_2$ and $PhP(S)Cl_2$ to high energy radiation, together with some data for related radicals

Symbol	Radical	^{31}P Hyperfine coupling/G			$^{35/37}Cl$ Isotropic hyperfine coupling/G	*g*-Values		
		$A_{\parallel}$	$A_{\perp}$	A_{iso}		$g_{\parallel}$	$g_{\perp}$	g_{av}
A	$PhP(O)Cl_2^-$	*ca.* 1150	925	1000	51	2·004	2·012 [a]	2·009
A′	$PhP(S)Cl_2^-$	*ca.* 1120 [a]	900 [a]	973	43	2·008 [a]	2·016 [a]	2·013
B	$Ph\dot{P}(O)Cl$	⩾550 [a]	*ca.* 450			2·004 [a]	2·012	
B′	$Ph\dot{P}(S)Cl$	550	370	430		2·006	2·020	2·015
C	$PhP(O)Cl_2$ ' dimer '			700				*ca.* 2·03
C′	$PhP(S)Cl_2$ ' dimer '			700				*ca.* 2·03
	PCl_4 [b]			1206	62(two) 7(two)			2·013
	$OPCl_3^-$ [c]			1359	67(two)15(one)			2·018
	$SO_2Cl_2^-$ [d]				67			2·018
	$POCl_2$ [c]	893	692	759	18	1·971	2·0176	2·002
	HPO_2^- [e]	550	383	495				
	$Et_3P{-}PEt_3^+$ [f]	540	412	454·7		2·00	2·012	2·008

[a] Possible values based on the overall anisotropy (see text). [b] G. F. Kokoszka and F. E. Brinckman, *J. Amer. Chem. Soc.*, 1970, **92**, 1199. [c] Ref. 4. [d] Ref. 7. [e] J. R. Morton, *Mol. Phys.*, 1962, **5**, 217. [f] Ref. 9.

Radicals B *and* B′.—Weak doublets separated by *ca.* 500 G were always detected after irradiation at 77 K, and these were generally enhanced during the initial annealing stages. Only in the case of the sulphur compound, *B′*, however, were we able to obtain conditions that resulted in dominance by this species (Figure 2*a*). In the oxy-compound, annealing gave mainly Cl_2^-, as indicated in Figure 1. When the sulphur compound was irradiated in the good anion solvating medium CD_3OD, *B′* was the major primary product at 77 K.

These species (*B* and *B′*) are thought to be PhP(O)Cl and PhP(S)Cl respectively, and are formed from the anions (*A* and *A′*) by loss of chloride ion. This identification rests strongly upon comparison with results for many similar radicals. Thus the data for HPO_2^- given in the Table are very close to those now found for radical *B′* (the parallel features for *B* were never clearly defined because of overlap with neighbouring lines from other radicals). Also, recent results of Geoffrey and Lucken[13] for $PhPO_2^-$ and PhP(O)OH radicals accord very well with those now reported. As stressed by Geoffrey and Lucken, it is interesting to view these radicals as benzene derivatives and to compare them with the well known nitrobenzene anions. The latter have a high spin-density in the aromatic ring and, unless steric factors intervene, the benzene ring is co-planar with the nitro-group. There is some evidence for a tendency to become pyramidal at the nitrogen centre,[14] but this is undoubtedly small. In contrast, the phosphorus analogues are strongly pyramidal at phosphorus, and the extent of delocalisation into the aromatic ring seems to be very small.

Radicals C *and* C′.—The features indicated in Figures 1 and 2*a* as *C* and *C′* only appeared during the annealing process, and never in good relative yields. Since they were always somewhat overlapped by the lines assigned

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[11] P. W. Atkins and M. C. R. Symons, ' The Structure of Inorganic Radicals,' Elsevier, Amsterdam, 1967.

[12] J. Higuchi, *J. Chem. Phys.*, 1969, **50**, 1001.

[13] M. Geoffrey and E. A. C. Lucken, *Mol. Phys.*, 1972, **24**, 335.

[14] J. H. Sharp and M. C. R. Symons, *Nature*, 1969, **224**, 1297.

to $PhP(O)Cl_2^-$ or $PhP(S)Cl_2^-$ (A or A'), it was never possible to estimate more than an average ^{31}P splitting (Table) although considerable structure, presumably from $^{35/37}Cl$, usually appeared on the high field lines.

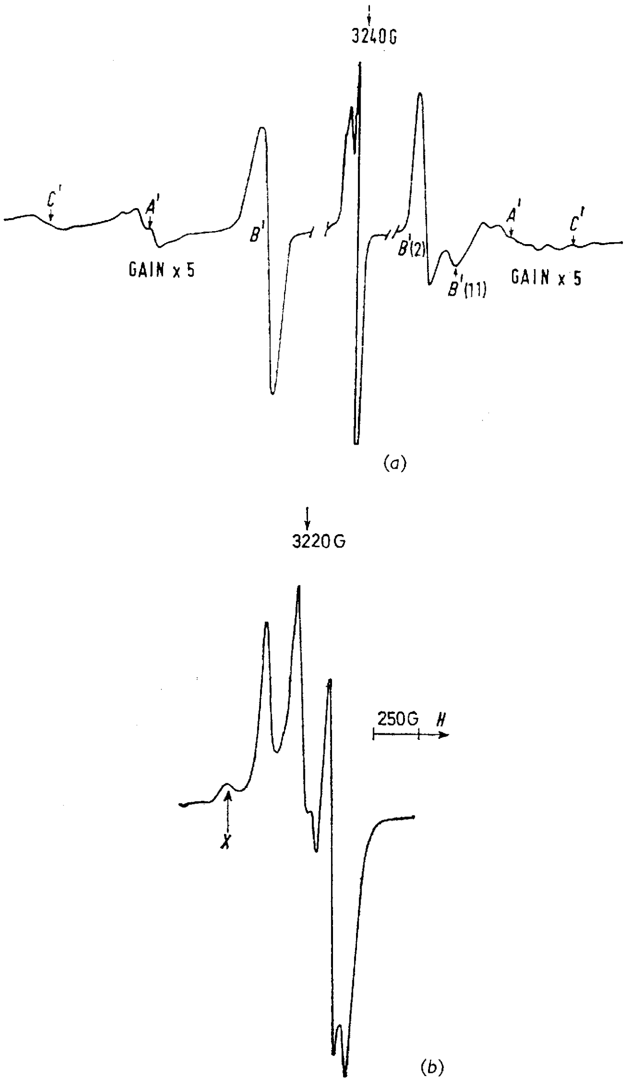


FIGURE 2 First derivative X-band e.s.r. spectra for $PhP(S)Cl_2$ after exposure to ^{60}Co γ-rays at 77 K and partial annealing; (a) features (A'), assigned to $PhP(S)Cl_2^-$ radicals, have decayed, and features (C'), assigned to 'dimers,' and (B'), assigned to PhP(S)Cl radicals, have grown during the annealing process; (b) expanded central region showing extra feature (X) possibly associated with species (C'), which was selectively lost, together with (C') on further annealing

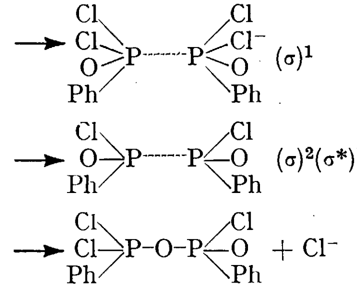
If this large coupling is caused by a single ^{31}P nucleus, we need to discover some species which has a considerably higher spin-density (3s-character) on phosphorus than is the case for the parent anions. One possible pair would be the chlorine atom adducts, $PhP(O)Cl_3$ or $PhP(S)Cl_3$. We know of no authenticated examples of such adducts, but do not consider them to be very probable chemically, nor that they would have the required large ^{31}P hyperfine interaction.

There is, however, one explanation that removes the need to postulate such a large hyperfine coupling, namely the formation of dimers. In previous work we have established that the reaction

$$R_3P^+ + PR_3 \longrightarrow R_3P\text{-}PR_3^+ \qquad (1)$$

is of some importance, but we have never needed to invoke similar dimer formation from four-co-ordinated species. If dimers of some sort are responsible, the real ^{31}P hyperfine coupling is *ca.* 700 G, and the g_{av} value must be considerably greater than that of the free spin (Table). Both the ^{31}P couplings and the g-values are rather greater than those assigned to $R_3P\text{-}PR_3^+$ radicals, so that the structures may well be different. The following reactions seem to be reasonable:

$PhP(O)Cl_2^- + PhP(O)Cl_2$



(2)

(3)

(4)

The radical product in (2) has a one electron σ bond between the two phosphorus atoms, which, in view of the steric crowding, is unlikely to be formed. That in (3) is isostructural with $(R_3P\text{-}PR_3)^+$, and should have a larger ^{31}P hyperfine coupling for reasons similar to those that make the ^{31}P coupling of the parent R_3P^+ radicals increase with increase in the electronegativity of the ligands.

The radical product in (4) is of a type not previously postulated, so far as we know. The unpaired electron would be expected to be almost evenly distributed despite the lack of symmetry but the distortions from local tetrahedral symmetry at the phosphorus atoms are likely to be less than in the monomer anions because of the lower spin densities. This structural feature could well be responsible for the rather large g-shift, and we are inclined to favour process (4) for this reason. We have as yet been unable to devise effective experiments which would help to distinguish between these different formulations.

The central lines obtained in these studies are probably caused by positive hole centres such as $PhP(S)Cl_2^+$ in which the spin is largely confined to the sulphur ligand, but spectra were never sufficiently clear to prove this suggestion.

Reactions.—The reactions of the parent anion resemble those studied by Kerr and Williams for $SO_2Cl_2^-$.[7] Thus, on annealing in various solvents, clear features for Cl_2^- were obtained both for $SO_2Cl_2^-$ and $PhPOCl_2^-$. (The suggestion [7] that SO_2^- is also formed during the thermal annealing process is one that we have not been able to confirm: also, no evidence for PhPO$^-$ was obtained in the present study.)

In marked contrast, Cl_2^- radicals were not obtained from $PhP(S)Cl_2^-$, which clearly dissociates to give $Ph\dot{P}SCl + Cl^-$ in preference. This contrast is a subtle one, and the only contributing factor which we can discern at present is the fact that the spin density on the two chloride ligands in $PhP(O)Cl_2^-$ is greater than that in $PhP(S)Cl_2^-$, which presumably has an appreciable spin density on the sulphur ligands. We hope to learn more about this interesting contrast by studying a range of dihalide anions of this type.

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