Phosphoranyl (PH_4) and Diphosphine ($P_2H_6^+$) Radicals

By **Thomas A. Claxton, Brian W. Fullam, Eric Platt,** and **Martyn C. R. Symons,*** Department of Chemistry, The University, Leicester LE1 7RH

Theoretical computations for the ^{31}P and ^{1}H isotropic coupling constants for PH_4 and $[P_2H_6]^+$ radicals suggest that a species recently identified as PH_4 is more probably $[P_2H_6]^+$. Comparisons with the data for structurally similar species strongly support this suggestion. In particular, the radical anions formed from $Me_2(S)P{-}P(S)Me_2$ and $Et_2(S)P{-}P(S)Et_2$ have e.s.r. spectra remarkably similar to that now assigned to $[P_2H_6]^+$. E.s.r. results for acidic aqueous solutions containing both PH_3 and $[PH_4]^+$ after exposure to ^{60}Co γ rays at 77 K give evidence for the formation of $[P_2H_6]^+$ radicals during the annealing process.

IN a recent paper, McDowell *et al.*[1] described an e.s.r. spectrum obtained from phosphine in krypton at *ca.* 10 K by u.v. photolysis, which comprised a central doublet assigned to $\dot{P}H_2$ radicals, a normal hydrogen-atom doublet, and a 974 G doublet assigned to $\dot{P}H_4$ radicals. These outer lines appeared as poorly resolved quintets with a proton coupling of 21·0 G. Although the assignment of these lines to $\dot{P}H_4$ radicals is, at first sight, compelling, nevertheless there are several factors which make the data appear highly anomalous. (*i*) The isotropic hyperfine coupling to ^{31}P was far larger than expected in the light of results for similar species. A wide range of radicals in this class show that $A_{iso}(^{31}P)$ decreases as the ligand electronegativity decreases. In particular, $\dot{P}(OR)_4$, $R_2\dot{P}(OR)_2$, and $R_3\dot{P}(OR)$ radicals in the liquid phase have $A(^{31}P) \approx 920$, 710, and 630 G,† respectively[2,3] (R = alkyl or H). It seems reasonable to extrapolate to $\dot{P}R_4$ and suggest a ^{31}P coupling in the 500—600 G region. This should also be approximately correct for $\dot{P}H_4$. (*ii*) The (average) proton hyperfine coupling of 21 G was surprisingly low. Again, using the results of Krusic *et al.*[2] one can predict that for the static radical two protons show a coupling of *ca.* 140 G and the other two *ca.* -10 G. In the fast-exchange limit this would give *ca.* 65 G each. (*iii*) The centre of the phosphorus doublet assigned to $\dot{P}H_4$ [*cf.* Figure 1(*a*)] was very close to that of the hydrogen-atom doublet. This is most unexpected for such a large hyperfine splitting and is not in accord with the results for a large range of radicals of this class.[2,3] Using the data given in Figure 1 (internally calibrated by the H-atom doublet), and the Breit–Rabi equation, we estimate $g \approx 1{\cdot}988$ for the 974 G doublet. We have found, for at least 12 radicals in this class, that $g_{\parallel} \approx 2{\cdot}002$ and $g_{\perp} > 2{\cdot}0023$, and conclude that, if this species is indeed $\dot{P}H_4$, it has most unexpected magnetic properties.‡

We have recently encountered similar problems in our studies of radiation damage in alkylphosphines.[4] We detected parallel and perpendicular features separated by *ca.* 1 000 G which seemed to be incompatible with the species to be expected. It seemed that dimeric radicals were involved, but it was impossible to confirm this concept by detecting the $M_I = 0$ components because of the invariable presence of strong features in the central region of the spectra. However, when similar arsenic compounds were studied, clear seven-line spectra were obtained, thus confirming the formation of dimeric

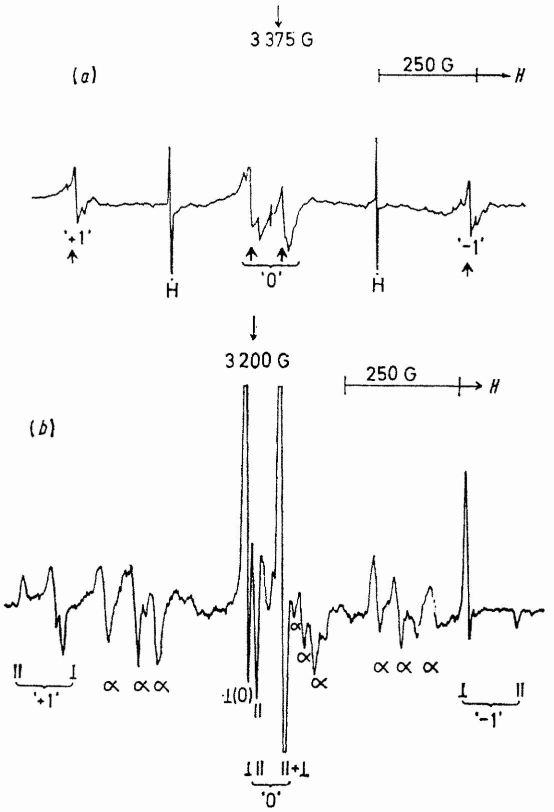

FIGURE 1 (*a*) First-derivative *X*-band e.s.r. spectrum originally assigned to $\dot{P}H_4$ (outer features) and $\dot{P}H_2$ radicals (central doublet), together with traces of $\dot{H}$ and $\dot{P}$ atoms (see ref. 1). Using the hydrogen-atom doublet for calibration, this spectrum is reassigned to the radical cation $[P_2H_6]^+$, the arrows showing the predicted transitions based on the parameters given in the text. (*b*) Spectrum for γ-irradiated $Et_2(S)P{-}P(S)Et_2$ on approximately the same scale, showing features assigned to the anion $[Et_2(S)P{-}P(S)Et_2]^-$. [Other features (α) are not discussed herein]

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† 1 G = 10^{-4}T, 1 bohr $\approx 5{\cdot}29 \times 10^{-11}$ m, 1 rad = 10^{-2} J kg^{-1}.

‡ *Note added in proof:* Since this paper was submitted, a report on authentic PH_4 radicals has appeared (A. J. Colussi, J. R. Morton, and K. F. Preston, *J. Chem. Phys.*, 1975, **62**, 2004). These radicals have $A_{iso}(^{31}P) = 519.3$ G, $A_{iso}(^{1}H)$ (two) = 198.7 G, and $A_{iso}(^{1}H)$ (two) = 6.0 G, in good agreement with expectation.

[1] C. A. McDowell, K. A. R. Mitchell, and P. Raghunathan, *J. Chem. Phys.*, 1972, **57**, 1699.

[2] P. J. Krusic, W. Mahler, and J. K. Kochi, *J. Amer. Chem. Soc.*, 1972, **94**, 6033.

[3] I. S. Ginns, S. P. Mishra, and M. C. R. Symons, *J.C.S. Dalton*, 1973, 2509.

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

radicals. We concluded that the species responsible were of the general type $[R_3P{-}PR_3]^+$ and $[R_3As{-}AsR_3]^+$,[4] having the outer electron in a P–P or As–As σ^* orbital. When the parent compounds (R_3P and R_3As) were progressively diluted with inert solvents these dimer features diminished in intensity and were ultimately lost; however, in the 5 : 1 mol ratio, which was most significantly found to be necessary by McDowell *et al.*,[1] dimer cations were still readily detected.

One possible alternative to the $\dot{P}H_4$ formulation is, therefore, the σ^*-radical $[H_3P{-}PH_3]^{+\cdot}$. This would then require the presence of a central doublet (because of second-order splitting), each line being split further by the six equivalent protons, together with outer septets, the ^{31}P coupling constant now being in the region of 487 G. This tentative alternative certainly accommodates many of the factors that are anomalous on the $\dot{P}H_4$ theory: (*i*) it explains the need to use high concentrations of PH_3; (*ii*) the g value is now close to the free-spin value, as found for the $[R_3P{-}PR_3]^+$ dimers; (*iii*) the ^{31}P hyperfine coupling of *ca.* $0{\cdot}5 \times 974 = 487$ G is very close to that found for $[R_3P{-}PR_3]^+$ radicals (*ca.* 460 G); and (*iv*) the ^1H hyperfine coupling is reasonable for the radical $[H_3P{-}PH_3]^+$.[5] [The outermost lines of the expected septet would be lost in noise in the spectrum reported [Figure 1(*a*).]

The central doublet was assigned [1] to rotating $\dot{P}H_2$. This radical, previously detected by Gordy and his coworkers,[6,7] has $A_{\mathrm{iso}}(^{31}P) = 80$ [6] ($81{\cdot}79$ [7]) G, $A_{\mathrm{iso}}(^1H) = 18$ [5] (17 [7]) G, and $g_{\mathrm{av}} = 2{\cdot}0087$ [6] ($2{\cdot}0050$ [7]). If the central doublet in Figure 1(*a*) is assigned to $\dot{P}H_2$, we find (using the phosphorus- and hydrogen-atom lines for calibration) $A_{\mathrm{iso}}(^{31}P) = 78$ G ($82{\cdot}3$ G reported [1]), $A_{\mathrm{iso}}(^1H) \approx 20$ G ($18{\cdot}0$), and $g_{\mathrm{av}} = 2{\cdot}022$ ($2{\cdot}0090$). Thus there seems to be a major discrepancy in the g values if these lines are really due to $\dot{P}H_2$ radicals. Our alternative, $[P_2H_6]^+$, theory requires the presence of central features from the '$M_I = 0$' transition which are split by the Breit–Rabi shifts. To second order, the splitting between these features (1,0) and (0,0) is given by $A_{\mathrm{iso}}{}^2(^{31}P)/H_0$, which gives 70 G for a hyperfine coupling of $974/2 = 487$ G. Furthermore, the high-field component should be close to the free-spin g value as found. It is noteworthy that the poorly resolved proton structure on the wing lines was reproduced on the central lines. We conclude that the central lines are far better accommodated as the $M_I = 0$ features for $[P_2H_6]^+$ than as the $M_I = \pm\frac{1}{2}$ lines for $\dot{P}H_2$.

In an attempt to verify these prognostications, we have calculated the isotropic coupling constants for both $\dot{P}H_4$ and $[P_2H_6]^+$ in the expected geometries. Furthermore, we have devised conditions for the preparation of $[P_2H_6]^+$ radicals under entirely different conditions and, in order to study the central features experimentally for compounds of this type, we have prepared $[R_2(S)P{-}P(S)R_2]^{\cdot}$ radicals from $R_2(S)P{-}P(S)R_2$ molecules for which the presence of two phosphorus nuclei strongly coupled to the unpaired electron is unambiguous.

CALCULATIONS

The *ab initio* UHF method in the LCAO–MO approximation with spin annihilation, as described previously,[8] was used. A minimal basis set of Slater-type orbitals, represented on phosphorus by four *s*-type and four *p*-type and on hydrogen by six *s*-type completely contracted gaussian-function expansions,[9] was used in the calculations on $[P_2H_6]^+$. The calculations on $\dot{P}H_4$ were made using, in addition to the above minimal basis set, a Slater-type *d* orbital on phosphorus represented by a 2*d*-type completely contracted function expansion. The choice of Slater-type orbitals as basis orbitals was made in order that *d*-type orbitals could easily be introduced in the calculation of $\dot{P}H_4$. Bond angles for $\dot{P}H_4$ radicals were chosen as those of a perfect trigonal bipyramid, while tetrahedral angles about each phosphorus atom of $[P_2H_6]^+$ were used. The P–H bond length in all calculations was chosen as 2·7 bohr (*i.e.* close to the experimental P–H bond length in PH_3). The P–P bond length was chosen to be 4·72 bohr, some 0·3 bohr longer than that expected for a P–P single bond. The H exponent was chosen to be 1·2, while the P exponents (1*s* 14·56, 2*s* 4·91, 3*s* 1·77, 2*p* 5·48, 3*p* 1·7, and 3*d* 0·48) were obtained from a paper by Marsmann *et al.*[10] For each radical, the results were obtained from ψ, the wave function which minimises the UHF energy, and from $A_{s+1}\,\psi$ (UHFAA), where A_{s+1} is the annihilator which removes the spin component $(s + 1)$ from ψ.[11] For these radicals $s = 0{\cdot}5$.

EXPERIMENTAL

Preparation of Diphosphine Radical Cations. Exposure of pure phosphine to ^{60}Co γ rays at 77 K yielded no detectable radicals having large ^{31}P hyperfine coupling constants. In dilute neutral solutions only PH_2 radicals were detected, and in dilute solution in 100% sulphuric acid only $[PH_3]^+$ radicals were detected. We concluded that conditions in which $[PH_3]^+$ radicals could co-exist in the presence of PH_3 molecules were required, and this was achieved using a range of aqueous H_2SO_4 glasses in which $[PH_4]^+$ and PH_3 were originally present. (These were cooled to 77K immediately after preparation in order to avoid oxidation of the phosphine.) Irradiation gave e.s.r. spectra characteristic of $[PH_3]^+$ radicals, but after slight annealing shoulders appeared in exactly the regions predicted for the $M_I = 1$ lines for $[P_2H_6]^+$ radicals [Figure 1(*b*)]. We suggest that reaction (1) occurs under these conditions. Unfortunately the relative concentration of these new radicals remained low compared with those of species absorbing in the central spectral region and completely concealed any $M_I = 0$ lines.

$$[PH_3]^+ + PH_3 \longrightarrow [P_2H_6]^+ \qquad (1)$$

However, after exposing the two diphosphorus species $Me_2(S)P{-}P(S)Me_2$ and $Et_2(S)P{-}P(S)Et_2$ to ^{60}Co γ rays at 77 K, spectra containing all the expected features for the radical anions were obtained (Figure 2). These anions are

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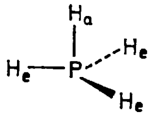
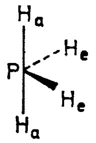
Calculated energies and hyperfine parameters for PH_4 and $[P_2H_6]^+$ radicals

Radical	Method	$a_{iso}(P)/G$	$a_{iso}(H_a)/G$	$a_{iso}(H_e)/G$	Energy/hartree	$\langle s^2 \rangle$
PH_4	UHF	124·58	310·73	16·31	−341·223083	0·7667832
Equatorial	UHFAA	194·75	260·64	23·36	−341·226556	0·7499574
PH_4	UHF	179·71	104·42	149·66	−341·204786	0·7621319
Axial	UHFAA	238·89	87·58	117·88	−341·206780	0·7499384
$[P_2H_6]^+$	UHF	457·22	−28·32		−681·281160	0·7582504
	UHFAA	414·33	−5·03		−681·282330	0·7500631



Axial



Equatorial

isostructural with $[P_2H_6]^+$, and the e.s.r. spectra were remarkably similar to those assigned to $[P_2H_6]^+$, apart from the clear anisotropy in the ^{31}P hyperfine interaction in these cases. Clear features for the (1,0) and (0,0) central components appeared in these spectra, and our theoretical values based on the second-order equations $\delta_{\parallel} = A_{\perp}^2/H_0$ and $\delta_{\perp} = (A_{\perp}^2 + A_{\parallel}^2)/2H_0$ are included in Figure 1(*b*).

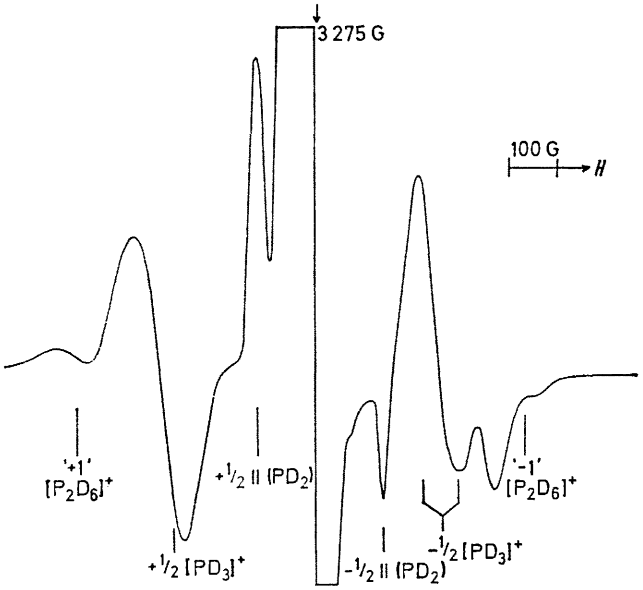


FIGURE 2 First-derivative *X*-band e.s.r. spectrum for a solution of PH_3 in a D_2SO_4–D_2O glass at 77 K after exposure to ^{60}Co γ rays for *ca.* 2 h at a dose rate of *ca.* 4 Mrad h^{-1}, showing features assigned to $[PH_3]^+$ and $[P_2H_6]^+$ radicals. The central features are assigned to various solvent radicals and possibly to $\dot{P}D_2$

DISCUSSION

Calculation of hyperfine coupling constants (Table) using the *ab initio* UHF method has proved to be most successful, especially for protons, and is generally superior to semi-empirical methods. Both theory and experiment show that the species whose e.s.r. spectra are illustrated in Figure 1(*a*) could well be $[P_2H_6]^+$. Furthermore, the theoretical calculations strongly support our comparative conclusions that the data to be expected for $\dot{P}H_4$ radicals are very different from those derivable from Figure 1(*a*) and hence we would like to conclude that the species is not $\dot{P}H_4$ but $[P_2H_6]^+$. We have reservations which are particularly based on the claim that new data rule out the $[P_2H_6]^+$ hypothesis.[12] If this is the case, then the problem remains: either, the species *is* $\dot{P}H_4$, in which case its properties are anomalous, or it is not $\dot{P}H_4$ in which case what is it? One possibility is P_2H_5 (H_2P–$\dot{P}H_3$). This species might still have the extra electron in the σ^* orbital and hence might qualitatively resemble $[P_2H_6]^+$. However, it would be most surprising if this species had two equivalent phosphorus atoms, as seems to be required if the central doublet in Figure 1(*a*) is correctly linked with the outer lines. Also the form of the proton hyperfine lines, although poorly defined, seems to be wrong for such a species.

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