Radiation Mechanisms. Part II.[1] Electron Spin Resonance Studies of the Mechanism of Radiation Processes in Trivalent Phosphorus Derivatives

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A range of phosphites (trimethyl phosphite, trimethyl and tripropyl thiophosphite, di-isopropylphosphinyl chloride, diphenylphosphinyl chloride, and dithioethylphosphinyl chloride) have been exposed, either pure or in a range of solvents, to ^{60}Co γ-rays at 77 K. The radical products have been analysed by e.s.r. spectroscopy. We conclude that, after electron addition, the radical anions may protonate on phosphorus, lose an anionic ligand to give a phosphinyl radical or lose a neutral ligand (alkyl, alkoxy, thiyl, or chlorine radicals). These radicals may subsequently add to adjacent molecules to give a range of phosphoranyl species. It is also suggested that the primary anion may sometimes rearrange to give an alkylphosphoranyl radical directly.

The primary cation-radicals, $\cdot PL_3^+$, react efficiently with PL_3 neighbours to give the dimer-cations, $P_2L_6^+$, but in dilute solution this is suppressed. Addition of methyl bromide suppresses anion formation and the resulting less complicated e.s.r. spectra show one of the $M_I = 0$ components (1,0) for the dimer-cations.

CHARACTERISATION of phosphinyl radicals ($\dot{P}L_2$),[2,3] phosphonyl radicals ($\dot{P}L_3$),[3-6] and phosphoranyl radicals ($\dot{P}L_4$)[7-11] by e.s.r. spectroscopy is now reasonably well established, although difficulties may arise in distinguishing between $\dot{P}L_3$ and $\dot{P}L_4$ species.[12] However, many aspects of the free radical chemistry of phosphorus

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[1] Part I, I. S. Ginns and M. C. R. Symons, *J.C.S. Dalton*, 1975, 514.

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[3] D. Griller, B. P. Roberts, A. G. Davies, and K. U. Ingold, *J. Amer. Chem. Soc.*, 1974, **96**, 554.

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[9] M. C. R. Symons, *J. Chem. Phys.*, 1970, **53**, 857.

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

[11] M. C. R. Symons, *Mol. Phys.*, 1972, **24**, 885.

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compounds remain obscure,[13] and this applies particularly to radiation mechanisms.

Very recently, Griller *et al.*,[3] using liquid-phase e.s.r. spectroscopy, have shown that all three classes of radicals react at, or close to, diffusion-controlled rates. They, and others,[7,8] usually generate these radicals by photolysis of di-t-butyl peroxide (BOOB) in the presence of suitable substrates, *e.g.*:

$$\mathrm{BOOB} \xrightarrow{h\nu} 2\mathrm{BO}\cdot$$

$$\mathrm{BO}\cdot + \mathrm{PL}_3 \longrightarrow \mathrm{BO\dot{P}L_3}\cdot \qquad (1)$$

Secondary processes are often significant, including

$$\mathrm{RO\dot{P}L_3} \longrightarrow \mathrm{R}\cdot + \mathrm{OPL_3} \qquad (2)$$

and

$$\mathrm{RO\dot{P}L_3} \longrightarrow \mathrm{L}\cdot + \mathrm{ROPL_2} \qquad (3)$$

Teranchi and Sakuri[14] have used e.s.r. spectroscopy to study the solid-state photolysis of pure triethyl phosphite and detected the ethyl radical together with two phosphorus-containing radicals which they identified as $(\mathrm{EtO})_2\mathrm{PO}\cdot$ and $\mathrm{O\dot{P}(OEt)_2}$. These results are discussed below. We have carried out extensive radiation studies of trialkylphosphines at 77 K, both pure and in various solvents,[15-17] but we failed to detect any primary radical anions or their breakdown products. Cation-radicals were not detected as such (except in sulphuric acid, when the substrate was $\mathrm{HPR_3}^+$ rather than $\mathrm{PR_3}$), but in the pure materials dimeric cations

$$\mathrm{R_3P}^{\cdot +} + \mathrm{PR_3} \longrightarrow \mathrm{R_3P \overset{\cdot}{-} PR_3}^+ \qquad (4)$$

were well characterised.[17]

A preliminary study of γ-irradiated trimethyl phosphite in methanol[11] indicated that a wide range of interesting radicals can be formed from such substrates, and we have therefore extended this work to include several similar compounds in a range of solvents.

EXPERIMENTAL

Di-isopropylphosphinyl chloride and diethylthiophosphinyl chloride were kindly donated by Professor S. Trippett. Trimethyl thiophosphite and tri-n-propyl thiophosphite were prepared by the reaction of the respective disulphide with powdered white phosphorus.[2] Trimethyl phosphite (B.D.H. Chemicals Ltd.) and diphenylphosphinyl chloride (Maybridge Chemicals) were used as received. All samples were irradiated in evacuated silica tubes, having been thoroughly degassed by freeze–pump–thaw cycles. Solvents were added by vacuum distillation directly onto the samples and the solutions frozen immediately to prevent any solvolysis. All samples were irradiated at 77 K in a Vickrad $^{60}\mathrm{Co}$ γ-source for periods up to 2 h.

Samples of trimethyl thiophosphite and trimethyl phosphite were frozen to 77 K, in silica tubes, under a nitrogen atmosphere before being photolysed, using a Wooten 200 W super-high pressure mercury lamp. E.s.r. spectra were obtained using a Varian E3 X-band spectrometer.

RESULTS AND DISCUSSION

Identification.—Spectral features were generally separated into three groups. The first covers the free-spin region with features from alkyl and substituted alkyl radicals together with the perpendicular features for $\mathrm{\dot{P}L_2}$ radicals and the $M_\mathrm{I} = 0$ features for the dimer cations. The second spans *ca.* 300 G and is dominated by the parallel features for $\mathrm{\dot{P}L_2}$ radicals and the third spans the 700—1000 G region, with parallel and perpendicular features from $\mathrm{\dot{P}L_3}$, $\mathrm{\dot{P}L_4}$, and $\mathrm{L_3P{-}PL_3}^+$ radicals.

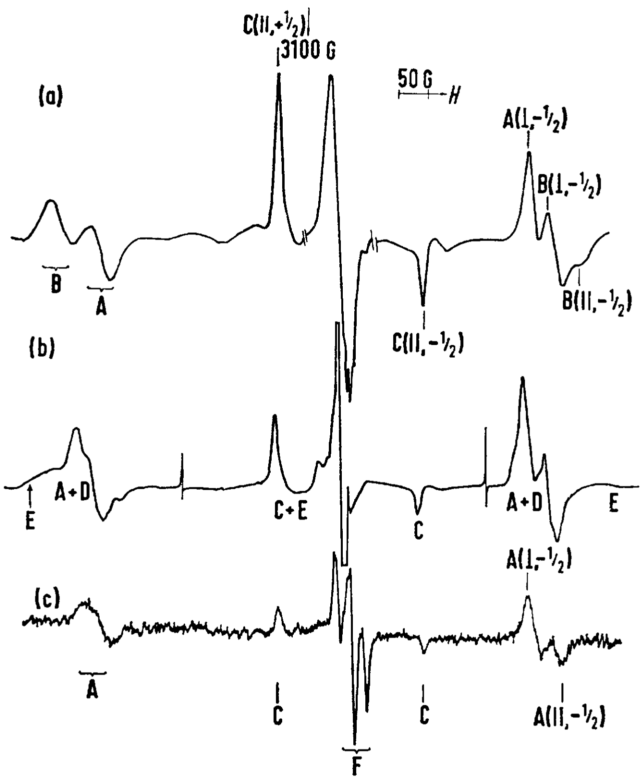

FIGURE 1 First derivative X-band e.s.r. spectra for $(\mathrm{MeS})_3\mathrm{P}$, (a) after exposure to $^{60}\mathrm{Co}$ γ-rays at 77 K showing features assigned to $\mathrm{Me\dot{P}(SMe)_3}$ and/or $\mathrm{Me\dot{P}S(SMe)_2}^-$ (A), $(\mathrm{MeS})_4\dot{\mathrm{P}}$ (B), and $(\mathrm{MeS})_2\dot{\mathrm{P}}$ (C); (b) after exposure of a dilute solution in methanol to $^{60}\mathrm{Co}$ γ-rays at 77 K and slight annealing to remove trapped methyl radicals and some $(\mathrm{MeS})_2\dot{\mathrm{P}}$ radicals, showing features assigned to residual $(\mathrm{MeS})_2\dot{\mathrm{P}}$ (C), $\mathrm{Me\dot{P}(SMe)_3}$ or $\mathrm{Me\dot{P}S(SMe)_2}^-$ (A), together with $(\mathrm{MeS})_2\mathrm{P{-}\dot{P}(SMe)_3}$ (D), and $(\mathrm{MeS})_3\mathrm{\dot{P}{-}P(SMe)_3}^+$ radicals (E); (c) after photolysis and annealing showing features assigned to $\mathrm{H_2\dot{C}SP(SMe)_2}$ (F)

Interpretation for the first two regions was generally unambiguous. However, the third region was often difficult to interpret because of the presence of several overlapping features. The dimer-cations were usually clearly defined because of the large separation between the $M_\mathrm{I} = \pm 1$ features and the fact that these are almost symmetrically placed about the centre ($g = 2$) region in contrast with features for $\mathrm{\dot{P}L_3}$ and $\mathrm{\dot{P}L_4}$ species which, of course, exhibit large second-order shifts.

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[13] See, for example, C. Walling and M. S. Pearson, *Topics Phosphorus Chem.*, 1966, **3**, 1; J. I. G. Cadogan, *Adv. Free-Radical Chem.*, 1967, **2**, 203.

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[15] A. Begum, A. R. Lyons, and M. C. R. Symons, *J. Chem. Soc.* (*A*), 1971, 2290.

[16] A. Begum, A. R. Lyons, and M. C. R. Symons, *J. Chem. Soc.* (*A*), 1971, 2388.

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

Progressive annealing frequently resulted in selective loss of sets of features and, at temperatures above 77 K, rotations or librations resulted in better resolution, thus, for example, revealing superhyperfine coupling to chlorine nuclei. In some cases, addition of methyl bromide resulted in marked reduction in the concentrations of species formed by electron-capture processes, whilst leaving cationic species unaffected. However, this had the side effect of generating methyl adducts in most instances.

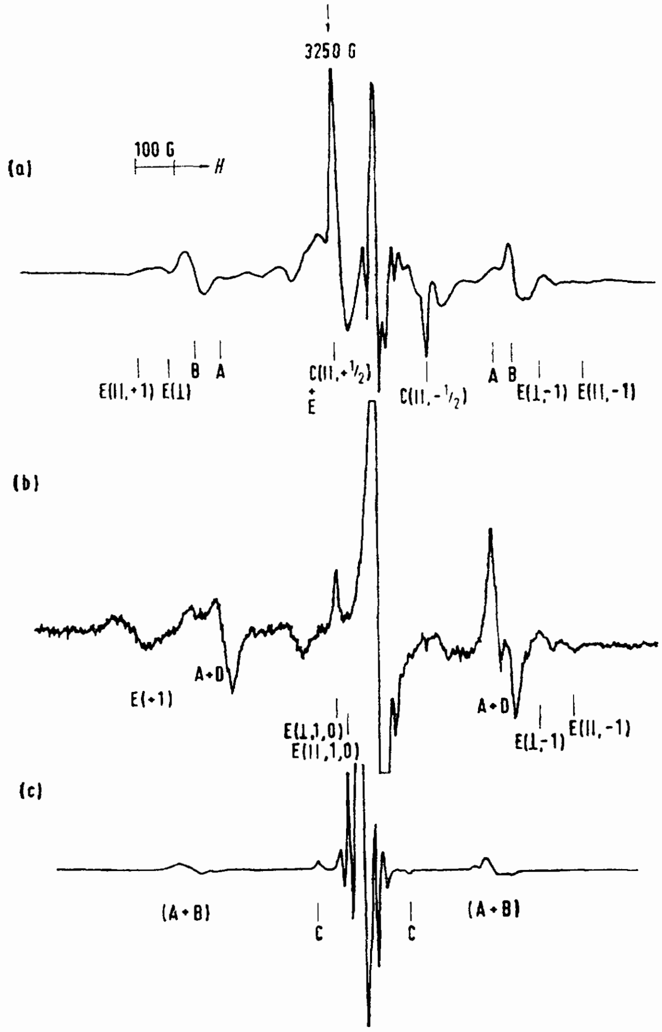


FIGURE 2 First derivative X-band e.s.r. spectra for $(PrS)_3P$ after exposure to ^{60}Co γ-rays at 77 K, (a) for the pure material showing features assigned to $(PrS)_2\dot{P}$ (C), $Pr–\dot{P}(SPr)_3$ or $Pr\dot{P}S(SPr)_2$ (A), $(PrS)_4\dot{P}$ (B), and $(PrS)_3P–P(SPr)_3^+$ (E). In addition, features for trapped Pr· radicals are indicated in the centre. Other weak features have not been clearly identified, but may include those for $H\dot{P}(SPr)_3$ and $S\dot{P}(SPr)_2$ radicals; (b) for a mixture of $(PrS)_3P$ and MeBr, after slight annealing, showing, in particular, features assigned to the (1,0) feature for $(PrS)_3P–P(SPr)_3^+$; (c) for a dilute solution in methanol before annealing, showing dominating features for Pr· and $\dot{C}D_2OD$ radicals

A selection of typical spectra is shown in the Figures and data relevant to the task of identification together with brief comments on the basis of our identifications are given in the Table.

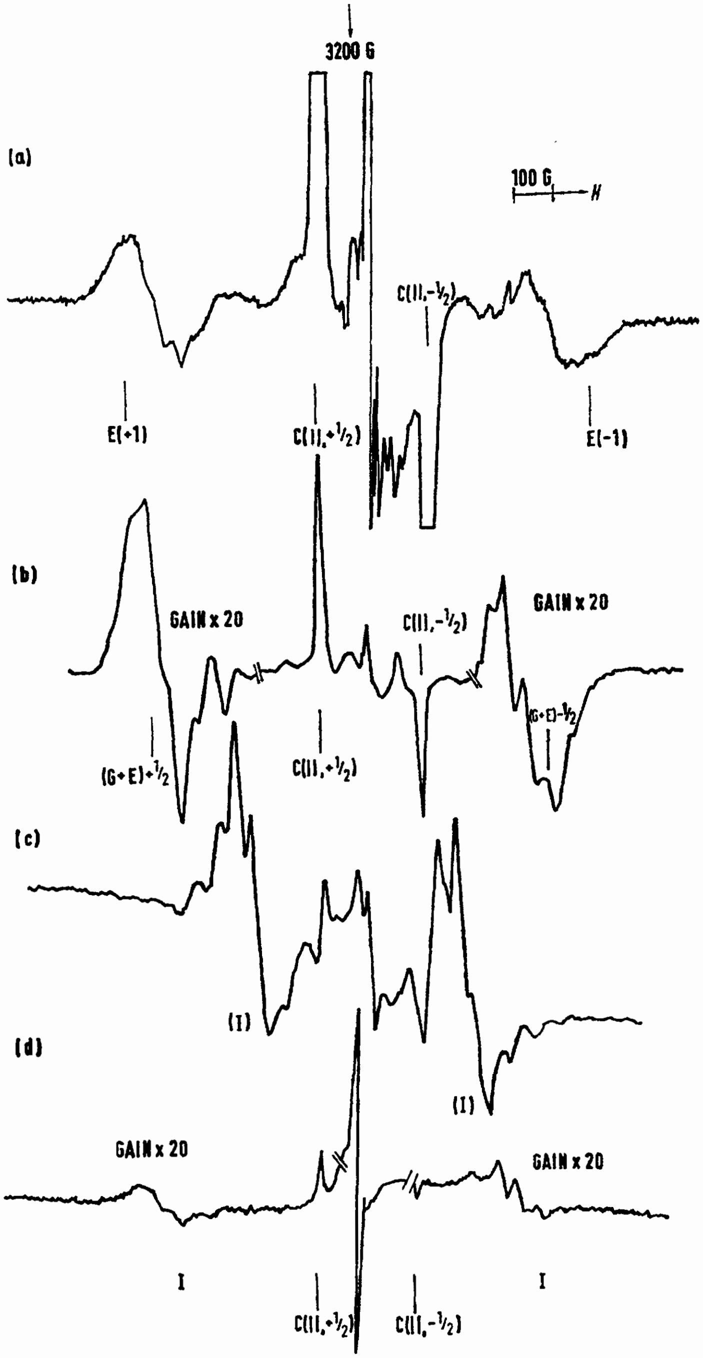
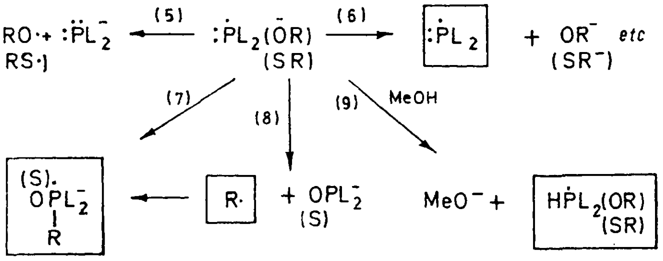


FIGURE 3 First derivative X-band e.s.r. spectra for various R_2PCl derivatives after exposure to ^{60}Co γ-rays at 77 K, (a) $Pr^i{}_2PCl$ before annealing, showing features assigned to the dimer-cations (E) overlapping those assigned to the dichloride, $Cl_2\dot{P}Pr^i{}_2$, together with those for $Pr^i\dot{P}_2$ (C) and Pr^i· radicals (central lines); (b) for Ph_2PCl before annealing, showing features assigned to the dimer-cations (E) which partially obscure those for the dichloride (G) (these were well defined during the annealing process); (c) as (b), after annealing, showing features assigned to the monochloride, $Ph_3\dot{P}Cl$ or $Ph_2P–\dot{P}(Ph)_2Cl$ (I); (d) for $(EtS)_2PCl$ after annealing, showing features assigned to $(EtS)_2\dot{P}(Et)Cl$ or $(EtS)_2P–(S\dot{P}Et)_2Cl$ (I) radicals and $(EtS)\dot{P}_2$ (C) radicals

Aspects of Mechanism

Electron-trapping.—In no instance have we been able to identify the primary anionic species, $\dot{P}L_3^-$. We know of no well defined phosphorus radicals in this class, which can be viewed as phosphoranyl radicals with a ' lone-pair ' of electrons occupying one of the ligand sites. We therefore predict a relatively small hyperfine coupling to ^{31}P using the usual ligand-electronegativity arguments,[12] and such spectra were not detected. The following Scheme summarises the processes which we require in order to accommodate the results:



SCHEME

In addition we include the formation of phosphoranyl radicals by the following steps

$$R\cdot + PL_3 \longrightarrow R\dot{P}L_3 \qquad (10)$$

$$RO\cdot + PL_3 \longrightarrow RO\dot{P}L_3 \qquad (11)$$

and possible additions of the type

$$\dot{P}L_2 + PL_3 \longrightarrow L_2P\text{-}\dot{P}L_3 \qquad (12)$$

We conclude that $P(OMe)_3^-$ reacts to give $\dot{P}(OMe)_2$ as a major path. However, methyl radicals are formed either by step (8) or by an excitation process followed by dissociation

$$P(OMe)_3 \longrightarrow Me\cdot + O\dot{P}(OMe)_2 \qquad (13)$$

and then add efficiently by step (10) to give $Me\dot{P}(OMe)_3$ radicals. In our view step (13) is unlikely in systems in which electron trapping is efficient, as in the present study. Certainly we have not been able to detect features for $O\dot{P}(OMe)_2$ radicals in any of our spectra. (However, see below.)

In methanol, $\dot{P}(OMe)_3^-$ may also be protonated since the species $H\dot{P}(OMe)_3$ is clearly trapped. Since $A(^1H) = 157$ G this species must have H in an axial site, and we have previously suggested that it is formed by H atom attack on the parent material.[11] Whilst this is probable, it is also possible that $\dot{P}(OMe)_3^-$ when first formed at 77 K adopts a structure in which the lone-pair is placed axial because this involves the smallest net ligand movement. In that case, rapid protonation would give the required products. Since methyl bromide suppresses this species, we believe that this is a significant mechanism.

In a range of experiments with careful temperature control, attempts were made to detect the change from the unstable isomer of $H\dot{P}(OMe)_3$ with H axial to the stable form with H equatorial. In no instance could this change be detected. The axial species remained as such until the glass began to soften, at which temperature all features rapidly decayed with no new one developing.

Also in methanolic solution, the phosphoranyl radical $\dot{P}(OMe)_4$ was detected,[11] but this is not formed in the pure material. Therefore step (5) is thought to be insignificant.

The sulphides $P(SMe)_3$ and $P(SPr)_3$ also form anions which readily dissociate to give $\dot{P}L_2$ radicals at 77 K. They also give Me· and Pr· radicals which are clearly trapped in solvents but add to give $R\dot{P}(SR)_3$ radicals in the pure materials. Indeed, for the isopropyl derivative we were able to control the annealing stage so that the loss of features for R· was seen to parallel the growth in those assigned to the $R\dot{P}(SR)_3$ adduct. In all these cases the hyperfine coupling to ^{31}P suggests that the alkyl adducts have R in an equatorial site, so that we must conclude either that axial attack is not favoured or that rearrangement to place R equatorial can occur efficiently at 77 K. The latter is a surprising result in the light of the stability of the HPL_3 species having hydrogen in the axial site. Equatorial attack is equally surprising because it requires greater adjustment of the existing ligands.

In methanolic solution RO· addition does not occur, in contrast with the results for $P(OMe)_3$. However, there seem to be two very similar species having ^{31}P coupling constants for alkyl adducts, one of which is formed at 77 K, the other growing in as $[R\cdot]_t$ falls. We suggest that an efficient internal rearrangement occurs (7) which may proceed *via* (8) and a cage back-reaction, to give $S\dot{P}(SR)_2R^-$ which should be quite similar in magnetic properties to $R\dot{P}(SR)_3$. Again, the R-group is in the equatorial site. Unfortunately electron scavenging by MeBr results in the formation of methyl radicals which also attack the substrate to give $Me(\dot{P}SR)_3$ radicals.

In several cases during annealing, loss of $\dot{P}L_2$ radicals resulted in a clear growth in the $R\dot{P}L_3$ features and we suggest that reaction (12) occurs. In most cases no clear coupling to a second ^{31}P nucleus was detected, but since several different species are thought to be present this is not surprising. However, in a few instances the high-field perpendicular features exhibited a splitting of *ca.* 35 G, which we tentatively attribute to a second phosphorus atom, probably in an equatorial site.

In the pure sulphides, but not in dilute glasses, an adduct with a ^{31}P coupling in the 800—900 G region was formed. The only reasonable candidate for this is $\dot{P}(SR)_4$, so that process (5) must have occurred, in contrast with the results for $P(OMe)_3$. This probably reflects the lower electronegativity of the RS group compared with that for the RO group.

We have also briefly studied the solid-state photolysis of $P(SMe)_3$. Methyl radicals were clearly trapped and during the annealing stage were converted into $Me\dot{P}(SMe)_3$ radicals having identical parameters with those detected in the radiolyses. Some $H_2\dot{C}SP(SMe)_2$ radicals were also formed at 77 K (F in Figure 1c), and traces of $\dot{P}(SMe)_2$ radicals were also detected. However, no clear features for $S\dot{P}(SMe)_2$ radicals were observed, unless these fall underneath those for $Me\dot{P}(SMe)_3$ radicals. This is, in our view, unlikely, since it would require that $S\dot{P}(SMe)_2$ radicals have a larger coupling to ^{31}P than do $O\dot{P}(OMe)_2$ radicals.

We recall that Teranchi and Sakurai, in their work on $P(OEt)_3$ detected two phosphorus radicals, one of which they described as $\cdot O{-}P(OEt)_2$ and the other $O\dot{P}(OEt)_2$. We stress that these species can hardly be expected to co-exist as separate entities, and that the phosphonyl structure undoubtedly is the better approximation. In fact, their results (as interpreted from their figures, and using the ethyl radical spectra for calibration) suggest that one of their radicals was $\dot{P}(OEt)_2$ (parallel features) and the other $Et{-}\dot{P}(OEt)_3$. Thus their results agree with ours. We suggest that absence of $O\dot{P}(OEt)_2$ and $S\dot{P}(SMe)_2$ radicals can be understood if these also add to neighbouring substrate molecules, since, as discussed above, the resulting phosphoranyl radicals would have spectra very similar to those for the alkyl adducts.

Some magnetic data for various phosphorus radicals

Parent material	Radical	^{31}P and ^{35}Cl Hyperfine coupling constants (G) [a, b] $A_{\parallel}$	$A_{\perp}$	A_{iso}	Comments
$P(OMe)_3$	$\dot{P}(OMe)_2$	285	~0	~95	Suppressed by MeBr
	$Me\dot{P}(OMe)_3$ [c]	882	722	775	Formed by Me· from MeBr
	$\dot{P}(OMe)_4$	990	840	890	Only formed in MeOH
	$P_2(OMe)_6^+$	720	615	650	Suppressed in dilute solutions
	$H\dot{P}(OMe)_3$	680	535	583	$A(^1H) \doteqdot 157$ G
$P(SMe)_3$	$\dot{P}(SMe)_2$	237·6	~0	~79·4	Suppressed by MeBr
	$Me\dot{P}(SMe)_3$ [d, e]	775	670	705	Formed by Me· from MeBr
	$\dot{P}(SMe)_4$	870	770	803	Suppressed in solvents
	$P_2(SMe)_6^+$	595	480	518	Suppressed in solvents
	$\dot{P}(SMe)_3^+$	690	785	720	Only in MeOH
$P(SPr)_3$	$\dot{P}(SPr)_2$	246	−15	71·8	Suppressed by MeBr
	$Pr\dot{P}(SPr)_3$ [f, g]	800	670	713	$Me\dot{P}(SBr)_3$ formed by MeBr
	$\dot{P}(SPr)_4$	890	790	823	Suppressed in solvents
	$P_2(SPr)_6^+$	590	480	516	Suppressed in solvents
	$\dot{P}(SPr)_3^+$	785	690	720	Only in MeOH
$Pr^i{}_2PCl$	$\dot{P}(Pr^i)_2$	246	−15	71·8	
	$Cl_2\dot{P}(Pr^i)_2$	←	~850	→	When coupling to ^{35}Cl and ^{37}Cl was detected, $\parallel$ and $\perp$ features were not sufficiently resolved to justify precise extraction of data
	$Cl\dot{P}(Pr^i)_3$ [h]	←	~650	→	
	$Cl_2P_2(Pr^i)_4^+$	←	~600	→	
Ph_2PCl	$Ph_2\dot{P}$	286	−13	78·7	For all phosphoranyl chlorides $A_{\parallel}(^{25}Cl) \doteqdot 70$ and $A_{\perp}(^{35}Cl) \doteqdot 25$, ± *ca.* 5 G
	$Cl_2\dot{P}Ph_2$	←	~840	→	
	$Cl{-}\dot{P}Ph_3$ [i]	←	~690	→	
	$Cl_2P_2(Ph)_4^+$	←	~600	→	
$(EtS)_2PCl$	$(EtS)_2\dot{P}$				All dichlorides rapidly lost on annealing, but no Cl_2^- formed
	$Cl_2\dot{P}(SEt)_2$	←	~1150	→	
	$Cl{-}\dot{P}(SEt)_2Et$ [j]	←	~880	→	
	$Cl_2P_2(SEt)_4^+$	←	~600	→	

[a] G = 10^{-4} T. [b] Corrected using the Breit Rabi equation. [c] And/or $Me\dot{P}O(OMe)_2^-$. [d] And/or $Me\dot{P}S(SMe)_2^-$. [e] The species $(MeS)_2P_{(1)}{-}\dot{P}_{(2)}(SMe)_3$ having $A(^{31}P_{(1)}) \doteqdot 35$ G is also thought to be formed. $A(^{31}P_2)$ Is approx. as recorded above. [f] And/or $Pr\dot{P}S(SPr)_2^-$. [g] The species $(Pr)_2P_{(1)}{-}\dot{P}_{(2)}(SPr)_3$ having $A(^{31}P_{(1)}) \doteqdot 35$ G is also thought to be formed. [h] And/or $(Pr^i)_2P{-}\dot{P}(Pr^i)_2Cl$. [i] And/or $Ph_2P{-}\dot{P}(Ph)_2Cl$. [j] And/or $(EtS)_2P{-}\dot{P}(SEt)_2Cl$.

The major electron-capture process for the chlorides results in dissociation (6) to give $\dot{P}L_2$ radicals. However, two chlorine-containing phosphoranyl radicals were formed in all three cases studied [$Pr^i{}_2PCl$, Ph_2PCl, and $(PrS)_2PCl$], one being almost certainly an axial dichloride (the results were obscured by overlap with the dimer features, but at least five components could be detected for these species during the annealing experiments) and the other a mono-chloride.

We therefore suggest that some chlorine atom transfer occurs to give $R_2\dot{P}Cl_2$ having both chlorine ligands axial, as expected. The data suggest that the mono-chloro-species are formed by alkyl (or phenyl) radical attack on the parent molecules.

Cationic Centres.—In all cases, the pure compounds gave no evidence for primary $\dot{P}L_3^+$ radicals, but clear outer features for $L_3P{-}PL_3^+$ dimer-cations were obtained. In our original studies [11,17] we were unable to detect the two '$M_I = 0$' components of the ^{31}P hyperfine structure because of overlap with features from other radicals. However, in the present experiments with added methyl bromide, many of these interfering lines were removed and the low-field component (1,0) of the split central line was clearly revealed. The splittings ($\delta_{\parallel}$ and $\delta_{\perp}$) between the (1,0) and (0,0) components of the central feature can be estimated approximately from the hyperfine parameters ($A_{\parallel}$ and $A_{\perp}$ for ^{31}P) deduced from the $M_I = \pm 1$ lines, using $\delta_{\parallel} \doteqdot A_{\perp}{}^2/H$ and $\delta_{\perp} \doteqdot (A_{\parallel}{}^2 + A_{\perp}{}^2)/2H$.[18,19] Unfortunately, the (0,0) features were never clear because of the presence of other radicals, but the (1,0) parallel and perpendicular lines lie in the correct region, *ca.* 135 G downfield from the central lines. This confirms our original identification,[17,19] and we conclude that such dimer-adducts are likely to be extremely important intermediates in radiolyses involving trivalent phosphorus compounds.

For the sulphides in dilute methanolic solution, dimer-cation formation was suppressed, and a new pair of asymmetric lines in between those for species A and B appeared. These were rapidly lost on annealing, and we tentatively assign them to the parent cations $(RS)_3P^{\cdot +}$ (Table).

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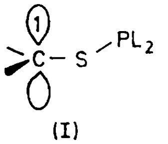
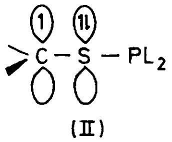
[18] B. Bleaney, *Phil. Mag.*, 1951, **42**, 441.

[19] Similar results have been obtained by T. Gillbro, C. M. L. Kerr, and F. Williams, personal communication.

In most cases, in addition to the species discussed above, weak features assignable to $R_2\dot{C}-S-PL_2$ or $R_2\dot{C}-O-PL_2$ radicals were detected. These are of particular interest in the light of the possibility that a configuration (I) might be adopted, favouring hyperconjugative interaction with the S–P σ-bond,[20] in preference to (II) which favours π-conjugation.



(I)



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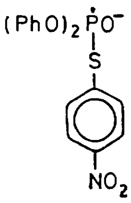

(III)

We were prompted to look for such a situation by the results of Gulik,[21] who observed an unusually large ^{31}P isotropic coupling for the radical (III). However, in no case were we able to detect such a species which should exhibit a large, nearly isotropic, coupling to ^{31}P, and we conclude that for our radicals P–S conjugation (II) is preferred.

Trends in Hyperfine Coupling to ^{31}P.—If these assignments are correct, we would expect to observe consistent trends in $A_{iso}(^{31}P)$ similar to those found for replacing OR groups by R.[12] An inspection of the data in the Table shows that such trends are indeed found. Thus replacing OR by SR in phosphoranyl radicals results in a decrease of *ca.* 15—25 G in $A(^{31}P)$. Also, replacing R by Cl results in an increase of *ca.* 150—200 G. These results are in good qualitative accord with expectation based upon electronegativity differences.[12]

The dimer-cations are not very sensitive to ligand changes, but the ^{31}P coupling constants for $(RS)_3P-P(SR)_3^+$ cations are appreciably smaller than those for the corresponding oxo-species. Once again it seems that ligand electronegativity is the controlling factor. We should comment also on the gross difference in the properties assigned to the symmetrical 'dimers' $R_3\dot{P}_{(1)}-P_{(2)}R_3^+$ and those for the more tentatively identified but apparently very similar species $R_2P_{(1)}-\dot{P}_{(2)}R_3$, (Table). Whilst in the dimer-cations the excess electron is clearly equally shared between $P_{(1)}$ and $P_{(2)}$, and is therefore thought to be in a P–P σ^* orbital, that for the asymmetric species $R_2P-\dot{P}R_3$ is almost completely confined to $P_{(2)}$. These are not structurally equivalent species with the excess electron differently distributed, but are two quite dissimilar structures, the latter being a normal phosphoranyl radical with the unpaired electron in an equatorial hybridised orbital and the R_2P group acting as an almost non-interacting ligand. It is not clear why these alternative structures should be adopted, although symmetry is probably a controlling factor. We stress that the dimer-cations could also have the asymmetric phosphoranyl radical structure $(R_3P_{(1)})-\dot{P}_{(2)}R_3$ in principle since distortion at $P_{(1)}$ would trap the electron on this atom. [A rapid jump of the electron (and distortion) from $P_{(1)}$ to $P_{(2)}$ would make these atoms appear to be equivalent, but this is not thought to be the case for the dimer-cations considered here since the spectra are not temperature dependent, and the averaged parameters are not in agreement with expectation for the phosphoranyl species.]

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