Radiation Mechanisms. Part VII.[1] Electron-loss and -capture Processes in Phenylphosphinic Acid and Related Compounds

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Exposure of phenylphosphinic acid and related compounds to ^{60}Co γ-rays at 77 K resulted in electron addition to the aromatic ring, since the characteristic e.s.r. spectra of the alternative phosphoranyl radicals were absent except for that assigned to $\mathrm{Ph\dot{P}H(O)OH}$ radicals. The anions were protonated on annealing, or directly at 77 K in methanolic glasses, to give cyclohexadienyl radicals which exhibited a hyperfine coupling of 22 G to ^{31}P nuclei. However, the aromatic anion of PhPH(O)OH probably undergoes a 1,2-hydrogen atom shift from phosphorus to the ring carbon, the resulting adduct having A (^{1}H) 40 and A (^{31}P) 200 G. This species is unstable and either breaks down to give benzene and $\cdot\mathrm{PO(OH)}^-$ radicals, or undergoes a further hydrogen shift to give a normal cyclohexadienyl species.

RADIATION processes in aromatic compounds have not been systematically studied using temperature-resolved e.s.r. spectroscopy.[2] Various cyclohexadienyl radicals have been detected,[3,4] which are readily characterised by the large (*ca.* 50 G) hyperfine coupling exhibited by the methylene protons. Such radicals are also readily formed by direct hydrogen atom addition.[5] Liquid-phase e.s.r. studies of aromatic compounds have been dominated by the ease with which the π-electronic systems can gain or lose electrons. Dixon and Norman,[6] in their pioneering studies of hydroxyl radical reactions, obtained the e.s.r. spectrum for hydroxyl radical adducts of aromatic compounds using a flow system. These hydroxyl adducts have recently been studied during radiolysis of aqueous solutions of benzene.[7] Phenyl radicals have also been detected by e.s.r. spectroscopy.[8,9]

Our interest in phenylphosphorus compounds has been twofold, to examine the competition for added electrons between the aromatic ring and the phosphorus atom, and to study adducts of type (I),[10] in the expectation that hyperconjugative interaction with the $\mathrm{PR_3}$ (or $\mathrm{PR_2}$) groups, as first postulated by Eaborn and his co-workers for the corresponding cations,[11] would give rise to a relatively large hyperfine coupling to ^{31}P.[12]

In our earlier study of the molecules $\mathrm{PhP(O)Cl_2}$ and $\mathrm{PhP(S)Cl_2}$ we found that electron addition was at phosphorus.[13] However, preliminary studies showed that when chlorine was replaced by oxygen, ring addition dominated.[10] In a related study Bockestein *et al.*[14] found that addition of RO· radicals to $\mathrm{PhP(OMe)_2}$ resulted in a radical having a zwitterion structure with the unpaired electron in the π-system of the benzene ring. This has recently been confirmed by Davies *et al.*[15] who also found that normal addition to give phosphoranyl radicals occurred when more electronegative substituents such as chlorine were present. [It is noteworthy that the electron also remained on phosphorus for the adduct $\mathrm{RO\dot{P}H_2(Ph)}$.[15]]

Irradiated phenylphosphinic acid and its salts have been studied by Lucken *et al.*[16] who were only interested in the e.s.r. spectrum of the electron-loss centre, $\mathrm{Ph\dot{P}O_2H(Ph\dot{P}O_2^-)}$. Their results showed that, in contrast with the anion $\mathrm{PhNO_2^-}$, electron-delocalisation in the ring was small. This was in accord with their previous study of $\mathrm{Ph_2\dot{P}O}$ radical formed from $\mathrm{Ph_2PH(O)}$.[17]

EXPERIMENTAL

Phenylphosphinic acid, diphenylphosphinic acid, and phenylphosphoric acid were of the highest grade available and were recrystallised from water ($\mathrm{D_2O}$) or methanol ($\mathrm{CD_3OD}$). Samples were irradiated as fine powders in a ^{60}Co Vickrad γ-ray source at a dose rate of 1.7 MCi h^{-1} for up to 2 h, either at 77 K or at ambient temperature (*ca.* 40°). E.s.r. spectra were measured with a Varian E3 spectrometer at 77 K. Samples were annealed in the insert Dewar after decanting the liquid nitrogen, and recooled to 77 K whenever significant changes were noticed in the rapidly scanned e.s.r. spectra. Samples irradiated at ambient temperatures were studied both at this temperature and at 77 K.

RESULTS AND DISCUSSION

Phenylphosphinic Acid.—Exposure at ambient temperatures gave e.s.r. spectra of two well defined species, one being for $\mathrm{Ph\dot{P}O(OH)}$ radicals, as shown in Figure 1 of ref. 16, and the other being assigned to a cyclohexadienyl radical (Figure 1). Data extracted from these spectra are listed in the Table. The most noteworthy aspect of the spectrum for $\mathrm{Ph\dot{P}O(OH)}$ is the extra, isotropic, doublet splitting of *ca.* 15 G, which must come from the hydroxy proton since it is lost on deuteriation.[16] This coupling is larger than is usually observed for hydroxy protons and implies a very specific orientation which must maximise orbital overlap probably by a 'hyperconjugative' mechanism.

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[1] Part VI, S. P. Mishra and M. C. R. Symons, *Internat. J. Radiation Phys. Chem.*, submitted for publication.

[2] I. S. Ginns and M. C. R. Symons, *J.C.S. Dalton*, 1976, in the press.

[3] H. Fischer, *Kolloid-Z.*, 1962, **180**, 64.

[4] S. Ohnishi, T. Tanei, and I. Nitta, *J. Chem. Phys.*, 1962, **37**, 2402.

[5] D. Campbell and M. C. R. Symons, *J. Chem. Soc. (A)*, 1969, 2480.

[6] W. T. Dixon and R. O. C. Norman, *J. Chem. Soc.*, 1963, 3119.

[7] K. Bhatia, *Radiation Res.*, 1974, **54**, 537.

[8] J. E. Bennett, B. Mile, and A. Thomas, *Proc. Roy. Soc.*, 1966, **A293**, 246.

[9] P. H. Kasai, E. Hedaya, and E. B. Whipple, *J. Amer. Chem. Soc.*, 1969, **91**, 4364.

[10] S. P. Mishra and M. C. R. Symons, *Tetrahedron Letters*, 1973, **41**, 4061.

[11] R. W. Bott, C. Eaborn, and P. M. Creasley, *J. Chem. Soc.*, 1964, 4804.

[12] A. R. Lyons and M. C. R. Symons, *J.C.S. Faraday II*, 1972, 622.

[13] S. P. Mishra and M. C. R. Symons, *J.C.S. Dalton*, 1973, 1494.

[14] G. Bockstein, E. H. J. M. Jansen, and H. M. Buck, *J.C.S. Chem. Comm.*, 1974, 118.

[15] A. G. Davies, M. J. Parrott, and B. P. Roberts, *J.C.S. Chem. Comm.*, 1974, 973.

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

[17] M. Geoffrey and E. A. C. Lucken, *Mol. Phys.*, 1971, **22**, 257.

The cyclohexadienyl radicals probably have structures (II) and (III). The proton hyperfine coupling constants are normal, suggesting a spin-density on C-1 (the carbon directly bonded to phosphorus) of *ca.* $\frac{1}{3}$. However, radicals of type $R_2\dot{C}$-PR_3 have isotropic ^{31}P coupling constants in the region of 40 G.[18,19] The high value of 22 G probably reflects an increase in the proportion of phosphorus 3*s* character in the C–P σ-bond, induced by the electronegative oxygen substitutes. Similar trends have been noticed previously and attributed to changes in *sp* hybridisation.[20,21]

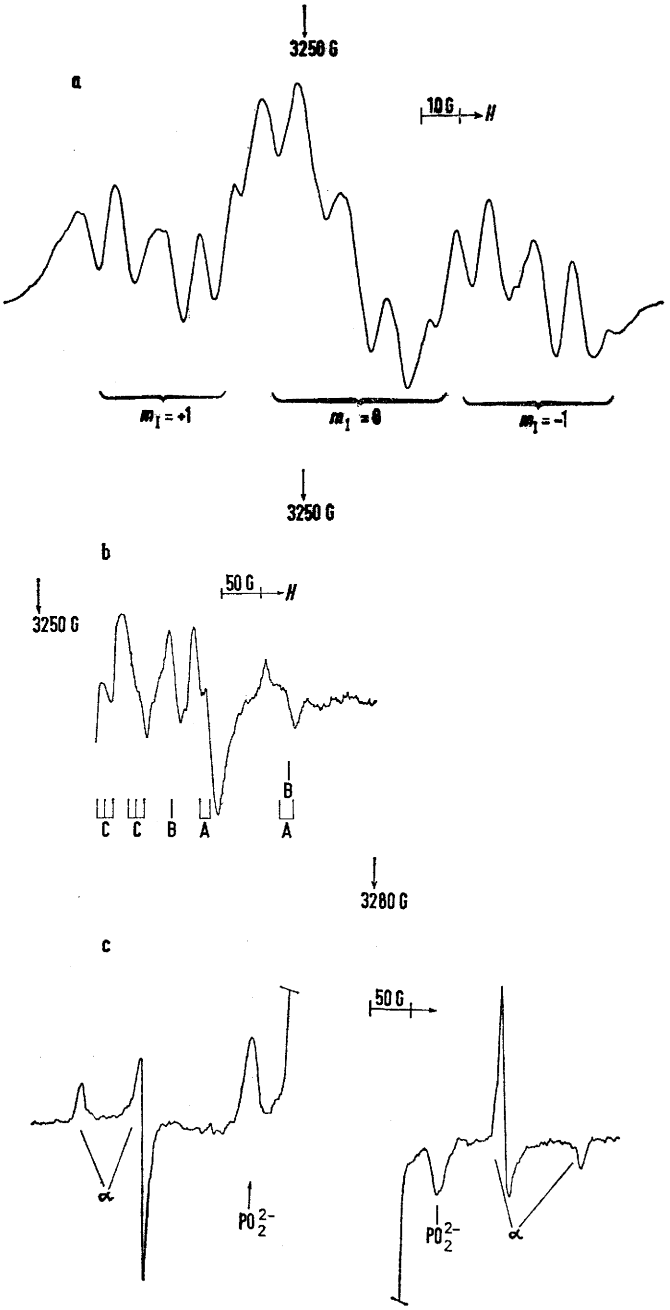

FIGURE 1 First derivative X-band e.s.r. spectrum for phenylphosphonic acid after exposure to ^{60}Co γ-rays: a, at ambient temperature, showing features assigned to cyclohexadienyl radicals (II) and (III); b, at 77 K, showing high-field ($M_I = -\frac{1}{2}$) features assigned to (A) $Ph\dot{P}O_2H$ radicals, (B) $[Ph\dot{P}HO(OH)]^-$ radicals (IV), and (C) cyclohexadienyl radicals of structure (I); and c after annealing, showing features assigned to $\dot{P}O_2^{2-}$ ($\dot{P}O_2H^-$) radicals, and $Ph\dot{P}O(OD)$ radicals (α)

Irradiation at 77 K gave a complex e.s.r. spectrum, the more intense centre ($g=2$) region being dominated by a broad singlet assigned to substituted benzene anions,

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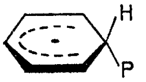
[18] E. A. C. Lucken and C. Mazeline, *J. Chem. Soc.* (*A*), 1966, 74; 1967, 439.

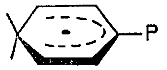
[19] A. Begum, A. R. Lyons, and M. C. R. Symons, *J. Chem. Soc.* (*A*), 1971, 2388.

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

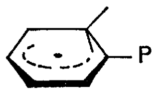
[21] S. Subramanian and M. C. R. Symons, *J. Chem. Soc.* (*A*), 1970, 2367.



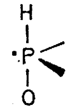
(I)



(II)



(III)



(IV)

E.s.r. parameters for radicals formed in γ-irradiated phenylphosphorus compounds

Compound	Radical	T/K[c]	^{31}P Hyperfine coupling (G)[a] $A_{\parallel}$	$A_{\perp}$	A_{iso}	^{1}H Hyperfine coupling (G)
$PhPO(OH)_2$	(II), (III)	323	*ca.* 26	*ca.* 20	22	8 (2 H), 48 (2 H) (7.4, 2 H)
$PhPO(OH)_2$	$PhPO_2^-$	323	620	435	497	
$PhPO(OH)_2$	$O\text{-}PO_2Ph$	77	*ca.* 10			
PhPH(O)OH	(II), (III)	323	*ca.* 26	*ca.* 20	22	9 (2 H), 48 (2 H) (7.4, 2 H)
PhPH(O)OH	(I)	77	*ca.* 200			40 (1 H), *ca.* 10 (3 H)
PhPH(O)OH	(IV)	77	*ca.* 600			*ca.* 150 (1 H)
PhPH(O)OH	$Ph\dot{P}O(OH)$	323	666	475	539	15 (1 H)
PhPH(O)OH	PO_2^{2-}	323	270	*ca.* 0	*ca.* 90	
PhPH(O)OH + CD_3OD	$Ph\dot{P}O_2^-$	77	560	385	443	
$Ph_2PO(OH)$	$\dot{O}PPh_2(OH)$	77	*ca.* 10			

[a] G = 10^{-4} T. [b] g Values were close to that of the free-spin (2.00). [c] Temperature of irradiation.

and an asymmetric doublet assigned to $\dot{O}PH(PH)OH$ radicals similar to those formed by electron loss from phosphate ions.[20] The outer regions contained many poorly defined features. The high-field region is shown in Figure 1b; the low-field region being very similar. Controlled annealing studies established that the A features are broadened perpendicular lines for the $M_I = -\frac{1}{2}$ part of the spectrum for $Ph\dot{P}O(OH)$ radicals. The B features comprise a pair of perpendicular lines, separated by 150 G, that decay together on slight annealing. A similar 150 G doublet was lost simultaneously on the low-field side. This 150 G doublet was replaced by poorly defined triplet for the deuteriated compound. The magnitudes of the ^{31}P and ^{1}H hyperfine coupling constants are typical of phosphoranyl radicals having an axial hydrogen ligand (IV), and we therefore identify this species as a parent anion in which the electron is centred on phosphorus rather than on the phenyl group. Another pair of doublets (C), which became momentarily very much better defined during the annealing process prior to decaying together irreversibly, were also shown, by deuteriation, to be caused by coupling to ^{31}P (*ca.* 200 G) and ^{1}H (*ca.* 40 G). The lines were slightly asymmetric, but absence of defined shoulders made any estimate of the anisotropic part of the hyperfine tensor components unreliable. Some indication of a small (*ca.* 10 G) quartet splitting was also observed for these features (C), which are therefore assigned to the adduct (I). It is significant that use of the partially deuteriated material, PhPH(O)OD gave the same e.s.r. features, so the hydrogen atom responsible for the 40 G hyperfine coupling must have been originally bound to phosphorus.

After prolonged irradiation and annealing to room temperature, clear parallel features separated by *ca.* 270 G were detected (Figure 1c). These are characteristic of phosphinyl radicals,[22] $\cdot PL_2$, having the unpaired electron in a pure π-level. The perpendicular components for phosphinyl radicals almost coincide in the free-spin region and would be completely hidden by the intense central lines in the present work. The radicals responsible for these features must be either $\dot{P}O_2^{2-}$ [$\dot{P}O(OH)^-$], or possibly $Ph\dot{P}O^-$ ($Ph\dot{P}OH$), both of which are expected to give rise to similar e.s.r. features.[22] We favour the former, for reasons given below.

In CD_3OD solution broad features assigned to $Ph\dot{P}O_2^-$ radicals were obtained, together with clear wing-lines for the deuterium atom adducts (II) and (III). Intense central lines for trapped electrons and $D_2\dot{C}OD$ radicals were also observed.

Phenylphosphonic Acid.—After irradiation at ambient temperature, central features very similar to those for phenyl phosphinic acid were obtained (Figure 2a). This species is undoubtedly the same type of cyclohexadienyl radical [(II) and (III)], the ^{31}P hyperfine coupling constants being equal within our experimental error. The outer lines (Figure 2b) are assigned to $Ph\dot{P}O_2^-$ radicals, since the alternative phosphoryl radical $Ph\dot{P}O(OH)$ is expected to have larger ^{31}P coupling constants, and, by analogy with the results for phenyl phosphinic acid, an extra doublet splitting from the hydroxy proton.

Irradiation at 77 K gave only intense central lines, which were interpreted in terms of a singlet from the aromatic radical anions, and an asymmetric doublet from the $\dot{O}PL_3$ hole-centres. No outer lines of any sort were obtained. On annealing, the room temperature features grew in at the expense of these central features. Solutions in methanol (CD_3OD), gave the deuterium atom adducts (II) and (III) directly at 77 K.

Diphenylphosphinic Acid.—Again, the e.s.r. spectra obtained after irradiation at ambient temperature was dominated by that for the cyclohexadienyl radicals (II) and (III) being almost identical with that shown in Figure 2a. However, the central spectral region still contained a strong absorption from radicals thought to be $\dot{O}P(OH)$-Ph_2. In the other two compounds these radicals were unstable at ambient temperatures. No outer lines were

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[22] B. W. Fulham, S. P. Mishra, and M. C. R. Symons, *J.C.S. Dalton*, 1974, 2145.

observed. This was also true after exposure at 77 K, the central features being then assigned to the substituted aromatic anions and the $\dot{O}P(OH)Ph_2$ species.

Reaction Mechanisms.—The results show that, at 77 K and room temperature, electron addition at the benzene ring is favoured. Taken in isolation, these results could mean that the distortions required to trap the electron at phosphorus are too slow at 77 K compared with the minor distortions involved in aromatic anion formation. That is to say that kinetic rather than thermodynamic control could be involved. (This is an intramolecular phenomenon, not one resulting from matrix constraints.) This would accord with the observation that low concentrations of the phosphoranyl radical with axial hydrogen were formed, since only the hydrogen needs to move extensively and this can be rapid even at 77 K. One would have anticipated that electron transfer from phenyl to phosphorus would then occur on annealing and this was never detected. (A similar electron-transfer from N–O to Fe was observed for irradiated sodium nitroprusside.[23]) However, this might be because ring protonation to give (II) and (III) occurred more rapidly than electron transfer.

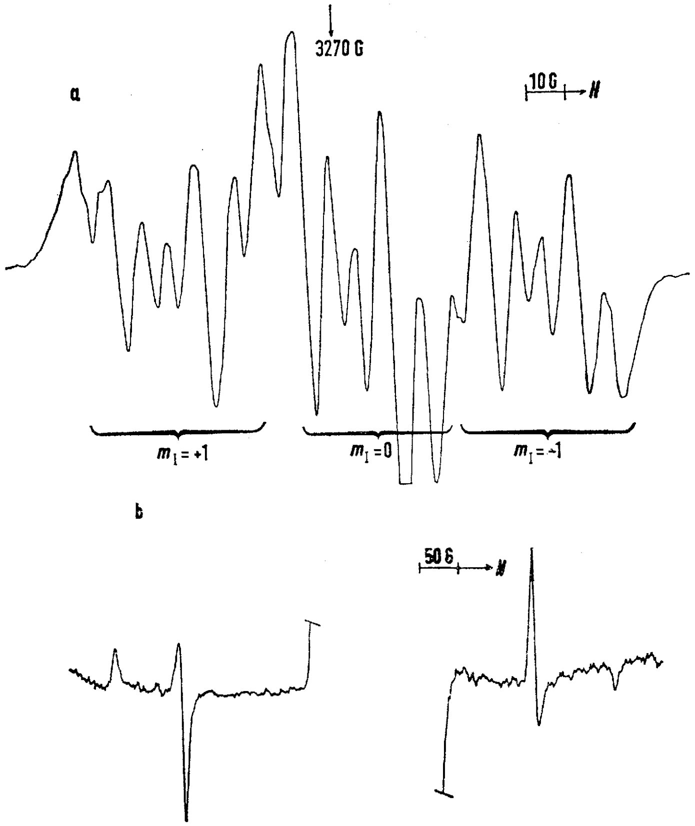


FIGURE 2 First derivative X-band e.s.r. spectrum for phenylphosphonic acid after exposure to ^{60}Co γ-rays at ambient temperature showing: a, features assigned to cyclohexadienyl radicals (II) and (III) and b, features assigned to $Ph\dot{P}O_2^-$ radicals

We do not favour this interpretation, however, because of the results obtained with the t-butoxy adducts.[14,15] These establish that the reverse electron transfer is in fact favoured for such compounds. Also, the results of Davies *et al.*[15] show that the presence of P–H bonds favours the phosphoranyl species, as we have now observed. Thus it seems that electron addition to the aromatic ring is thermodynamically favoured in the present compounds.

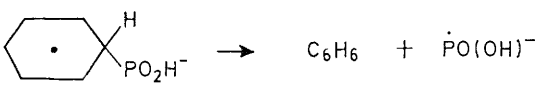
The reactions of phenylphosphinic acid are noteworthy. It seems that the aromatic anions experience an intramolecular proton transfer since it is the P–H proton that migrates into the ring. This is surprising from an acid–base viewpoint since this proton is non-acidic.

It is unlikely that this is the major mechanism for cyclohexadienyl formation [(II) and (III)] since similar radicals are formed from all three compounds. Also, the adducts of type (I) were only detected for the compound containing a P–H bond. We conclude that normal protonation is not favoured at C-1, but at the *ortho*- and *para*-positions of the anion.

It is also noteworthy that when protonation occurs at low temperature the methylene group clearly becomes $>CHD$ on replacing protons by deuterons. However, at ambient temperatures an intramolecular scrambling occurs so that radicals containing $>CH_2$ groups predominate after deuteron addition. This scrambling is slow on the e.s.r. time scale, but fast with respect to the time for measurement (*ca.* 0.1 h) at room temperature. It can be accomplished by migration of the hydrogen atom between the *ortho*- and *para*-positions of the cyclohexadienyl radicals.

We postulate that the $\dot{P}L_2$ species (Figure 2c) is PO_2^- or $PO(OH)^-$, formed from adduct (I) by loss of benzene [reaction (1)]. We were unable to discover any other chemically expected process that would form phosphinyl radicals.

Formation of $Ph\dot{P}O_2^-$ radicals from $PhPO(OH)_2$ probably proceeds *via* the anion [reaction (2)]. This process, which only occurs after considerable annealing above 77 K, probably involves incipient or complete formation of the phosphoranyl radical in low concentration, but we were unable to detect this species.


(1)

$$[PhPO(OH)_2]^- \longrightarrow Ph\dot{P}O_2^- + H_2O \qquad (2)$$

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[23] M. C. R. Symons, D. X. West, and J. G. Wilkinson, *J.C.S. Chem. Comm.*, 1973, 917.