

40. *Unstable Intermediates. Part XVI.¹ Hyperfine Coupling from α -Protons in Non-planar Free Radicals: the HPO_2^- Radical.*

By P. W. ATKINS, N. KEEN, and M. C. R. SYMONS.

Analysis of the ^{31}P hyperfine coupling tensor derived from the electron-spin resonance spectrum of the radical HPO_2^- in γ -irradiated $\text{Mg}(\text{H}_2\text{PO}_2)_2$ shows that this radical is non-planar, the $3p:3s$ ratio for the unpaired electron's orbital population on phosphorus being 4.07. Hyperfine coupling to the proton is almost isotropic and remarkably large for an α -hydrogen. It is suggested that, in contrast with planar π -electron radicals, this coupling is positive, and reasons for this are discussed. Spin-resonance data for silyl radicals are interpreted in terms of a pyramidal configuration.

THE radical PO_3^{2-} has been identified in γ -irradiated $\text{Na}_2\text{HPO}_3 \cdot 5\text{H}_2\text{O}$ by its electron-spin resonance spectrum,² which can be analysed in terms of the $3s$ - and $3p$ -character of the unpaired electron on phosphorus. We have independently detected this radical in several γ -irradiated phosphorus oxy-salts, together with other radicals of similar structure. One radical detected in various hypophosphites, and thought to be HPO_2^- , has a very similar spectrum except that each component of the ^{31}P doublet is further subdivided as a result of coupling to the proton. This subsidiary splitting of about 90 gauss is very large for an α -proton (that is, a proton directly attached to the atom on which the magnetic electron resides when coupling occurs), being close to that found for the formyl radical^{3,4} and very much larger than the normal isotropic coupling of 20–25 gauss for protons in planar π -electron radicals such as CH_3 or NH_3^+ .

Our main aim here is to discuss these results in terms of the coupling mechanism and the stereochemistry of the radical.

The results, obtained from spectra such as that depicted in the Figure, are summarised in Table 1, and the principal values for the hyperfine and g -tensors, derived therefrom by a second-order iterative process are given in Table 2, together with estimates of the $3p$ - and $3s$ -character of the unpaired electron on phosphorus and the $1s$ -character on hydrogen.

Identity of the Radical.—The major anisotropic hyperfine tensor must be associated with ^{31}P , and hence the $3s$ - and the $3p$ -character of the orbital on phosphorus can be estimated. The results show that, relative to PO_3^{2-} , the unpaired electron is somewhat more localised on phosphorus, and, since the $p:s$ ratio has increased from 3.31 to 4.07,

¹ Part XV, *J.*, 1962, 2582.

² Horsfield, Morton, and Whiffen, *Mol. Phys.*, 1961, **4**, 475.

³ Brivati, Keen, and Symons, *J.*, 1962, 237.

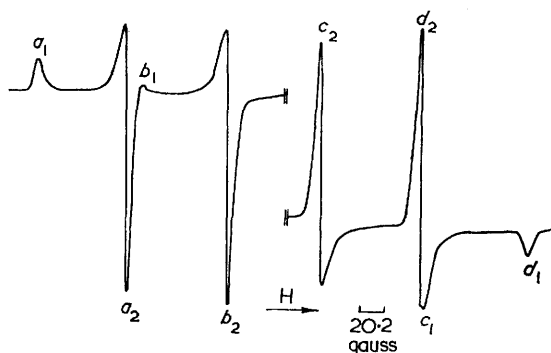
⁴ Adrian, Cochran, and Bowers, *J. Chem. Phys.*, 1962, **36**, 1661.

the new radical is, overall, somewhat flatter⁵ than PO_3^{2-} . These trends are in good accord with expectation for replacement of O^- by hydrogen, and hence support the formulation HPO_2^- .

It is common experience that exposure of crystalline solids composed of molecules or ions containing hydrogen to high-energy radiation results in loss of hydrogen atoms. These may be trapped and detected by spin-resonance methods if the temperature of the sample is in the region of 4°K , but under most conditions they react further to give molecular hydrogen or extract a hydrogen atom from another H_2PO_2^- ion. Hence it is most reasonable to expect that the reaction $\text{H}_2\text{PO}_2^- \rightarrow \text{H}\cdot + \text{HPO}_2^-$ would constitute an

Electron-spin resonance spectrum of γ -irradiated polycrystalline magnesium hypophosphite at room temperature.

Microwave frequency = 9463.8 Mc/sec.,
 $a_1 = 2993.9$ gauss, $d_1 = 3731.3$ gauss.
 For ease of representation, the central portion of the base line has been omitted.



important step in the decomposition of the salts under consideration. This step should be compared with that known to result in the formation of PO_3^{2-} radicals:



Since the radical must be bent, we should expect, by analogy with the formyl radical,³ to detect a large isotropic hyperfine coupling to the proton, and since the distance between the major density lobe of the electron and the proton is large, the anisotropic coupling should be quite small. These expectations are fulfilled. The isotropic coupling of about 90 gauss is very large for an α -proton, and should be compared with the result of about 130 gauss for formyl, HCO . The total anisotropy is probably less than 7 gauss, but cannot be accurately estimated from our spectra. This is again comparable with that for HCO .

TABLE I.

“Experimental” results for the hyperfine and g -tensors of the HPO_2^- radical.

System	g' -values			³¹ P Hyperfine splitting (gauss)			Average proton hyperfine splitting (gauss)
	g'_1	g'_{11}	g'_{av}	Anisotropic A'_1	Isotropic A'_{11}	A'_{1so}	
$\text{Mg}(\text{H}_2\text{PO}_2)_2$ γ -irradiated and measured at 300°K	2.0159	2.0109	2.0142	-60.8	+121.5	+520.7	92.6
$\text{Ca}(\text{H}_2\text{PO}_2)_2$ γ -irradiated at 77°K and measured at 300°K	2.0171	2.0088	2.0143	-60.5	+121.1	+511.8	88.0
$\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$ γ -irradiated and measured at 77°K	2.0146	2.0059	2.0117	-57	+114	+472	88.6

Thus our identification is firmly based, and in the following its correctness is assumed. The only alternative which could explain the spin-resonance results is HPO^+ . This is so unreasonable chemically that further consideration is unwarranted.

⁵ Coulson, Victor Henri Volume Commemoratif, Contribution à l'Étude de la Structure Moléculaire, 1948, p. 15.

TABLE 2.

Corrected hyperfine and g -tensors and orbital spin-densities for the HPO_2^- radical in magnesium hypophosphite at room temperature.

$A_{\parallel} = 366$ Mc./sec.	$g_{\parallel} = 2.0020$
$A_{\perp} = -183$ Mc./sec.	$g_{\perp} = 2.0035$
$A_{\text{iso}} = 1453$ Mc./sec.	$g_{\text{av}} = 2.0030$
$a_{p^3} = 0.61.$	$a_{s^3} = 0.15.$
	$a_{\text{H}^1} = 0.18.$

a_{p^3} , a_{s^3} , and a_{H^1} are the spin populations of the P $3p_z$ and $3s$ and the H $1s$ orbitals, respectively.

Stereochemistry.—It is noteworthy that the $p:s$ ratio for HPO_2^- is somewhat greater than that for PO_3^{2-} . Whilst wishing to postpone detailed consideration of this trend until more results are available, we recall that the radical NH_3^+ is almost certainly planar,⁶ whereas NO_3^{2-} is probably bent,⁷ though the $p:s$ ratio for this radical is relatively large and the identification somewhat uncertain. Also, if our reasoning in the next section is correct, the silyl radical, which is isoelectronic with PH_3^+ , is not planar although the bond angle must be large compared with that in HPO_2^- . These facts are in accord with the present results and lead to the generalisation that in radicals of this type, replacement of O^- by H results in a decrease in the angle between the X-H bond and the density axis of the orbital of the unpaired electron on X.

Proton Hyperfine Coupling.—We stress that the hyperfine coupling to the proton is unusually large. As with the structurally similar formyl radical,^{3,4} the unpaired electron density on the proton is almost certainly positive, so that one can say that the unpaired electron is about 16% on the proton. Positive coupling has been established experimentally by Adrian *et al.*,⁴ and is required by theory for both radicals. This is important in that it suggests that the results for formyl are not a peculiar feature of this radical, but that a large proton coupling is to be expected for radicals such as $\text{H}\dot{\text{X}}\text{A}$, $\text{H}\dot{\text{X}}\text{A}_2$, etc., in which the unpaired electron has considerable s -character on X. In the following sections we consider this generalisation qualitatively, in terms of simple valence-bond and molecular-orbital theory.

Valence-bond Treatment.—In a planar XH_3 seven-electron molecule, the X-H bonds are formed by the spin-pairing of the electrons in the H $1s$ - and X sp^2 -atomic orbitals, the unpaired electron being in the orthogonal $2p_z$ -orbital on X. For the isolated X-H bond there is no preference *a priori* for a particular spin alignment. Introduction of the odd electron into the X $2p_z$ -orbital gives rise to an energetically more favourable situation with the electron in the X sp^2 -orbital aligned parallel to the unpaired electron. This is a consequence of the exchange interaction between two electrons closely approaching each other. By the Pauli principle the electron predominantly in the H $1s$ orbital is necessarily antiparallel to the other bonding electron and hence also to the unpaired electron. Therefore a negative spin-density arises at the proton.

When the angle between the unpaired electron orbital and the X-H bond increases, s -character migrates from the X sp^2 -orbitals to the $2p_z$ -orbital. Since the s -orbital has a large magnitude in the vicinity of the nucleus, when the bonding electron is near the unpaired electron, both will have some s -character. In these circumstances these electrons tend to pair with their spins antiparallel, which leaves a positive spin-density at the proton. This effect will gain in importance as the s -character of the unpaired electron increases.

Molecular Orbital Approach.—An alternative explanation may be offered in terms of molecular-orbital theory for seven-electron radicals of the type XH_3 .

The ground state of a planar XH_3 molecule (symmetry group D_{3h}) is

$$(1a'_1)^2(2a'_1)^2(1e')^4(1a''_2)^1, {}^2A''_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

⁶ Cole, *J. Chem. Phys.*, 1961, **35**, 1169.

⁷ Symons, "Inorganic Free Radicals," ed. R. F. Gould, A.C.S. Monograph, 1962.

The $1a'_1$ orbital is largely the $1s$ -atomic orbital in X, $2a'_1$ and $1e'$ are X-H bonding orbitals, and $1a''_2$ is a non-bonding orbital centred on X and is predominantly an X $2p_z$ -atomic orbital. This z -axis is the C_3 symmetry axis.

The bent molecule has reduced symmetry and belongs to the group C_{3v} . The ground state has the orbital classification

$$(1a_1)^2(2a_1)^2(1e)^4(3a_1)^1, {}^2A_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The odd electron is now in the $3a_1$ -orbital which has increasingly more X $2s$ -character as the HXH angle approaches 90° . The proton interaction term depends on mixing of excited states with the ground state, the permitted mixing being governed by symmetry requirements. Since the symmetry of the orbital containing the unpaired electron changes from $1a''_2$ to $3a_1$ on bending, the states involved in the two cases will differ.

For planar methyl Padgett and Krauss⁸ and Higuchi and Aono⁹ have shown by an LCAO-SCF molecular-orbital calculation that the pertinent excited states which contribute are

$$(1a'_1)^2(2a'_1)^2(1e')^3(1a''_2)^1(2e')^1, {}^2A''_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

$$(1a'_1)^2(2a'_1)^1(1e')^4(1a''_2)^1(3a'_1)^1, {}^2A''_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

The mixing of (3) with (1) gives only a small contribution, the major interaction arising from the mixing of (4) with (1). The effective excitation involved is $3a'_1 \leftarrow 2a'_1$ which is tantamount to a movement of charge outwards. To a first approximation the electron in the $1a''_2$ -orbital is unaffected by this migration. The electron in the $3a'_1$ -orbital is predominantly near the hydrogens, and since it has an antiparallel spin to the electron in the $2a'_1$ -orbital, and hence also to the electron in the $1a''_2$ -orbital, a net negative spin-density will arise on the hydrogen atoms.¹⁰

In the bent molecule a similar situation occurs except that, as described above, the symmetry of the orbital containing the odd electron becomes $3a_1$. Since this level is already half full, only a state with opposite spin can mix with it. This entails that the electron remaining in the lower level has the same sign as the previously unpaired electron. Since the $3a_1$ -orbital is non-bonding it is more strictly confined to the central atom than any of the lower $n a_1$ orbitals with which it interacts, so there will be a considerable positive spin-density on the hydrogens. As the molecule bends, the s -character of the $3a_1$ -orbital increases and so this level deepens in energy; interaction involving this orbital, therefore, becomes more important and so the proton interaction becomes larger and more positive. Thus the essential difference between the coupling mechanisms for planar and bent radicals is that, for the former, interactions involving excitations from filled to unoccupied orbitals are involved, whereas for the bent radicals excitation into the half-filled level is involved.

[Note added in proof: Morton (*Mol. Phys.*, 1962, 5, 217) has also studied the radical HPO_2^- . His data are very similar to ours.]

Conclusions.—The effect of bending on the proton hyperfine coupling in methyl radicals has been discussed by Karplus.¹¹ In terms of the present scheme, the magnitude of this interaction should become less negative, pass through zero and increase to a value several times larger than the original on progressive bending towards the tetrahedral configuration.

It is perhaps relevant that the isotropic proton hyperfine coupling for trapped silyl radicals is only 7.6 gauss.¹² The relative sign of this coupling cannot be estimated from the results, but, if our analysis is correct, the small magnitude can be understood if these radicals are pyramidal, in contrast to methyl radicals.

⁸ Padgett and Krauss, *J. Chem. Phys.*, 1960, **32**, 189.

⁹ Higuchi and Aono, *J. Chem. Phys.*, 1960, **32**, 52.

¹⁰ McConnell and Chesnut, *J. Chem. Phys.*, 1958, **28**, 107.

¹¹ Karplus, *J. Chem. Phys.*, 1959, **30**, 15.

¹² Cochran, 4th Internat. Symposium on Free Radicals, 1959, D11.

EXPERIMENTAL

Materials.—The salts listed in Table 1 were kindly given by Messrs. Albright and Wilson, and were used without further purification.

Gamma-irradiation.—Samples were irradiated at room temperature or 77°K with a 1900 c ⁶⁰Co source, the total dosages being about 6.5 Mrad.

Electron-spin Resonance.—Measurements were made at room temperature and 77°K with a 3 cm. spectrometer described previously.³

Derivation of the Hyperfine and g-Tensors from the Spectra attributed to HPO₂⁻.—The large doublet splitting is assigned to ³¹P ($I = \frac{1}{2}$), and the secondary splitting, assigned to a proton, is assumed to be isotropic.

It is also assumed that there is axial symmetry for both the ³¹P hyperfine and *g*-tensors, and measurements were made from points of extreme slope as recommended by Kneubühl.¹³ Thus,

$$a'_{\perp}({}^{31}\text{P}) = \frac{c_2 + d_2}{2} - \frac{a_2 + b_2}{2}; \quad a'_{\parallel}({}^{31}\text{P}) = \frac{c_1 + d_1}{2} - \frac{a_1 + b_1}{2};$$

$$a({}^1\text{H}) \quad (d_1 - c_1) \doteq (d_2 - c_2) \quad (b_2 - a_2) \doteq (b_1 - a_1),$$

and g'_{\perp} at $\frac{c_2 + d_2}{2} - \frac{a'_{\perp}}{2}$, g'_{\parallel} at $\frac{c_1 + d_1}{2} - \frac{a'_{\parallel}}{2}$.

The primed values are not the true values because the nuclear interaction from ³¹P is large, and are thus described as "experimental" to distinguish them from the true components of the tensors. Parameters derived from these spectra are given in Table 1. True values for the magnitudes of these tensors have been calculated for the radical in magnesium hypophosphite and are given in Table 2, together with relevant orbital spin-densities.

Experimental Details.—The ability of different hypophosphites to yield HPO₂⁻ on γ -irradiation was dependent on the cation and the temperature. Irradiation of the calcium salt at 300°K gave no HPO₂⁻; however, a multicomponent spectrum, of total spread about 260 gauss centred on $g = 2.003$, was observed. When the calcium salt was irradiated at 77°K an appreciable amount of HPO₂⁻ was detected, together with a trace of the 260 gauss species; warming to 300°K had very little effect on the relative amounts of the two species.

Irradiation of the magnesium salt at 300°K gave rise to a large concentration of HPO₂⁻, the 260 gauss species being just detectable; similar behaviour was observed when the irradiation was carried out at 77°K and the spectrum measured either at this or at room temperature. Some HPO₂⁻ was detected at 77°K in the sodium salt after prolonged irradiation at this temperature, but the signal was weak; no signal was detected from the sodium salt irradiated at room temperature.

We thank Dr. Chapman of Albright and Wilson Ltd. for supplying the phosphorus salts, D.S.I.R. and Imperial Chemical Industries Limited for financial assistance, and D.S.I.R. and The Esso Petroleum Company for maintenance grants to P. W. A. and N. K.

DEPARTMENT OF CHEMISTRY,
THE UNIVERSITY, LEICESTER.

[Received, June 12th, 1962.]

¹³ Kneubühl, *J. Chem. Phys.*, 1960, **33**, 1074.