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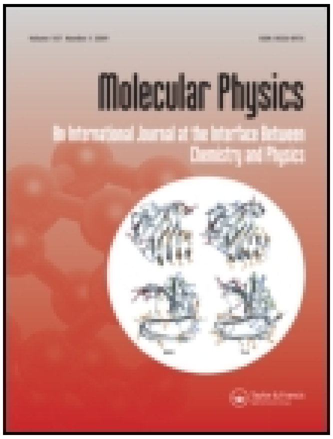

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The electron spin resonance spectrum of X-irradiated phenylphosphinic acid and its salts

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The electron spin resonance spectrum of X-irradiated phenylphosphinic acid and its salts

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Irradiation of single crystals of phenylphosphinic acid, $C_6H_5P(H)(O)OH$, gives rise to a radical to which the structure $C_6H_5\dot{P}(O)OH$ is ascribed. The radical exists in four different symmetry-related orientations and the average principal values of the g-tensor and of the ^{31}P coupling tensor are 2·0023, 2·0034, 2·0034 and 1865, 1346, 1320 MHz.

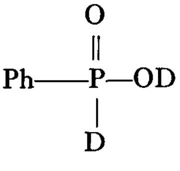
Irradiation of the polycrystalline acid gives identical results for the E.S.R. parameters. Irradiation of various polycrystalline salts of phenylphosphinic acid gives rise to spectra attributed to $C_6H_5PO_2^{\cdot -}$, the phosphorus analogue of the nitrobenzene radical anion. The E.S.R. parameters are similar to those of the radical arising from the corresponding acid but vary with the nature of the cation. They indicate that unlike $C_6H_5NO_2^{\cdot -}$ the radical is non-planar and has the unpaired electron largely localized on the phosphorus atom.

1. Introduction

In a previous communication [1], we have reported the E.S.R. parameters of the radical Ph_2PO, the phosphorus analogue of the well-known stable radical diphenylnitroxide, which was prepared by X-irradiation of crystalline diphenyl phosphine oxide. In continuation of this work we report here the E.S.R. spectra of the radicals produced by X-irradiation of phenylphosphinic acid and certain of its salts, and present evidence that the radicals produced from the salts are the phosphorous analogues, $Ph\dot{P}O_2^-$, of the nitrobenzene radical anion.

2. Experimental

Commercial (Fluka) phenylphosphinic acid gave monocrystals of appropriate dimensions (∼5 mm) on slow recrystallization from water. Deuterated phenylphosphinic acid,



$$Ph\text{—}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle D}{|}}{P}}\text{—}OD$$

is obtained by recrystallization from D_2O (99 per cent D), the extent and positions of deuteration being verified by proton N.M.R. spectroscopy at 60 MHz (Perkin–Elmer R.12). The salts were prepared according to the method of Michaelis [2] with the exception of the potassium salt which was prepared by the action of metallic potassium on a solution of phenylphosphinic acid in benzene saturated with water.

The monocrystals of phenylphosphinic acid and the polycrystalline salts were sealed in glass tubes in an atmosphere of Argon and these were placed as close as possible to the window of a Phillips type 1559 X-ray tube fitted with a tungsten cathode, for periods of seven and twelve hours respectively at room temperature.

Electron spin resonance spectra were measured on a J.E.O.L. ME–1X X-band spectrometer using 100 HKz field-modulation. The field sweep was calibrated by means of the spectrum of Mn^{2+} in polycrystalline calcium oxide [3] and the g-factors measured with respect to D.P.P.H. ($g = 2{\cdot}0036$).

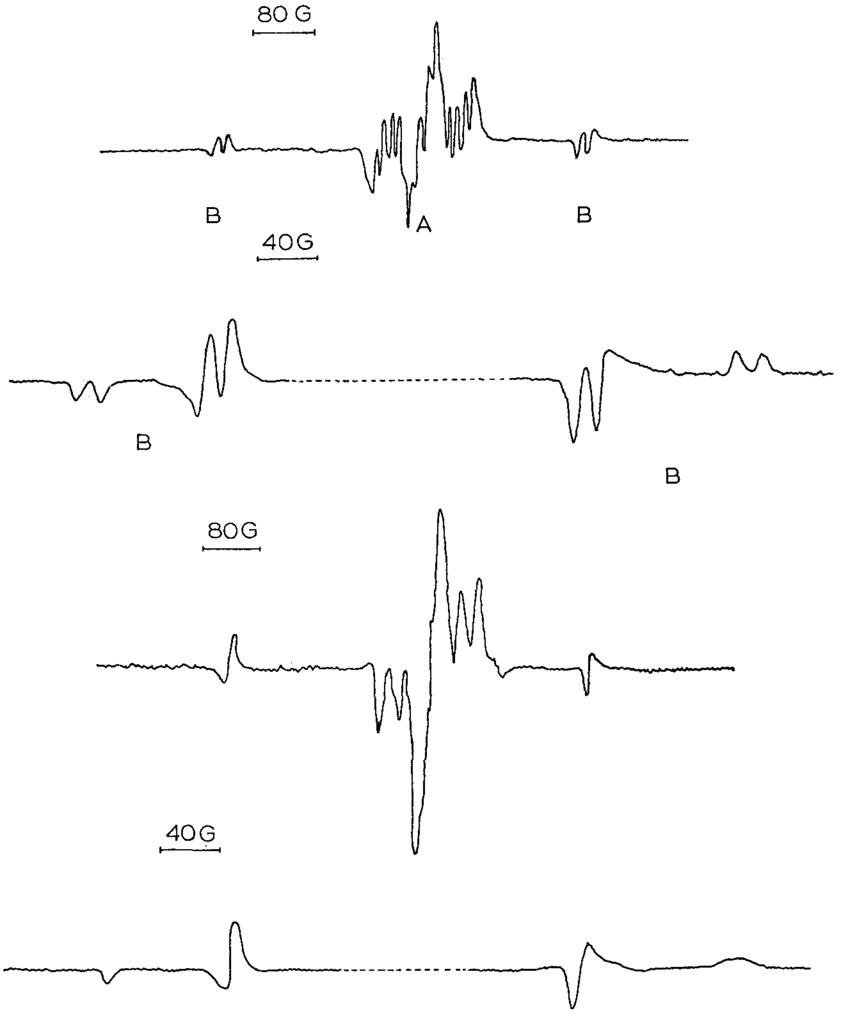
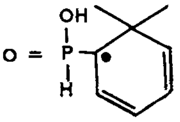


Figure 1. Spectra of irradiated polycrystalline phenylphosphinic acid. (*a*) Material of normal isotopic constitution. (*b*) As (*a*) but at higher gain to show extreme satellites. (*c*) As (*a*) but of the deuterated compound, Ph(D)P(O)OD. (*d*) As (*c*) but at higher gain to show outer satellites.

3. Results

3.1. *Powder spectra*

A typical spectrum (figure 1) shows the presence of at least two radical species. The central spectrum (A) contains abundant fine structure with relatively small coupling constants, which is difficult to analyse and for the present these spectra have not been studied in detail. A spectrum (B) with one strong doublet cylindrically symmetric splitting is present however, and yields at once values for the perpendicular and parallel components of the hyperfine splitting and g-tensors. A further splitting into two components is noted in the B-spectrum of polycrystalline phenylphosphinic acid which is not present in the deuterated compound. It is therefore due to one of the two hydrogen atoms which have been substituted by the deuterium isotope. In connection with the central spectrum (A) it is noteworthy that the central spectrum (A) has also undergone considerable simplification in the deuterated material. A possible structure for radical (A) is one resulting from attack of a hydrogen atom on the benzene ring e.g.



These results are summarized in table 1.

Cation	^{31}P coupling constant (MHz) $A_\parallel$	$A_\perp$	$g_\parallel$	$g_\perp$
Na$^+$	1525	1055	2·0001	2·0020
	1758	1243	1·9991	2·0020
K$^+$	1724	1231		
Mg^{++}	1791	1262	2·0011	2·0024
Ca^{++}	1763	1259	2·0009	2·0023
Sr^{++}	1702	1209	2·0010	2·0021
Ba^{++}	1646	1156	1·9997	2·0015
Ph(H)P(O)OH	1867	1332	2·0023	2·0034

Table 1. E.S.R. spectral parameters for irradiated powders of salts of phenylphosphinic acid. The free acid shows an additional coupling from a proton $A_\parallel = 49$ MHz, $A_\perp = 42$ MHz.

4. Spectra of single crystals phenylphosphinic acid

A typical spectrum of the deuterated material is shown in figure 2. Study of the central spectrum (A) has been left aside for the moment and attention concentrated on the outer spectrum (B). In general the spectrum consists of two pairs of widely-separated lines and the usual study of the rotation pattern together with the result for the polycrystalline powder, shows that these pairs arise from two symmetry-related radical sites. In certain orientations a further splitting occurs (*figure* 3) showing that in fact four symmetry related sites are present. This observation is consistent with the observation that the crystal is orthorhombic[†].

The values of the hyperfine and *g*-tensors for these species are shown in table 2 ; they are identical with those obtained from the polycrystalline material. We were unsuccessful in obtaining large single crystals with well-developed characteristic faces and for this reason do not give values of direction cosines. Furthermore as stated above the splitting from two to four components only occurs for rotation about one axis and the positions of the extrema of the rotation patterns are badly defined. This is the reason for the rather poor precision (~ 1 per cent) in the values of the four coupling constants which should certainly be all identical.

Figure 2. Spectrum of monocrystalline Ph(D)P(O)OD, showing the presence of two radical sites.

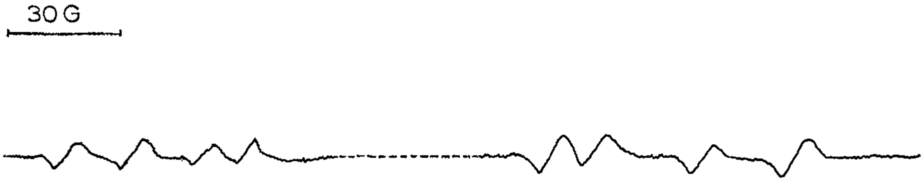


Figure 3. Spectrum of monocrystalline Ph(D)P(O)OD showing further splitting into four components.

	^{31}P coupling constant (MHz)			*g*-tensor		
Site (1)	1878	1349	1330	2·0023	2·0034	2·0034
Site (2)	1878	1349	1330	2·0023	2·0034	2·0034
Site (3)	1853	1344	1311	2·0023	2·0034	2·0034
Site (4)	1853	1344	1311	2·0023	2·0034	2·0034

Average $A_{\parallel}$ 1865, $A_{\perp}$ 1333.

Table 2. ^{31}P coupling constants and *g*-tensors from irradiated monocrystalline Ph(D)P(O)OD.

The spectrum of the non-deuterated material shows, as in the case of the polycrystalline substance, a further splitting due to a spin ½ nucleus. This splitting is

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[†] We thank Dr. R. Gerdil and Mr. A. Dunant of the Organic Chemistry Department who have kindly determined the following parameters by x-ray diffraction : $a = 5{\cdot}70 \pm 0{\cdot}01$ A, $b = 7{\cdot}77 \pm 0{\cdot}02$ A, $c = 15{\cdot}364 \pm 0{\cdot}006$ A, $D_m = 1{\cdot}401$ gm cm^{-3}, $Z = 4$. Systematic absences show the space group is Pmn2_1 or Pmmn.

almost isotropic and the values essentially the same as those reported above; although a complete rotation study of the non-deuterated material was not carried out. The spectrum of this material was also measured at 77 K: no significant change in the spectrum was apparent in any of the several orientations studied.

5. DISCUSSION

A variety of previous investigations have shown that homolytic fission of the Phosphorus–Hydrogen bond is a frequent consequence of X-radiolysis of solid materials containing this structural unit. This hypothesis also explains well the spectra obtained here, the large doublet splitting arising from the ^{31}P nucleus with which the resulting unpaired electron is largely associated. The measurements on the deuterated material shows that the large splitting cannot arise from the hydrogen directly bonded to the phosphorus atom and no other spin $\frac{1}{2}$ nucleus, apart from ^{31}P, is likely to give such a considerable interaction. It seems certain therefore that the B radical in the salts arises from the radical-anion $\mathrm{PhPO_2}^{\underset{\cdot}{-}}$ while in the free acid the neutral species $\mathrm{Ph\dot{P}(O)OH}$ is present.

	^{31}P coupling constants (MHz)			Phosphorus valence orbital spin densities			
Cation	A iso	$B_\parallel$	$B_\perp$	3*s*	3*p*	3*s* + 3*p*	3*s*/3*p*
Na^+	1212	313	−157	0·12	0·54	0·66	0·22
	1414	344	−172	0·14	0·59	0·73	0·24
K^+	1397	327	−163	0·13	0·56	0·69	0·23
Mg^{++}	1439	327	−177	0·14	0·61	0·75	0·23
Ca^{++}	1428	336	−168	0·14	0·58	0·72	0·24
Sr^{++}	1372	330	−165	0·13	0·57	0·70	0·23
Ba^{++}	1318	327	−163	0·13	0·56	0·69	0·23
Ph(H)P(O)OH	1512	356	−178	0·15	0·61	0·76	0·25

Table 3. Break-down of ^{31}P coupling constants into their isotropic and anisotropic components. A spin density of unity in a ^{31}P-3*s* orbital is assumed to give an isotropic coupling of 10 190 MHz and in a ^{31}P 3*p* orbital a parallel anisotropic coupling of 577 MHz.

The assumption that the radical anion is $\mathrm{PhPO_2}^{\underset{\cdot}{-}}$ and that the splitting arises from the ^{31}P nucleus leads to the further assumption that the parallel and perpendicular components of the hyperfine coupling tensor both have the same sign. They may then be split up into isotropic and anisotropic components, the former arising from the 3*s* and the latter from the 3*p* electron density at the phosphorus atom, and hence yield values for these densities from the theoretically evaluated couplings for an electron in a pure 3*s* or 3*p* orbital of neutral ^{31}P.[4]. The results of such calculations are shown in table 3.

They show that in contrast to the nitrobenzene radical anion which is most probably planar, the radical $\mathrm{PhPO_2}^{\underset{\cdot}{-}}$ is undoubtedly pyramidal although the bond angle is certainly greater than the tetrahedral angle. Furthermore, and in agreement with the non-planar structure, the total spin–density on the phosphorus atom is approximately 0·7 while for the nitrobenzene radical anion in solution the spin-density has been estimated [5] as approximately 0·24.

The difference between $PhPO_2^{\bar{\cdot}}$ and $PhNO_2^{\bar{\cdot}}$ is thus similar to the difference between Ph_2PO and Ph_2NO [1].

The electron spin resonance parameters of $PhPO_2^{\bar{\cdot}}$ are dependent on the nature of the cation ; similar behaviour has already been noted with the analogous $PO_3^{2\bar{\cdot}}$ and $HPO_2^{\bar{\cdot}}$ radical [6] and the environmental dependence of ^{14}N splittings in $PhNO_2^{\bar{\cdot}}$ is likewise well-known [5].

The results presented here complete the series of related radicals $PO_3^{2\bar{\cdot}}$, $PhPO_2^{\bar{\cdot}}$, $Ph_2PO^{\bar{\cdot}}$. The $3s/3p$ ratio decreases steadily from an average value of 0·31 for $PO_3^{2\bar{\cdot}}$ to 0·18 for the last member of the series. We have so far been unsuccessful in attempts at obtaining $Ph_3P^{+\cdot}$; the isoelectronic Ph_3Si [7] has however an $3s/sp$ ratio of 0·1. Thus substitution of oxygen by phenyl in this system makes the radical increasingly flat. This behaviour is analogous to that found in diamagnetic molecules and is possibly due to reduction of bond–bond interelectronic repulsion as the more electronegative substituent pulls the centre of gravity of the bonding electrons away from the central atom.

It could also be due to simply the greater bulk of the phenyl groups. It is not likely to arise from delocalization of the unpaired electron onto the phenyl rings since the total spin density on phosphorus remains almost constant throughout the series.

The structure of the radicals $Ph_{3-n}PO_n^{(n-1)\bar{\cdot}}$ thus appear to evolve in a regular and systematic fashion. In contrast to their nitrogen analogues none of them are planar, and the planarity of the nitrogen-containing compounds is no doubt due to the ability of this atom to form strong π bonds.

As far as can be judged from the ^{31}P hyperfine splitting the structure of the parent neutral radical, $PhP(O)OH^{\cdot}$ appears to be very similar to that of the radical anion. Coupling with the $-OH$ proton is of an unsurprising order of magnitude. The lack of an appreciable temperature dependence indicates either that at room temperature the proton occupies a well-defined fixed position in the molecule or that even at 77 K it is exchanging rapidly among several different sites.

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REFERENCES

[1] Geoffroy, M., and Lucken, E. A. C., 1971, *Molec. Phys.*, **22**, 257.

[2] Michaelis, A., 1876, *Justus Liebigs Annln Chem.*, **181**, 303.

[3] Abragam, A., and Bleaney, B., 1970, *Electron Paramagnetic Resonance of Transition Ions* (Clarendon).

[4] Watson, R. E., and Freeman, A. J., 1961, *Phys. Rev.*, **124**, 1117.

[5] Rieger, P. H., Fraenkel, G. K., 1963, *J. chem. Phys.*, **39**, 609.

[6] Horsfield, A., Morton, J. R., and Whiffen, D. H., 1961, *Molec. Phys.*, **4**, 475. Hanna, M. W., and Altman, L. J., 1962, *J. chem. Phys.*, **36**, 1788. Morton, J. R., 1962, *Molec. Phys.*, **5**, 217. Atkins, P. W., Keen, N., and Symons, M. C. R., 1963, *J. chem. Soc.*, p. 250.

[7] Geoffroy, M., and Lucken, E. A. C., 1970, *Helv. chim. Acta.*, **52**, 813.