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ELECTRON SPIN RESONANCE SPECTRA OF SOME PHOSPHONYL RADICALS AND RELATED SPECIES

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Summary

The isotropic ESR spectra of a number of phosphonyl radicals ($X_2\dot{P}O$), the dimethylphosphinyl radical, and the phosphoranyl radical $(MeO)_3\dot{P}OBu$-t, are described, and accurate values of the phosphorus hyperfine splittings and g-factors are reported. For $X_2\dot{P}O$, the value of a(P) increases and the g-factor decreases as the electronegativity of X increases. There is a linear relationship between a(P) for $X_2\dot{P}O$ and ^1J(P—H) for $X_2P(O)H$, but the same relationship does not hold for $Me_2P\cdot$ and Me_2PH. The spectrum of the di-n-hexylphosphonyl radical shows coupling to two pairs of α-methylene protons, and this non-equivalence is attributed to the pyramidal structure of the phosphonyl radical.

Some time ago we reported [1] the existence of a linear relationship between the NMR parameter ^1J(P—H) for compounds (phosphonates, phosphine oxides and phosphoranes) of the type L_nPH and the ESR parameter $a(^{31}P)$ for the phosphorus centred radicals $L_nP\cdot$. At that time our equipment was inadequate to allow accurate measurement of the g-factors and large phosphorus splittings shown by the radicals. Since then the g-factors of radicals have assumed new importance as a result of the extensive use of NMR spectroscopy in mechanistic studies of homolytic reactions, making use of CIDNP effects [2]. Reactions involving phosphorus centred radicals have been studied using this technique and hence we felt that it would be useful to report further details of the spectra, including more accurate measurements of g-values and phosphorus coupling constants, of some phosphonyl radicals in solution.

Experimental

The ESR spectra of radicals in fluid solution were obtained during continuous UV irradiation of appropriate samples directly in the cavity of a Varian E-4 spectrometer. The techniques employed have been described previously

[3]. Phosphonyl radicals, $X_2\dot{P}O$, were produced by photolysis of di-t-butyl peroxide in the presence of the appropriate phosphonate (eq. 1 and 2) [4].

$$\text{t-BuOOBu-t} \xrightarrow{h\nu} 2\ \text{t-BuO} \qquad (1)$$

$$\text{t-BuO}\cdot + X_2P(O)H \rightarrow \text{t-BuOH} + X_2\dot{P}O \qquad (2)$$

The phosphoranyl radical $(MeO)_3\dot{P}OBu$-t was generated by photolysis of di-t-butyl peroxide in the presence of trimethyl phosphite [5]. The dimethylphosphinyl radical was produced by X-irradiation of trimethylphosphine, included in solid adamantane, for 1 h at −145°C. The solid solution in adamantane was prepared by sublimation of the hydrocarbon in an atmosphere of trimethylphosphine at ca. 160°C (c.f. ref. 6). At −28°C an isotropic spectrum assigned to the dimethylphosphinyl radical was obtained.

Line positions were measured using a specially constructed proton magnetometer and the microwave frequency was measured using a calibrated wavemeter. Phosphorus splitting constants and g-values were calculated using the full Breit—Rabi equation [7] and are considered accurate to ±0.5 G and ±0.0002, respectively.

The phosphorus compounds employed were either commercially available or were prepared by standard methods.

Results and discussion

The ESR parameters for the phosphorus centred radicals are given in Table 1 and the spectrum of the di-n-hexylphosphonyl radical is shown in Fig. 1.

The large phosphorus splittings exhibited by the phosphonyl radicals $X_2\dot{P}O$ indicate that these species are pyramidal at the radical centre. The value of a(P)

TABLE 1

ESR PARAMETERS FOR PHOSPHONYL AND OTHER PHOSPHORUS-CENTRED RADICALS

Radical	Solvent [a]	Temp. (K)	g [b]	Hyperfine splitting (G)		^1J(P—H) for protic parent [c] (Hz)
				a(P) [b]	Others	
$(Me_3SiO)_2\dot{P}O$	C	215	2.0017	+727.6		+696 [d]
$(MeO)_2\dot{P}O$	P	251	2.0018	+697.1 [e]		+695 [f]
$(EtO)_2\dot{P}O$	C	215	2.0017	+688.6 [e]		+682 [f]
$(Me_2N)_2\dot{P}O$	P	276	2.0026	+523.6 [g]	12.0(2N); 1.5(12H)	+568 [f]
$Ph_2\dot{P}O$	C + B	280	2.0035	+361.6 [h]		+481 [i]
n-$Hex_2\dot{P}O$	C + B	276	2.0043	+350.4 [j]	8.1(2H); 2.5(2H)	+460 [k]
$Me_2\dot{P}$	A	245	2.0084	+95.7 [l]	13.9(6H)	+191 [m]
$(MeO)_3\dot{P}OBu$-t	C	187	2.0019	+886.5		

[a] C = cyclopropane, P = di-t-butyl peroxide, B = benzene, A = adamantane. [b] Calculated using the full Breit—Rabi equation. [c] At room temperature. [d] N. Fazal, Ph.D. Thesis, London, 1976. [e] In the solid state at 77 K, a(P) is 684 G for $(MeO)\dot{P}O$ and 673 G for $(EtO)_2\dot{P}O$; ref. 14. [f] Ref. 15. [g] a(P) = 491 G in the solid state at 77 K; ref. 16. [h] a(P) = 390 G in the solid state at room temperature; ref. 17. [i] Ref. 18. [j] For $Me_2\dot{P}O$ in the solid state at 140 K, a(P) = 373, a(6H) = 5.6 G; ref. 19. [k] Taken to be the same as ^1J(P—H) for n-$Bu_2P(O)H$; ref. 20. [l] For i-$Pr_2\dot{P}$ in the solid state at 77 K, a(P) = 96.7, a(2H) = 13 G; ref. 10. [m] Ref. 9.

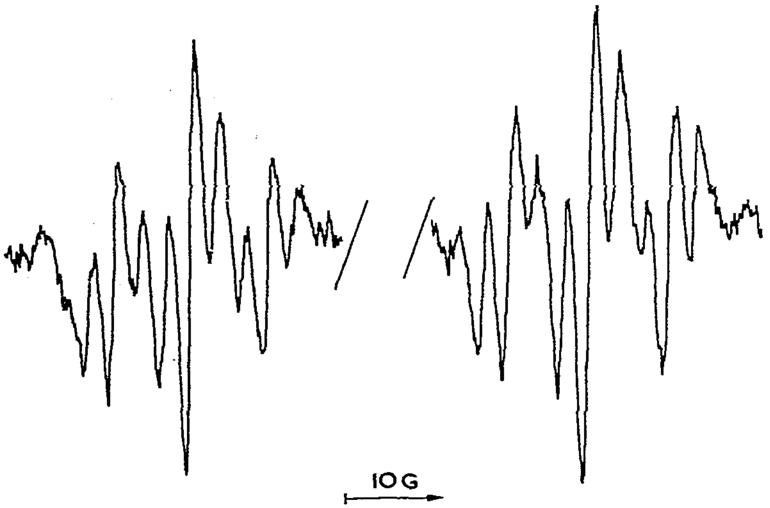


Fig. 1. ESR spectrum of the dihexylphosphonyl radical produced by photolysis of di-t-butyl peroxide in the presence of dihexylphosphine oxide in cyclopropane-benzene (1 : 1 by volume) solvent at 277K.

increases with the electronegativity of the substituent X and, as we have pointed out previously [1], there is an approximate linear relationship (eq. 3) between $a(\mathrm{P})$ and $^1J(\mathrm{P{-}H})$ for the protic parent, $X_2P(O)H$.

$$a(\mathrm{P})(\mathrm{G}) = 1.52\ ^1J(\mathrm{P{-}H})\ (\mathrm{Hz}) - 350 \qquad (3)$$

As the electronegativity of the substituent in $X_2\dot{P}O$ increases, the proportion of P-3*s* character in the orbital of the unpaired electron increases and the radical becomes more pyramidal [8]. Eq. 3 implies that the P-3*s* character of the P—H bonding MO in $X_2P(O)H$ is a linear function of the P-3*s* character in the orbital of the unpaired electron in $X_2\dot{P}O$. We have suggested that when $a(\mathrm{P})$ and $^1J(\mathrm{P{-}H})$ are related by eq. 3 homolysis of the P—H bond in the phosphonate occurs without appreciable electronic or nuclear reorganisation in the $X_2P{=}O$ residue, that is the structure of the phosphonyl group is similar in the radical and in its protic parent [1].

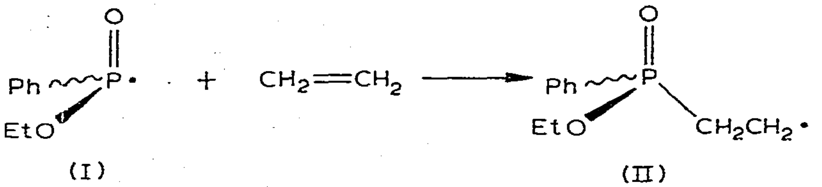
The diphenylphosphonyl radical exhibits a phosphorus splitting close to that predicted by eq. 3, taking $^1J(\mathrm{P{-}H})$ for $Ph_2P(O)H$ as 481 Hz. This suggests that there is negligible delocalisation of the unpaired electron onto the benzene rings in $Ph_2\dot{P}O$, which is in accord with the lack of resolvable proton splitting. The relatively large magnitude of the nitrogen splitting detected for $(Me_2N)_2\dot{P}O$ is probably a consequence of the non-planarity of the radical centre. The *N*-methyl proton splitting is small and there appears to be little delocalisation of the unpaired electron onto nitrogen, in agreement with the observation that $a(\mathrm{P})$ and $^1J(\mathrm{P{-}H})$ are related by eq. 3.

Eq. 3 holds only if there is appreciable P-3*s* character in the orbital of the unpaired electron in $L_nP\cdot$, such as is the case for phosphonyl and phosphoranyl radicals, and in the P—H bond of L_nPH. The values of $a(\mathrm{P})$ and $^1J(\mathrm{P{-}H})$ for $Me_2P\cdot$ and Me_2PH, respectively, are not related by eq. 3. There is relatively little P-3*s* character in the P—H bond of dimethylphosphine [9] and, to judge from its ESR spectrum and by analogy with other phosphinyl radicals [10], the unpaired electron in $Me_2P\cdot$ resides in a P-$3p_\pi$ orbital perpendicular to the CPC plane. The phosphorus splitting for $Me_2P\cdot$ thus arises by spin-polarisation of σ-orbitals rather than by the direct mechanism possible if the orbital of the unpaired electron has P-$3s$ character.

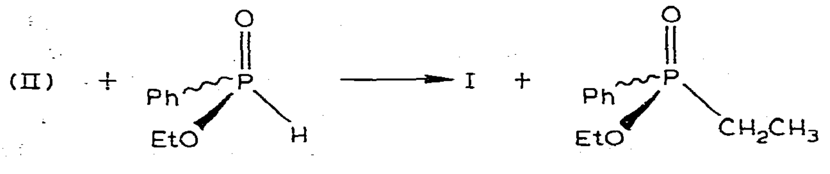
An isotropic splitting from six equivalent protons (13.9 G) was detected for the dimethylphosphinyl radical. This value may be compared with that obtained (13 G) for the β-hydrogen splitting in the diisopropylphosphinyl radical, produced by γ-irradiation of i-Pr_2PCl [10]. The similarity of these values implies that rotation about the C—P bonds is essentially free in both radicals. The proton splitting for $Me_2P\cdot$ probably arises predominantly by a hyperconjugative mechanism and is smaller than that detected for $Me_2N\cdot$ (27.36 G) [11], which would be expected since phosphorus is a second row element and the P-$3p_\pi$ orbital will overlap less effectively than the N-$2p_\pi$ orbital with the β-C—H group orbitals.

The g-factor of the dimethylphosphinyl radical is higher than that of $Me_2N\cdot$ (2.0044), and this difference may be related to the larger spin-orbit coupling constant of phosphorus compared with that of nitrogen. There is a steady increase in the g-factors of the phosphonyl radicals $X_2\dot{P}O$ as the electronegativity of X decreases and as the radicals become less pyramidal at the radical centre. For comparison, the g-factor of the monofluoromethyl radical (2.0045) is greater than that of the more pyramidal trifluoromethyl radical (2.0038) [12].

Product studies demonstrate that phosphonyl radicals possess considerable configurational stability. For example [13], optically active ethyl phenylphosphinate undergoes free radical chain addition to ethylene with complete retention of configuration at phosphorus (eq. 4 and 5).

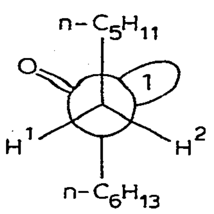


(4)

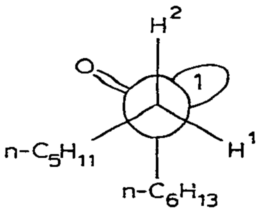


(5)

The pyramidal structure of the dihexylphosphonyl radical is probably responsible for the non-equivalence of the α-methylene protons of the hexyl groups. The spectrum at 277K, at which temperature rotation about the P—C bonds will probably be rapid on the ESR time scale, is shown in Fig. 1. For a pyramidal radical centre the α-methylene protons will be non-equivalent whatever the rate of rotation about the P—C bonds. It seems likely that exchange between the conformers III—V will be rapid, with III the most stable.



(III)



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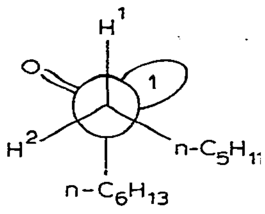

(V)

The phosphoranyl radical $(MeO)_3\dot{P}OBu$-t was included for comparative purposes. It exhibits a larger phosphorus splitting than $(RO)_2\dot{P}O$, but the *g*-factors of both radicals are very similar and slightly less than the free spin value (2.0023).

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