Unstable Intermediates. Part CLIII.[1] Electron Spin Resonance Spectra and Structure of Dichlorophosphoranyl Radicals

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A range of dichlorophosphoranyl radicals $[(RO)P(O)Cl_2]^{\cdot-}$ have been prepared by exposure of the neutral molecules, $(RO)P(O)Cl_2$, to ^{60}Co γ-rays at 77 K [R = Me, Et, Ph, $C_{10}H_7$ (α-naphthyl), $MeOCH_2CH_2$, or $ClCH_2CH_2$]. Well resolved e.s.r. spectra obtained from $[(MeO)POCl_2]^{\cdot-}$ and $[(EtO)POCl_2]^{\cdot-}$ have enabled the components of the ^{31}P and $^{35,37}Cl$ hyperfine-coupling tensors to be derived. The results show that both tensors are nearly axial, but their principal axes are at right angles to each other. The two chlorine ligands must be nearly coaxial with the phosphorus atom and they share *ca.* 50% of the total spin density, the remainder being confined to 3*s* and 3*p* orbitals on phosphorus.

ALTHOUGH a range of phosphoranyl radicals are now known, including $\dot{P}F_4$,[2] $\dot{P}Cl_4$,[3] $[PO_4]^{4-}$ and various $\dot{P}(OR)_xR_{4-x}$ species (R = H or alkyl),[5,6] the majority of reliable results relate to isotropic e.s.r. spectra from which only partial structural information can be obtained. It is clear that the unpaired electron is strongly delocalized onto two ligands only, which are thought to be axial or nearly so, with little or no delocalization onto the two equatorial ligands. The anisotropy of the ^{31}P hyperfine coupling, although sometimes clearly defined,[4,7] is small and often hard to estimate precisely.[8-10] The best evidence that spin delocalization onto the axial ligands is large stems from data for axial hydrogen atoms, which exhibit hyperfine-coupling constants in the 140—150 G region.[6,11] This corresponds, unequivocally, to 28—29% delocalization.

The next best ligands to study are the halides, but to date the only good hyperfine-coupling constants available are isotropic and since the halides bond primarily *via* their *p* orbitals this is not helpful. Our attempts to study the ^{19}F anisotropy for $\dot{P}F_4$ failed because the species thought to be $\dot{P}F_4$ turned out to be $[PF_5]^{\cdot-}$.[12] Previous results for chlorine appeared to be unsatisfactory,[8] but for the isostructural species $[SO_2Cl_2]^-$ fairly well defined powder [13,14] and crystal [15] spectra have been obtained. Unfortunately the crystal data, although by no means complete, seemed to contradict our interpretation of the powder spectra, so no strong reliance could be placed on the derived ligand spin densities. Also, our attempt to estimate the ^{33}S hyperfine interaction [14] was bedevilled by interference from features for $[Cl_2]^-$ [15] and the results, although reasonable, are suspect. On the other hand the crystal data [15] seemed to show the ^{33}S coupling tensor to be isotropic, which is most improbable.

For these reasons we returned to the phosphoranyl radicals and sought out parent compounds that would give well defined e.s.r. spectra. We were successful and are now able to offer a proper interpretation of spectra that have long defied correct analysis.

EXPERIMENTAL

Alkyl dichlorophosphates were prepared by addition of one equivalent of alcohol to three equivalents of phosphoryl

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chloride.[16] Aryl dichlorophosphates were prepared in a similar manner, although KCl was required as a catalyst.[17] The physical properties of all compounds were in agreement with those described in the literature. Aqueous solutions containing $[PO_2Cl_2]^-$ ions were prepared from phosphoryl chloride and aqueous sodium hydroxide.[18] These solutions were frozen immediately and used as such, no attempt being made to isolate the pure salt.

Glassy beads, prepared by pipetting freshly distilled material, neat or in solution, directly into liquid nitrogen, were irradiated at 77 K in a ^{60}Co Vickrad source for up to 1 h at a dose rate of 4 Mrad h^{-1}.* *X*-Band e.s.r. spectra were recorded at 77 K and above on a Varian E3 spectrometer.

RESULTS AND DISCUSSION

The best spectra were obtained from $(MeO)POCl_2$ and $(EtO)POCl_2$ (Figures 1 and 2). Other compounds listed in the Table gave clearly resolved features corresponding to ' parallel ' coupling to the two chlorine ligands, but, as with $[POCl_3]^-$,[8,19] no properly defined ' perpendicular ' features were resolved. We illustrate this in Figure 3 and show how, nevertheless, the limits of the ' perpendicular ' lines can be defined. It is noteworthy that in solvents such as methanol (or CD_3OD) or tetrahydrofuran (thf) spectra like that in Figure 3 were obtained even for $[(MeO)POCl_2]^{\cdot-}$ and $[(EtO)POCl_2]^{\cdot-}$. Our analysis in Figures 1 and 2 gave the results listed in the Table. We are confident that these are correct because every feature in both high- and low-field components is properly accommodated, both with respect to location, shape, and relative intensity. Also, the isotropic ^{31}P and ^{35,37}Cl hyperfine-coupling constants are close to those obtained for similar radicals in the liquid phase.[20]

These results lead us to estimates of spin densities. For phosphorus, using the best available wavefunctions,[21] we estimate A^0 (3*s*, ^{31}P) = 3 664, $2B^0$ (3*p*, ^{31}P) = 201·4, A^0 (3*s*, ^{35}Cl) = 1 666, and $2B^0$ (3*p*, ^{35}Cl) = 100·7 G. Using these values, we find *ca.* 30·7% spin in the 3*s* (P) orbital, 25·4 in the 3*p* orbital, and 28·5 in each 3*p* (σ) chlorine orbital, giving a total estimated spin density of 113 or 117·4% if the 3*s* (chlorine) contribution is included. This is a satisfactory result since no allowance was made for spin-polarization contributions, *etc.* Indeed, the result compares very well with results obtained for $[Cl_2]^-$ using the same approach.[22]

This result lends further support to the analysis and various pertinent conclusions can be drawn. The fact that the parallel ^{31}P features reveal perpendicular splitting for ^{35}Cl and ^{37}Cl and the perpendicular ^{31}P features have both parallel and perpendicular ^{35,37}Cl components means that the principal axes of the ^{31}P and ^{35}Cl orbitals must support an angle of *ca.* 90°. Another significant factor is that the smaller chlorine coupling on the ^{31}P perpendicular features equals that on the ^{31}P parallel lines. This must mean that the Cl–P–Cl angle is close to 180°.[23] It is interesting that the spin density on the chlorine ligands is almost equal to that on axial hydrogen in phosphoranyl radicals. This suggests that the large systematic trends observed in $A_{iso}(^{31}P)$ as the nature of the ligands varies [7] is not primarily caused by various extents of delocalization onto the axial ligands. We have previously suggested that the main factor is admixture of 3*s* and 3*p* atomic orbitals in the wavefunction on phosphorus, which is expected to be a function of the ligand electronegativity. Thus, with ligands such as hydrogen or alkyl the available 3*s* character is low but the 3*p* character is high, whilst with ligands such as fluorine the reverse applies. This admixture is to various extents a function of the electronegativity of all four ligands, as shown by trends discussed previously.[7]

Another conclusion that can be drawn is that the extent of delocalization onto the equatorial ligands is small or zero. This is not an obvious result in terms of simple molecular-orbital theory, but is reminiscent of the results for $\dot{S}F_5$ [24] and $[PF_5]^{\cdot-}$ [12] which show almost zero hyperfine coupling to the *trans* ligand.

We can now turn to the problem of interpreting the e.s.r. powder spectra of other phosphoranyl chlorides, such as that in Figure 3. We can, by inspection, set fair limits to the range of the ' perpendicular ' features for chlorine, but, in most cases this limit contains the anisotropy of the ^{31}P interaction for which some allowance must be made. Approximate values deduced in this way are given in the Table for the radicals involved in the present study. We also include revised values for $[POCl_3]^{\cdot-}$, based on our present analysis, since it is clear that the previous values assigned to the isotropic coupling to chlorine [8,19] were in fact close to the parallel values. We have also returned to our $[SO_2Cl_2]^{\cdot-}$ spectra. Our previous analysis gave 22·7% spin density on each 3*p*(σ)chlorine orbital, but suggested a lack of symmetry not observed in the present study. Using the spectra in Figures 1 and 2 as models, we have obtained revised perpendicular data for ^{35}Cl which now tie in most satisfactorily with the present work. It is clear also that some of the ' average ' values for ^{35}Cl for phosphoranyl radicals reported in ref. 10 are somewhat too high, but unfortunately the spectra are too poorly resolved for us to obtain useful estimates of the real values, except to say that they will not differ greatly from those presently reported.

Other Radical Centres.—Generally, we detected relatively low concentrations of $\dot{P}L_3$ species such as (MeO)-$\dot{P}$OCl after irradiation at 77 K. These species had, as expected, large ^{31}P hyperfine-coupling constants and also

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[*] 1 rad = 10^{-2} J kg^{-1}.

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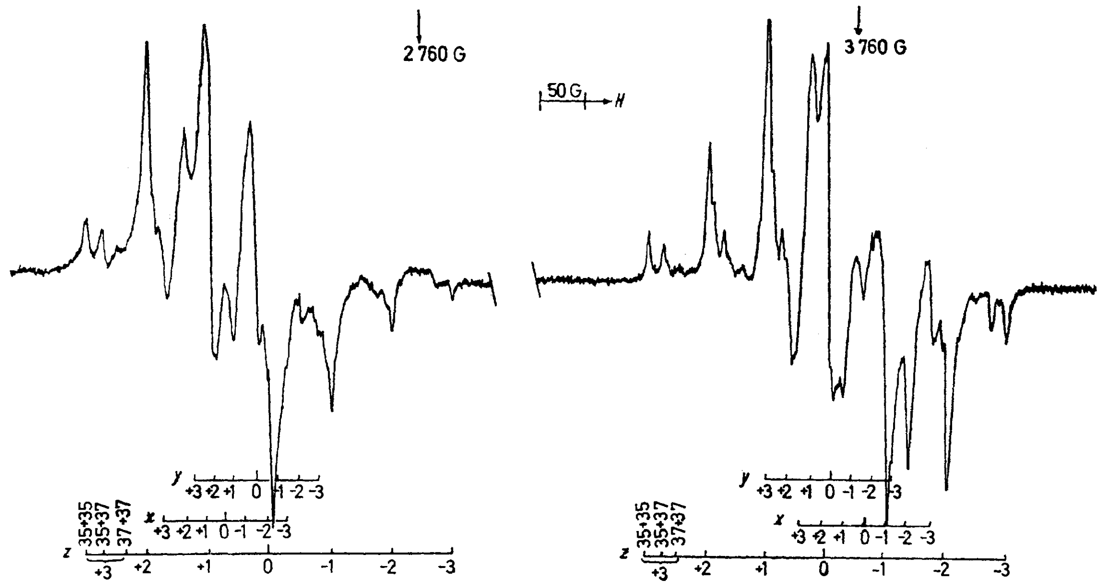

FIGURE 1 First-derivative X-band e.s.r. spectrum for (MeO)$POCl_2$ after exposure to ^{60}Co γ-rays at 77 K, showing features assigned to the radical anions $[(MeO)POCl_2]^{-}$. Features for ^{35}Cl only are indicated in the reconstruction, except as marked

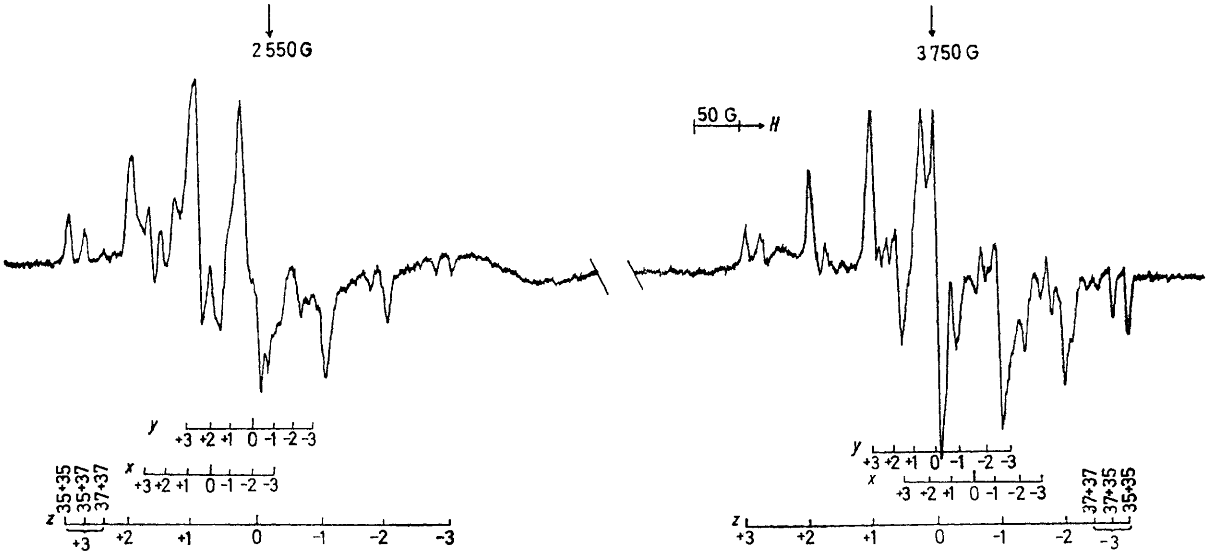

FIGURE 2 First-derivative X-band spectrum for (EtO)$POCl_2$ after exposure to ^{60}Co γ-rays at 77 K as in Figure 1

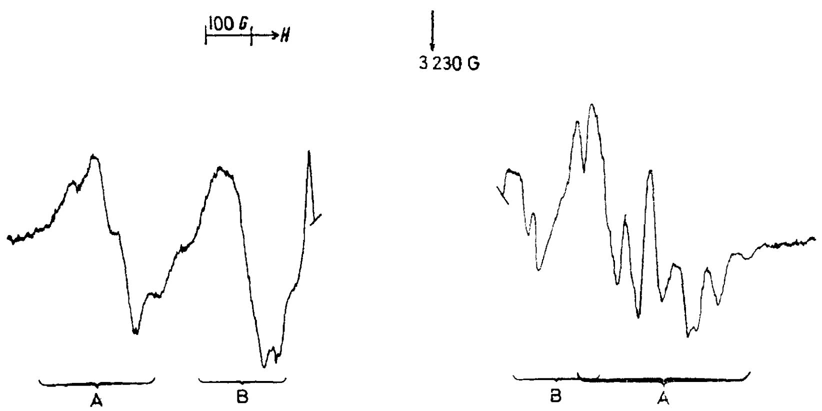

FIGURE 3 First-derivative X-band spectrum for an aqueous glass containing $[PO_2Cl_2]^{-}$ anions as in Figure 1

strong coupling to ^{35}Cl and ^{37}Cl, the overall effect being to cause severe overlap between their features and those for the phosphoranyl radicals. For this reason, and because the species are not clearly identified, we have not attempted to derive accurate spin-Hamiltonian parameters for these species. It is significant that these $\dot{P}L_3$ radicals were generally not formed from the phosphoranyl radicals during the annealing process. Sometimes, as for the methoxo- and ethoxo-compounds (Figures 1 and 2), the $\dot{P}L_3$ radicals were lost preferentially on annealing, and sometimes the reverse occurred, but we cannot state that the commonly postulated step (1) is of great thermal significance for these compounds. Certainly on going to

$$[R_2PCl_2]^{\overset{-}{\cdot}} \longrightarrow R_2\dot{P}Cl + Cl^- \qquad (1)$$

polar media such as methanol (or CD_3OD) the initial act caused more primary dissociation and the proportion of the $\dot{P}L_3$ species increased. These media also promoted another mode of dissociation [equation (2)] which seems to be important for *trans*-dihalides of this type.[13]

$$[R_2PCl_2]^{\overset{-}{\cdot}} \longrightarrow R_2P + [Cl_2]^{\overset{-}{\cdot}} \qquad (2)$$

E.s.r. data for $[(RO)P(O)Cl_2]^{\overset{-}{\cdot}}$ and some related species (at 77 K)

		^{31}P Hyperfine coupling [a]/G			^{35}Cl Hyperfine coupling/G					
Host	Radical	$A_{\parallel}$	$A_{\perp}$	A_{iso}	A_x	A_y	A_z	A_{iso}	$g_{\parallel}$ [a]	$g_{\perp}$ [a]
$(MeO)P(O)Cl_2$	$[(MeO)P(O)Cl_2]^{\overset{-}{\cdot}}$	1 175	1 098	1 149	23	23	67	37·0	2·0028	2·0001
$(EtO)P(O)Cl_2$	$[(EtO)P(O)Cl_2]^-$	1 236	1 172	1 215	25	25	69	39·7	2·0094	2·0074
$POCl_3$	$[POCl_3]^-$	*b*	1 359		25	25	69	39·7	2·006	2·018
$[PO_2Cl_2]^-$	$[POCl_2]^{2\overset{-}{\cdot}}$	*b*	1 050		*b*	*b*	66		*b*	2·005
$(MeOCH_2CH_2O)P(O)Cl_2$	$[(MeOCH_2CH_2O)P(O)Cl_2]^{\overset{-}{\cdot}}$	*b*	1 133		*b*	*b*	67		*b*	2·0080
$(ClCH_2CH_2O)P(O)Cl_2$	$[(ClCH_2CH_2O)P(O)Cl_2]^{\overset{-}{\cdot}}$	*b*	1 133		*b*	*b*	67		*b*	2·0056
$(PhO)P(O)Cl_2$	$[(PhO)P(O)Cl_2]^{\overset{-}{\cdot}}$	*b*	1 160		*b*	*b*	66		*b*	2·0052
$(H_{10}C_7O)P(O)Cl_2$	$[(H_{10}C_7O)P(O)Cl_2]^-$	*b*	1 160		*b*	*b*	66		*b*	2·0052
SO_2Cl_2	$[SO_2Cl_2]^{\overset{-}{\cdot}}$				21	21	64	35·3	2·005	2·027

[a] Calculated using the Brait–Rabi formula. [b] Spectra resolution did not permit assignment of parameter.

As expected the primary hole centres were in general converted by loss of an α proton into $(R_2\dot{C}O)POCl_2$ radicals having normal properties.[25] Sometimes alkyl radicals were also detected in low concentration, presumably formed during the electron-addition process (3).

$$e^- + (RO)POCl_2 \longrightarrow R\cdot + [PO_2Cl_2]^- \qquad (3)$$

It is significant that the compound $(ClCH_2CH_2O)POCl_2$ preferentially added the extra electron to phosphorus rather than suffering cleavage of the Cl–C bond, despite the high reactivity of alkyl halides towards electrons. It is also significant that the phenoxo-derivative also added an electron to phosphorus. This means that the benzene ring has a lower effective electron affinity than has phosphorus, although it is quite possible that some addition to the ring may have occurred. Still more significant is the detection of good yields of phosphoranyl radicals from the α-naphthyl derivative, despite the higher electron affinity of the aromatic system. These results contrast with those of Boekestein *et al.*[26] who demonstrated preferential electron addition to the aromatic ring in formation of the radical anions $[PhP(OR)Me_2]^-$ and $[PhP(OR)(OMe)_2]^-$. We have stressed elsewhere [27] that this contrast is probably associated with the need for the phosphorus atom to change the configuration of its ligands to increase its electron affinity. The preference for phosphorus in the present instance may well stem from the presence of strongly electronegative chloride ligands.

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