Unstable Intermediates. Part CXXXVI.[1] A Survey of the Magnetic Properties of $\cdot\mathrm{PL}_3$ and $\cdot\mathrm{PL}_4$ Radicals: The Radicals $\cdot\mathrm{P(OH)}_3^+$, $\cdot\mathrm{As(OH)}_4$, and $\mathrm{(MeO)}_3\dot{\mathrm{P}}\mathrm{O}^-$

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Hyperfine coupling constants for a wide range of radicals of type $\cdot\mathrm{PL}_3$ (related to $\cdot\mathrm{PO}_3^{2-}$) and $\cdot\mathrm{PL}_4$ (related to $\cdot\mathrm{PO}_4$-$^+$) are reviewed, and trends as L is varied are displayed and discussed. From these correlations it is concluded that a radical formed by exposure of rigid solutions of phosphoric acid in sulphuric acid to γ-rays is $\cdot\mathrm{P(OH)}_3^+$ rather than $\cdot\mathrm{P(OH)}_4$, whilst that formed from similar solutions of arsenic acid is $\cdot\mathrm{As(OH)}_4$ rather than $\cdot\mathrm{As(OH)}_3^+$. Also, two new radicals formed from trimethyl phosphate are shown to be $\mathrm{(MeO)}_3\dot{\mathrm{P}}\mathrm{O}^-$ and $\mathrm{(MeO)}_2\dot{\mathrm{P}}\mathrm{O}$. Two radicals whose properties appear to be anomalous in terms of these correlations are $\cdot\mathrm{PO}_4^{4-}$ and $\cdot\mathrm{PH}_4$. Possible reasons for these anomalies are considered.

DURING the past few years a wide range of phosphorus- and arsenic-centred radicals having relatively large isotropic coupling constants to the central atom have been detected, largely through the work of Krusic and his co-workers [2] and Davies and his co-workers.[3] These fall into two main classes, one, which we symbolise as $\cdot\mathrm{PL}_3$ contains radicals which are isostructural with $\cdot\mathrm{PO}_3^{2-}$, whilst the other ($\cdot\mathrm{PL}_4$) contains radicals isostructural with $\cdot\mathrm{PF}_4$.

The radical $\cdot\mathrm{PO}_3^{2-}$ was first detected by Whiffen and his co-workers [4] in γ-irradiated $\mathrm{Na_2HPO_3,5H_2O}$. The $\cdot\mathrm{PF}_4$ radical was first studied by Morton,[5] and was shown to contain two pairs of quite differently interacting fluorine atoms by Fessenden and Schuler.[6] The two related arsenic-centred radicals, $\cdot\mathrm{AsO}_3^{2-}$ and $\mathrm{H_2\dot{A}sO_4^{2-}}$, were both first detected by McDowell and his co-workers [7,8] in irradiated sodium and potassium arsenates, the latter species being of particular importance in relation to the study of ferroelectric materials.[9]

The aim of this study was to correlate the widespread data for these two families in the hope that the resulting trends would differ enough to provide a useful aid in assigning one or other structure to unknown phosphorus- or arsenic-centred radicals. This problem is illustrated by reference to unknown radicals formed in γ-irradiated rigid solutions of phosphoric and arsenic acids dissolved in sulphuric acid, and in γ-irradiated trimethyl phosphate.

It became clear that the results for a radical in phenacite ($\mathrm{Be_2SiO_4}$),[10] identified [11] as $\cdot\mathrm{PO}_4^{4-}$, were anomalous in terms of the clear correlations that apply to other species in this class. Also the results recently assigned to $\cdot\mathrm{PH}_4$ radicals [12] are seen to be unexpected in terms of these correlations. Possible reasons for these apparent discrepancies are outlined.

EXPERIMENTAL

All materials were of AnalaR grade, used as supplied. Outgassed samples were immediately frozen to 77 K and exposed to ^{60}Co γ-rays at 77 K in a Vickrad cell for up to 2 h at a nominal dose-rate of 4 Mrad h^{-1}.

E.s.r. spectra were measured with a Varian E3 spectrometer at 77 K. Samples were annealed in the insert dewar vessel with continuous monitoring of the e.s.r. spectra, and recooled to 77 K as soon as significant spectral modifications were observed. *Q*-Band spectra were measured on a

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[4] A. Horsfield, J. R. Morton, and D. H. Whiffen, *Mol. Phys.*, 1961, **4**, 475.

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[8] M. Hampton, F. G. Herring, W. C. Lin, and C. A. McDowell, *Mol. Phys.*, 1966, **10**, 565.

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

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superheterodyne instrument constructed in these laboratories.[13]

RESULTS AND DISCUSSION

Results for the particular radicals prepared are given in detail in the Table and various spectra are shown in Figures 1—3. These were derived using suitable forms of the Breit–Rabi equation.[14] Hyperfine coupling data for a wide range of $\cdot PL_3$ and $\cdot PL_4$ radicals, together with some for related arsenic radicals, are displayed in various ways in Figures 4—6. (Results for ^{31}P and ^{75}As are fortuitously almost directly comparable, because the estimated A^0 and $2B^0$ values are nearly equal.[15])

Hyperfine coupling constants for various radicals in γ-irradiated trimethylphosphate, and in sulphuric acid solutions of phosphoric and arsenic acid.

		^{31}P or ^{75}As Hyperfine tensor components/G [a]		
Host	Radical	$A_{\parallel}$	$A_{\perp}$	A_{iso} [b]
Me_3PO_4	$(MeO)_3\dot{P}O^-$	970	805	860
Me_3PO_4	$(MeO)_2\dot{P}O$	802	635	690·7
H_3PO_4–H_2SO_4	$\cdot P(OH)_3^+$	930	728	795
H_3AsO_4–H_2SO_4	$\cdot As(OH)_4$		*d*	*ca.* 1375
H_3AsO_4–MeCN	$H_2\dot{A}sO_4^{2-}$ [c]		*d*	*ca.* 1100

[a] Corrected by use of the Breit–Rabi formula: errors *ca.* ±5 G. [b] Based on the reasonable assumption that the signs of $A_{\parallel}$ and $A_{\perp}$ are the same. [c] The results are very similar to those for $H_2\dot{A}sO_4^{2-}$ in KH_2AsO_4 crystals, suggesting di-protonation in this case also. [d] The anisotropic features were not well enough resolved to warrant any attempt to estimate $A_{\parallel}$ and $A_{\perp}$.

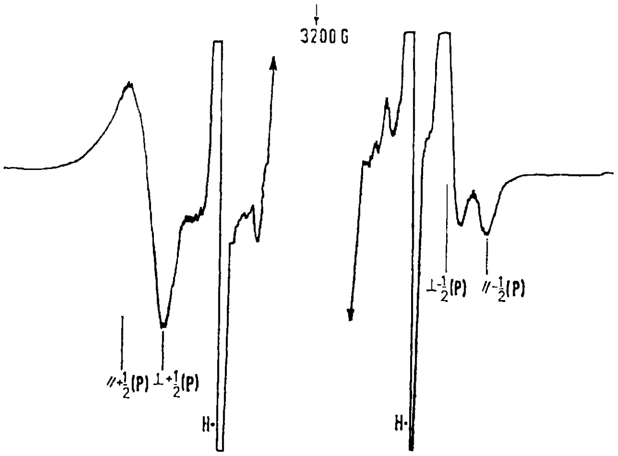

FIGURE 1 First derivative *X*-band e.s.r. spectrum for a solution of phosphoric acid in sulphuric acid after exposure to ^{60}Co γ-rays at 77 K, showing features assigned to $P(OH)_3^+$ radicals. The central features are mainly caused by HSO_4 and HSO_3 radicals

The spectrum obtained from irradiated rigid solutions of phosphoric acid in sulphuric acid (Figure 1) is dominated by an asymmetric doublet, clearly assignable to a hyperfine interaction with ^{31}P, and strong central features largely caused by various solvent radicals such as $HS\dot{O}_4$ and $HS\dot{O}_3$. On annealing, the doublet features were lost and no secondary species was detected. When D_2SO_4 was used, the lines narrowed appreciably, suggesting some interaction with protons, but no clearly defined subsidiary splitting of the lines from H_2SO_4 solutions could be detected.

Solutions of arsenic acid in sulphuric acid gave a well defined quartet of very broad lines, showing only slight evidence of asymmetry (Figure 2). For comparative purposes, we obtained a similar spectrum from solutions of arsenic acid in methyl cyanide, and this is also displayed in Figure 2.

Spectra for γ-irradiated trimethyl phosphate are so strongly dominated by features for methyl radicals and $H_2\dot{C}OPO(OMe)_2$ radicals[16,17] that both previous groups of workers failed to detect the weak, broad doublets shown in Figure 3. These are clearly caused by the presence of two distinct radicals, the one with the larger coupling (a) being lost first during the annealing process.

Identification.—When phosphoric acid is dissolved in sulphuric acid, the cationic species $\cdot P(OH)_4^+$ is formed,[18] and we had expected that $\cdot P(OH)_4$ would be an important radiation product. The results are, however, ambiguous. Thus we estimate $A_{iso}(^{31}P) =$ *ca.* 795 G which can be compared with *ca.* 900 G for typical $(RO)_4P\cdot$ radicals.[2,3] Alternatively, the species could be $\cdot P(OH)_3^+$, which can be compared, for example, with $(RO)_2\dot{P}O$ radicals, which have $A_{iso} =$ *ca.* 690 G.[3] Thus our value for A_{iso} falls nicely between these two examples, and identification by analogy would be unwise.

For this and similar reasons, we attempted to define the properties of these two classes of radical more precisely as a function of ligand. Since it has been shown that radicals of this type have properties that are often markedly dependent upon environment,[19,20] it was also necessary to attempt to eliminate possible environmental constraints in these correlations. Since many of the data pertain to radicals in the liquid phase, it was decided to treat A_{iso} (^{31}P) (or ^{75}As) as the major observable parameter.

Variation of A_{iso} *with Ligand.*—Our first correlation (Figure 4) is for the species $\cdot PO_3^{2-}$, $(RO)\dot{P}O_2^-$, $(RO)_2\dot{P}O$, and $\cdot P(OR)_3^+$. The radical $(RO)\dot{P}O_2^-$ was prepared in a variety of media from a neutral precursor,[21] so no allowance need be made for environmental constraints. In contrast, $\cdot PO_3^{2-}$ radicals have all been prepared from HPO_3^{2-} ions in salts in which cations are close to the

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

[14] G. Breit and I. Rabi, *Phys. Rev.*, 1931, **38**, 2082.

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[20] J. H. Sharp and M. C. R. Symons, *J. Chem. Soc.* (*A*), 1970, 3075.

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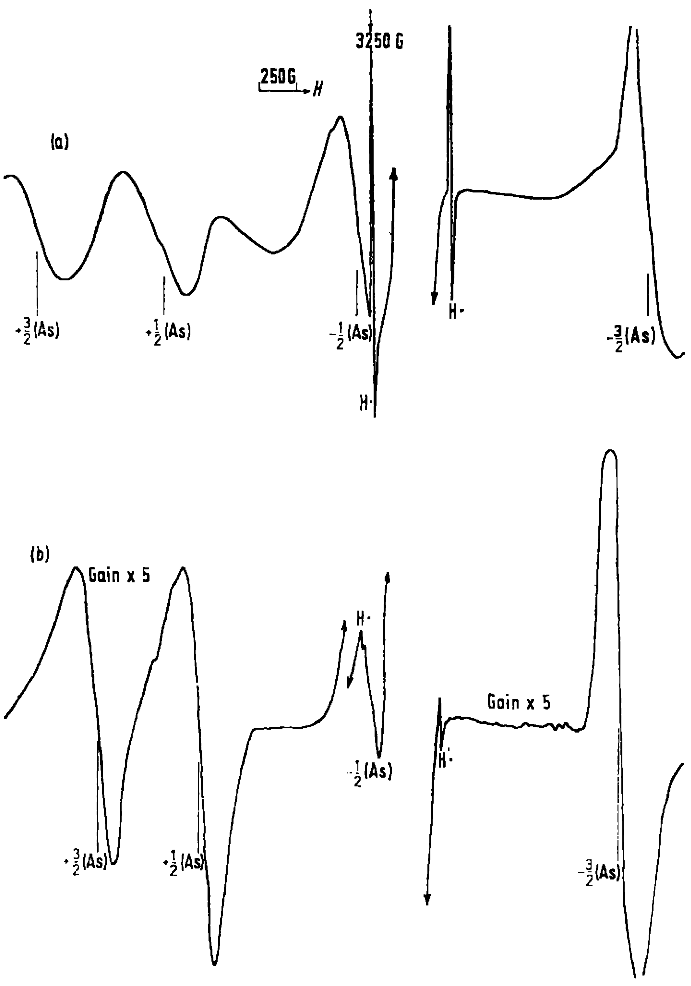

FIGURE 2 First derivative X-band e.s.r. spectrum for a solution of arsenic acid in sulphuric acid (a) and methyl cyanide (b), after exposure to ^{60}Co γ-rays at 77 K, showing features assigned to $\cdot$As(OH)$_4$ (a) and $H_2\dot{A}sO_4{}^{2-}$ (b)

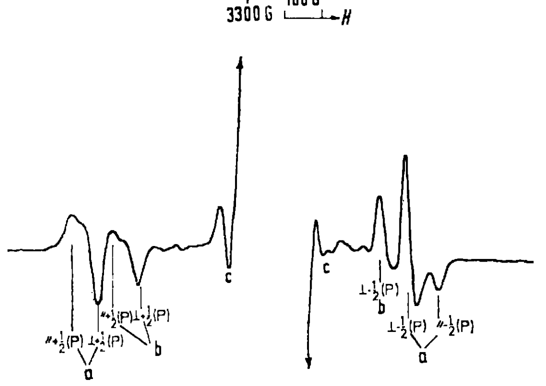

FIGURE 3 First derivative X-band e.s.r. spectrum for trimethyl phosphate after exposure to ^{60}Co γ-rays at 77 K, showing outer features assigned to (a) $(MeO)_3\dot{P}O^-$ and (b) $(MeO)_2\dot{P}O$ radicals. The central features are caused by $\cdot CH_3$ and $H_2CO\dot{P}(O)(OMe)_2$ radicals. (c) Probably ^{13}C satellites for HCO radicals

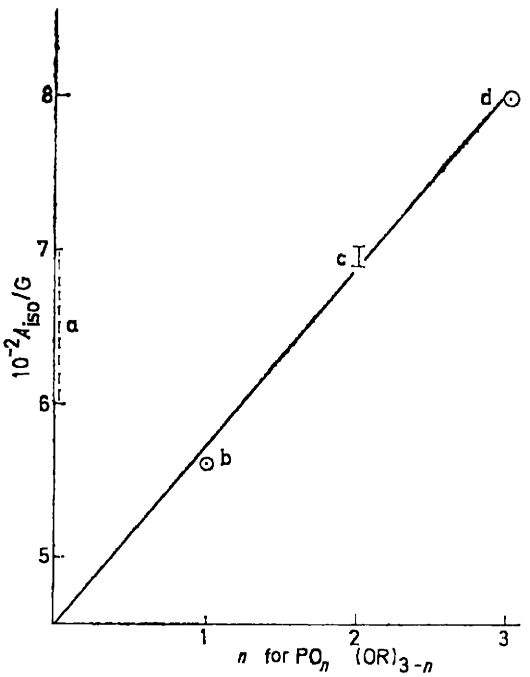

FIGURE 4 Trends in A_{iso} (^{31}P) as $PO_3{}^{2-}$ is protonated or alkylated; a, $PO_3{}^{2-}$ in various hosts (ref. 19); b, $MeOPO_2{}^-$ (ref. 21); c, $(MeO)_2PO$ (ref. 21, present work, and ref. 3); and d, $P(OH)_3{}^+$, present work

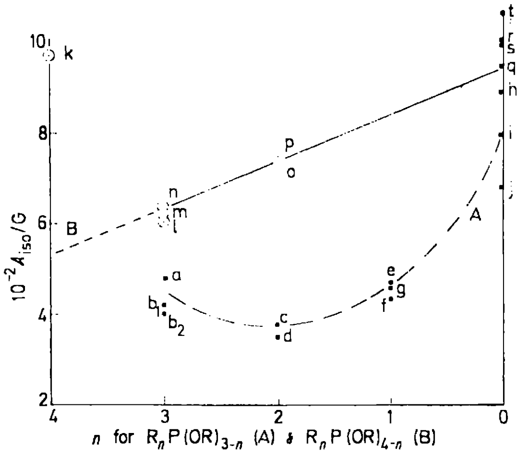

Figure 5 Trends in A_{iso} for A, various PL_3 radicals; and B, various $\cdot PL_4$ and $\cdot AsL_4$ radicals, as L is varied from –R to –O or –OR (a—j relate to PL_3 and k—t to PL_4 and AsL_4); a, $PH_3{}^+$ (ref. 25); b$_1$, b$_2$, $PMe_3{}^+$ + $PEt_3{}^+$ (ref. 25); c, Ph_2PO (M. Geoffrey and E. A. C. Lucken, *Mol. Phys.*, 1971, **22**, 257); d, Me_2PO (A. Begum and M. C. R. Symons, *J.C.S. Faraday II*, 1973, **69**, 43); e, $HPO_2{}^-$ (J. R. Morton, *Mol. Phys.*, 1962, **5**, 217); f, $PhPO_2{}^-$ (M. Geoffrey and E. A. C. Lucken, *Mol. Phys.*, 1972, **24**, 335); g, PhPO(OH) (M. Geoffrey and E. A. C. Lucken, *Mol. Phys.*, 1972, **24**, 335); h, $P(OH)_3{}^+$ (present work); i, $(MeO)_2\dot{P}O$ (ref. 3); j, $MeOPO_2{}^-$ (ref. 21); k, PH_4 (ref. 12); l, Me_3PO^- (A. Begum and M. C. R. Symons, *J.C.S. Faraday II*, 1973, **69**, 43); m, Me_3POR (ref. 2); n, R_3AsOR (E. Furimsky, J. A. Howard, and J. R. Morton, *J. Amer. Chem. Soc.*, 1972, **92**, 5932); o, $(RO)_2PR_2$ (refs. 2 and 3); p, $(RO)_2AsMe_2$ (A. G. Davies, D. Griller, and B. P. Roberts, *J. Organometallic Chem.*, 1972, **38**, c8); q, $P(OMe)_4$ (refs. 2 and 3); r, $AsO_4{}^{4-}$ (ref. 8); s, $PO_4{}^{4-}$ (refs. 10 and 11); and t, $As(OH)_4$ (present work)

anions and exert very strong electric fields thereon, which markedly modify the magnetic parameters for $\cdot PO_3^{2-}$.[19] It seemed worthwhile to attempt an approximate extrapolation to infinite cation radius since results for $\cdot PO_3^{2-}$ in a range of different salts are available.[19] To help discover the most suitable extrapolation procedure, we first studied the results for $\cdot CO_2^-$ in a range of alkali-metal formates,[20] since data for $\cdot CO_2^-$ in a non-solvating, non-ionic medium are available.[22]

Best results were obtained by plotting charge/(radius) ^{2} against A_{iso}, the radius chosen being the ' experimental ' values,[23] since these gave a better linear correlation than others. The extrapolated value was *ca.* 139 G, which is considerably larger than the 120 G reported for $\cdot CO_2^-$ in 3-methylpentane at 77 K.[22] If instead of using charge/(radius)^2, we plotted simply (radius)$^{-2}$ for all ions, a fair correlation was obtained, which extrapolated to *ca.* 120 G, provided the result for the lithium salt was ignored. Since this salt was hydrated,[20] its result may be unsuitable anyway. We have used both these correlations in an attempt to obtain an approximate value for $\cdot PO_3^{2-}$.

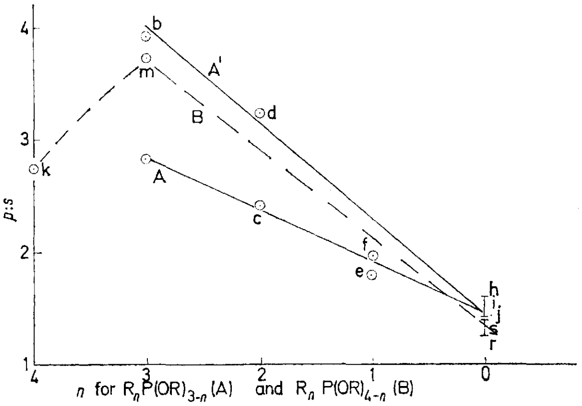

FIGURE 6 Trends in estimated $p:s$ ratios for various $\cdot PL_3$ radicals (A and A′), and $\cdot PL_4$ or $\cdot AsL_4$ radicals (B) as L is varied from $-R$ to $-O^-$ or $-OR$; key as in Figure 5

The result suggest limits between 450 and 490 G for non-interacting $\cdot PO_3^{2-}$ ions. Such values accord reasonably well with the trend indicated in Figure 4, and the resulting curve accommodates the value for the species formed from phosphoric acid in sulphuric acid, which supports the $\cdot P(OH)_3^+$ formulation.

A similar display for the family of radicals $R_3P^{+\cdot} \longrightarrow \cdot PO_3^{2-}$ is shown in Figure 5, curve A, which brings out several interesting facets of the collective results. These include the marked decrease in $A(_{iso}{}^{31}P)$ on going from $\cdot PH_3^+$ to $\cdot PMe_3^+$ and the further slight decrease on going to $\cdot PEt_3^+$. A similar trend is seen on going from $H\dot{P}O_2^-$ to $Me\dot{P}O(OMe)$. Results for radicals containing phenyl bonded to phosphorus also show a clear increase in $A_{iso}(^{31}P)$ relative to the alkyl derivatives, phenyl being very similar to hydrogen in its affect upon $A(^{31}P)$.

The curvature observed in this plot reflects the change in bond angle as $-R$ groups are replaced by $-OR$ groups, together with the increased ability of the $-OR$ groups to delocalise the unpaired electron by pseudo-π-bonding. An alternative display, which focuses attention on bond-angle changes, is given in Figure 6, in which the $p:s$ ratio, estimated from the hyperfine tensor components in the usual manner,[15] is used as a rough measure of the mean bond angle, or deviation from planarity. Here again the very marked effect of replacing alkyl by hydrogen or phenyl is notable (A and A′). However, the marked dependence of A_{iso} on oxygen protonation or alkylation is largely eliminated in this mode of display. Unfortunately, it can only be used when solid-state results are available.

Results for various $\cdot PL_4$ radicals are also in Figure 5 and 6. In Figure 5 there is a fairly linear progression if the datum for $\cdot P(OR)_4$ is used rather than that for $\cdot PO_4^{4-}$. The results for the species obtained from phosphoric + sulphuric acids are not well accommodated especially when the results for various arsenic central radicals are included (see later). Also, the recently reported results for $\cdot PH_4$ radicals[12] are seen to be somewhat anomalous. There is not enough information to test a linear relationship for the $p:s$ plot in Figure 6, but the result for $\cdot PH_4$ is included on the limiting assumption that there is 100% spin-density on the phosphorus atom. (This is not what would be predicted, but any delocalisation on to hydrogen would simply make the apparent discrepancy for $\cdot PH_4$ more marked.)

The Influence of Ligand Electronegativity.—$\cdot PL_3$ *radicals.* The surprisingly large dependence for PO_3 species upon protonation or alkylation can be qualitatively understood in terms of a change in the effective electronegativity of the ligand coupled with a change in pseudo-π-delocalisation. Thus as the ligand takes an increasing share of the σ-bonding electrons, so the phosphorus $3p$-orbitals are favoured increasingly for σ-bonding, thereby forcing the unpaired electron more into the $3s$-atomic orbital. This favours increasing deviation from planarity which, in turn, makes pseudo-π-delocalisation less efficient.

Similar arguments adequately explain the trends for $\cdot PL_3$ radicals shown in Figures 5 and 6, and we strongly favour this simple model, first suggested by Pauling,[24] over those based upon electron-repulsion effects or orbital expansion effects often used by others.

$\cdot PL_4$ *Radicals.* Ligand electronegativity effects are more difficult to accommodate in this case since there are essentially two different types of ligand, axial (L_{ax}) and equatorial (L_{eq}). We stress that L_{ax} will not be expected to lie along an axis passing through the central atom, because of the asymmetry of the radical (I). However, they are expected to be bonded to phosphorus by longer and weaker bonds than L_{eq}, the unpaired electron being

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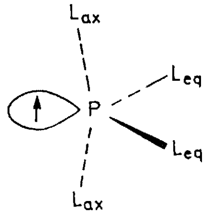
[22] J. M. Johnson and A. C. Albrecht, *J. Chem. Phys.*, 1966, **44**, 1845.

[23] M. J. Blandamer and M. C. R. Symons, *J. Phys. Chem.*, 1963, **67**, 1304.

[24] L. Pauling, *Proc. Nat. Acad. Sci. U.S.A.*, 1928, **14**, 359; L. Pauling, *J. Chem. Phys.*, 1969, **51**, 2767.

pictured as being the third equatorial ' ligand ' in this model.



(I)

This difference is well illustrated by the shifts observed on replacing H by Me in the two different sites for $RO\dot{P}R_3$ radicals.[2] Thus, for example, $(RO)\dot{P}H(Me)_2$ radicals with H axial gave $A(^{31}P) = 631{\cdot}4$ G, whilst $(RO)\dot{P}Me_3$ gave the somewhat smaller value of 618·7 G. This decrease is in line with the results for $\cdot PR_3^+$ radicals. However, $(RO)_2\dot{P}H_2$ and $(RO)_2\dot{P}Me_2$ radicals gave $A(^{31}P) = 672{\cdot}5$ and 713·7 G respectively, the relatively large increase being opposite to expectation. These differences, which, in our view, reflect a change in response of the methyl groups with the nature of the bonding similar to those observed for the series of radicals $\cdot AlH_3^-/\cdot AlR_3^-$, $\cdot SiH_3/\cdot SiR_3$, and $\cdot PH_3^+/\cdot PR_3^+$,[25] are important when considering the results for $\cdot PH_4$ radicals, and suggest that replacement of alkyl groups by hydrogen atoms should not cause a large net change in $A_{iso}(^{31}P)$. However, replacement of H or Me by ^-OR groups leads to a clear increase in $A(^{31}P)$ both for axial and equatorial sites. Again with respect to $\cdot PH_4$ these trends lead to a predicted value of *ca.* 580 G for $A_{iso}(^{31}P)$ in $\cdot PH_4$.

Returning to the identification of the phosphoric acid radical, we conclude from the comparisons in Figures 4 and 6 that this species is somewhat better described as $\cdot P(OH)_3^+$ rather than as $\cdot P(OH)_4$. Comparison with the results for arsenic acid lends credence to this, since the arsenic species is far more likely to be $\cdot As(OH)_4$ than $\cdot As(OH)_3^+$ in view of its very large ^{75}As coupling constant. This seems to rule out the $\cdot P(OH)_4$ formulation. Again, results for the trimethyl phosphate radicals (a and b of Figure 3) can be confidentally assigned to $(MeO)_3\dot{P}O^-$ (a) and $(MeO)_2\dot{P}O$ (b) from these correlations. The fact that the former gives way to the latter on annealing accords with expectation for such species [reaction (1)].

$$(MeO)_3PO^- \longrightarrow MeO^- + (MeO)_2\dot{P}O \qquad (1)$$

The last radical (b) has recently been detected in γ-irradiated dimethyl phosphite,[21] and the present results are in good agreement with those previously found. Somewhat surprisingly, it was not detected in irradiated trimethyl phosphite.[26]

The PO_4^{4-} Anomaly.—The problem is now well defined: as ligand electronegativity increases so, normally, A_{iso} (^{31}P or ^{75}As) increases. Thus, on protonation of $H_2AsO_4^{2-}$, one expects an increase in $A(^{75}As)$ and this is clearly observed (cf. a and b in Figure 2). Why then, is there a clear decrease in $A(^{31}P)$ on going from $\cdot PO_4^{4-}$ to $(MeO)_4P\cdot$? The problem is underlined by the increase in $A(^{31}P)$ on going from $(MeO)_3\dot{P}O^-$ to $(MeO)_4P\cdot$.

We think that the answer is to be found partly in the fact that *O*-protonation is seen to have a considerably greater effect on the ligand electronegativity than *O*-alkylation, and partly in the marked cation effects previously discussed for $\cdot PO_3^{2-}$ radicals, and also clearly observed for $H_2\dot{A}sO_4^{2-}$ radicals.[27] It might seem surprising that cations could have a greater effect than alkyl groups (R^+), but the cation in question for $\cdot PO_4^{4-}$ was Be^{2+}, and extrapolations by use of the cation-radius correlations mentioned above confirm that Be^{2+} ions should have an exceptionally large effect on $A_{iso}(^{31}P)$. We therefore confidentially predict that $\cdot PO_4^{4-}$ ions in weaker crystal-fields would have A_{iso} values less than the value of *ca.* 900 G found for $(MeO)_4P\cdot$ species. Unfortunately, all attempts to prepare these radicals in suitable host crystals or in aqueous glasses have so far failed.

The $\cdot PH_4$ Anomaly.—As mentioned above, we would expect $\cdot PR_4$ radicals to have $A_{iso}(^{31}P)$ in the 550—600 G region, whereas the results for a species formed from the photolysis of phosphine in krypton at *ca.* 10 K suggest $A = ca.$ 974 G.[12] Whilst this dramatic increase is clearly not ruled out by the present correlations, the result seems to have no ready explanation. Still more puzzling is the small (average) proton hyperfine coupling of *ca.* 21 G. Given that a tunnelling process can achieve rapid averaging of H_{ax} and H_{eq} even at 10 K, we would predict from the results for $(RO)\dot{P}H_3$ radicals (which are unambiguously not exchanging H_{ax} and H_{eq} even at —100 °C[2]) a mean coupling of $(139{\cdot}6 + 10{\cdot}8) \times 0{\cdot}5 = 75{\cdot}2$ G (or 64·4 G if H_{eq} has a negative coupling, which is most unlikely). Again, one must ask, why is the proton coupling, which is remarkably constant for H_{ax} and H_{eq} for a range of $(RO)\dot{P}R_3$ and $(RO)_2\dot{P}R_2$ radicals,[2] suddenly modified so dramatically on going to $\cdot PH_4$?

Another curious feature is that g_{av} (as estimated from the figure given in ref. 12, since the quoted value seems to be in error) is *ca.* 1·990, which is anomalously low for radicals in this class, which generally have $g_{av} > 2{\cdot}0023$. Probably there is a simple explanation involving $\cdot PH_4$ that will serve to explain all these factors, but we have not yet discovered one that is convincing. It did occur to one of us (M. C. R. S.) that the species might be $P_2H_6^+$ rather than $\cdot PH_4$. We have previously found that the process (2) is strongly favoured at 77 K,[27] and

$$\cdot PR_3^+ - PR_3 \longrightarrow P_2R_6^+ \qquad (2)$$

at the high concentrations of PH_3 needed to give the spectrum assigned to $\cdot PH_4$ such dimerisation seems to be possible. This would explain the apparently large

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

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

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

$A(^{31}P)$ since the split central component ($M_I = 0$) would be hidden by other features, and from our previous results we would predict $2A_{iso}(^{31}P) = ca.$ 920, with replacement of alkyl by hydrogen giving a slight increase, as observed. Also, if the absence of the $M_I(^1H) = \pm 3$ lines is allowed for because of the high noise level, the small proton coupling of 21 G is quite reasonable for this species. Yet again, the negative *g*-shift is no longer found if the species is dimeric, since the effective Breit–Rabi shift is very much smaller, the calculated *g*-value being now close to 2·003.

Against this suggestion is the absence of trapped $\cdot PH_3^+$ radicals, and one needs to postulate photo-ionisation (3) from pairs of PH_3 molecules in order to accommodate this.

$$PH_3 + PH_3^* \longrightarrow P_2H_6^+ + e^- \qquad (3)$$

However, we have been assured that more recent results rule out this alternative suggestion, and strongly support the $\cdot PH_4$ postulation.[28] Thus the anomalies remain an enigma.

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[28] C. A. McDowell, personal communication.