Electron Spin Resonance Studies. Part XXXV.[1] The Generation, and Some Reactions, of the Radicals $\cdot PO_3^{2-}$, $\cdot PO_2OH^-$, $HPO_2^{\cdot -}$, and $PhPO_2^{\cdot -}$ in Aqueous Solution

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Four phosphorus-containing radicals ($\cdot PO_3^{2-}$, $\cdot PO_2OH^-$, $HPO_2^{\cdot -}$, and $PhPO_2^{\cdot -}$) have been generated in aqueous solution by the abstraction of hydrogen from the parent anions and have been characterised by their e.s.r. spectra; the electronic structure of $PhPO_2^{\cdot -}$ contrasts markedly with that of $PhNO_2^{\cdot -}$. The radicals add readily to many olefinic compounds, oximes (to give nitroxides), and nitroalkane *aci*-anions; the resulting e.s.r. spectra provide information about the conformational preferences of the adducts and the angular dependence of the hyperfine interaction with ^{31}P.

THERE has been a number of studies of phosphorus-containing radicals in the liquid phase by e.s.r. spectroscopy, the results of which have led to conclusions about both the structures of the radicals and the mechanism of interaction of the spin with the phosphorus nucleus (^{31}P; $I = 1/2$); the following are illustrative. Radicals with the unpaired electron formally located at phosphorus, of the types $\cdot PR_3\cdot OBu^t$ and $\cdot P(OR)_3\cdot OBu^t$, have been generated by the photolysis of di-t-butyl peroxide in the presence of phosphines[2] and phosphites,[3] respectively; as expected, they are associated with very large values for a_P. Radicals with the unpaired electron formally associated with an atom bonded to phosphorus include $Ph_2PO\cdot$ (the large value of a_P for which provides evidence for non-coplanar bonding to phosphorus,[4] in contrast to the situation for the analogous $Ph_2NO\cdot$), species of the type $\cdot CR_2\cdot X$, where X is an alkyl-substituted phosphorus,[5] and the radical anion $PhPMe_2^{\cdot -}$;[6] the ring-proton splittings for the species $PhPMe_2^{\cdot -}$ suggest that the group PMe_2 is electron-attracting by way of p_π–d_π interaction,[6] but the data for the species $\cdot CR_2\cdot X$ have been accounted for in terms of the transmission of spin to phosphorus by spin polarisation, without the need to invoke p_π–d_π interaction.[5] Finally, radicals in which phosphorus is one atom further removed from one which is formally associated with the unpaired electron include $\cdot CHMe\cdot OPO(OEt)_2$ (from triethyl phosphite with the hydroxyl radical[7]), those of the type $\cdot CCl_2\cdot CH(OR)\cdot PO(OR')_2$ (from the corresponding trichloro-compound, by reductive elimination with the species $\cdot CO_2^-$),[8] and the radical anions from diethyl or diphenyl nitrophenyl phosphate (by electrochemical reduction[9]). It has been argued that the values of a_P

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[1] Part XXXIV, B. C. Gilbert, J. P. Larkin, and R. O. C. Norman, *J.C.S. Perkin II*, 1972, 1272.

[2] J. K. Kochi and P. J. Krusic, *J. Amer. Chem. Soc.*, 1969, **91**, 3944.

[3] A. G. Davies, D. Griller, and B. P. Roberts, *Angew. Chem. Internat. Edn.*, 1971, **10**, 738.

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

[5] A. Begum, A. R. Lyons, and M. C. R. Symons, *J. Chem. Soc.* (*A*), 1971, 2388.

[6] F. Gerson, G. Plattner, and H. Bock, *Helv. Chim. Acta*, 1970, **53**, 1629.

[7] E. A. C. Lucken, *J. Chem. Soc.* (*A*), 1966, 1354.

[8] W. Damerau, G. Lassmann, and K. Lohs, *J. Magnetic Resonance*, 1971, **5**, 408.

[9] W. M. Gulick, jun., and D. H. Geske, *J. Amer. Chem. Soc.*, 1966, **88**, 2928.

for radicals of the last two types are consistent with a dependence of a_P on $\cos^2\theta_P$ (θ_P = dihedral angle between the unfilled orbital and the X–P bond in a fragment of the type ·C–X–P); the inference from this is that the interaction of spin with phosphorus is of the hyperconjugative type.

Our success in characterising some simple inorganic sulphur-containing radicals, and their adducts with unsaturated carbon compounds, by e.s.r. spectroscopy in conjunction with a rapid flow technique [10] prompted us to embark on a similar investigation of some inorganic phosphorus-containing radicals. In the studies reported below we used the titanium(III) ion–hydrogen peroxide system to generate the hydroxyl radical in the presence of an appropriate phosphorus-containing anion. Hyperfine splitting constants and g-factors were determined to within ±0·01 mT and ±0·0001, respectively, except where stated otherwise (for radicals with large phosphorus splittings), and data were corrected to second order by the Breit–Rabi equation.

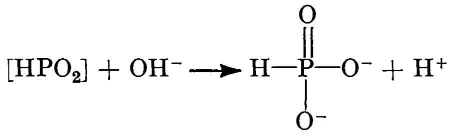
RESULTS AND DISCUSSION

The oxidation of sodium phosphite at pH 9 gave a spectrum consisting of a doublet (a 56·6 ± 0·1 mT, g 2·0011 ± 0·0004) which is attributed to the radical anion $\cdot PO_3^{2-}$ with splitting from phosphorus. This species has been generated previously in the solid state by γ-irradiation of various phosphites,[11,12] and the isotropic e.s.r. parameters obtained from those studies (*e.g.*, a_P 59·3 mT, g 2·001,[11] with small variations according to the nature of the phosphite [12]) are in good agreement with our results for aqueous solution.

When the oxidation was carried out at pH 2, a different spectrum [a(1) 64·4 ± 0·1 mT, g 2·0018 ± 0·0004] was observed which we ascribe to the conjugate acid, $\cdot PO_2OH^-$, of the species $\cdot PO_3^{2-}$. In accord with this, the spectra of both radicals were observed at pH between 2 and 9, the intensity of that of the species $\cdot PO_3^{2-}$ becoming relatively more intense as the pH was raised; thus, the relative concentrations of $\cdot PO_3^{2-}$ and its conjugate acid were 1 : 10 (pH 3), 1 : 2 (pH 5), and 1 : 0·4 (pH 6).

When sodium hypophosphite was oxidised at pH 9, the spectra of two radicals were observed. One spectrum was identical with that from sodium phosphite at this pH and is accordingly assigned to the species $\cdot PO_3^{2-}$. The other (g 2·0028 ± 0·0004) consisted of two doublets with splitting constants (47·8 ± 0·1 and 8·95 ± 0·02 mT) in reasonably close agreement with the isotropic values derived from a solid-state study of the radical anion $HPO_2{}^{\cdot -}$ (a_P 49·5, a_H 8·25 mT; g 2·0030 [13]); it is accordingly assigned to this species. The ratio of the observed concentrations of the radicals $HPO_2{}^{\cdot -}$ and $\cdot PO_3^{2-}$ varied as follows with the concentration of hydrogen peroxide: 4 : 1 (0·05M), 3 : 1 (0·1M), 2 : 1 (0·15M). This suggests that the latter radical is formed from the former with hydrogen peroxide, possibly as in reactions (1)—(3).

$$HPO_2{}^{\cdot -} + H_2O_2 \longrightarrow [HPO_2] + \cdot OH + OH^- \quad (1)$$



$$[HPO_2] + OH^- \longrightarrow H{-}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O^-}{|}}{P}}{-}O^- + H^+ \quad (2)$$

$$H{-}PO_3^{2-} + \cdot OH \longrightarrow \cdot PO_3^{2-} + H_2O \quad (3)$$

Oxidation of the phenylphosphinate anion at pH 9 gave a weak spectrum (g 2·0001 ± 0·0004) with a doublet splitting (a 46·8 ± 0·1 mT); it is ascribed to the radical anion $PhPO_2{}^{\cdot -}$ with splitting from phosphorus. This species contrasts strikingly with the analogous $PhNO_2{}^{\cdot -}$. Thus, for $PhPO_2{}^{\cdot -}$, the value for a_P, taken in conjunction with the splitting which would be expected if there were an unpaired electron in the outermost populated phosphorus s-orbital (364·0 mT [14]), indicates that *ca.* 13% of the spin is associated with this orbital. The $p : s$ ratio for the phosphorus atom cannot be evaluated in the absence of the anisotropic splitting, but the similarity between the isotropic splittings for $PhPO_2{}^{\cdot -}$ and $HPO_2{}^{\cdot -}$ (for which the $p : s$ ratio has been estimated as [15] 4·07), together with the essentially complete absence of delocalisation of the spin on to the aromatic ring of $PhPO_2{}^{\cdot -}$ (as judged by the lack of detectable proton splittings) suggests that the hybridisation in this species is similar to that in $HPO_2{}^{\cdot -}$ and that therefore it is pyramidal at phosphorus. On the other hand, significant delocalisation of the spin in $PhNO_2{}^{\cdot -}$ is indicated both by the far smaller value of a_N (*ca.* 1·5 mT, depending slightly on the conditions [16]) compared with aliphatic analogues such as $MeNO_2{}^{\cdot -}$ (*ca.* 2·5 mT) and by the ring-proton splittings; moreover, the $p : s$ ratio for nitrogen is large [17] (16·6). Thus, $PhPO_2{}^{\cdot -}$ is in these respects structurally more akin to $PhSO_2\cdot$ [18] than $PhNO_2{}^{\cdot -}$.

Addition to Olefinic Compounds.—When the species $\cdot PO_3^{2-}$ or $HPO_2{}^{\cdot -}$ were generated at pH 9 in the presence of one of the olefinic compounds in Table 1, their spectra were quenched and those of carbon-containing radicals were observed. The assignments of these spectra to the adducts tabulated are unambiguous and are based on the well established patterns of splitting constants observed for analogous radicals,[19] especially those formed by the sulphite radical anion; [10] for example, radicals of the type $\cdot CH(CO_2^-)\cdot CHRR'$ are normally associated with α-proton splitting constants close to 2·0 mT. The very large doublet splitting (>*ca.* 5 mT) is attributed to the

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[10] R. O. C. Norman and P. M. Storey, *J. Chem. Soc.* (*B*), 1971, 1009.

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

[12] P. W. Atkins and M. C. R. Symons, 'The Structure of Inorganic Radicals,' Elsevier, Amsterdam, 1967, p. 170.

[13] J. R. Morton, *Mol. Phys.*, 1962, **5**, 217.

[14] Ref. 12, p. 21.

[15] Ref. 12, p. 182.

[16] D. H. Geske, *Progr. Phys. Org. Chem.*, 1967, **4**, 125.

[17] W. M. Fox, J. M. Gross, and M. C. R. Symons, *J. Chem. Soc.* (*A*), 1966, 448.

[18] M. McMillan and W. A. Waters, *J. Chem. Soc.* (*B*), 1966, 422.

[19] A. J. Dobbs, B. C. Gilbert, and R. O. C. Norman, *J. Chem. Soc.* (*A*), 1971, 124.

^{31}P nucleus, and, in the adducts from the species $HPO_2^{\cdot-}$, the doublet splitting of 0·1—0·3 mT is attributed to the P–H proton. The spectrum from vinyl acetate and the radical $HPO_2^{\cdot-}$ proved too complex for analysis, and only very weak signals were detectable with acrolein, acrylamide, or 3,3-dimethylacrylate ion.

TABLE 1

Hyperfine splitting constants (mT) for adducts from phosphorus-containing radicals and olefinic compounds [a]

Phosphorus radical, X·	Olefinic compound	Adduct	$a_{\alpha\text{-H}}$(1H)	$a_{\beta\text{-H}}$	a_P	$a_{H(P)}$	a_{other}
$\cdot PO_3^{2-}$	$CH_2{:}CH{\cdot}CO_2^-$	$X{\cdot}CH_2{\cdot}\dot{C}H{\cdot}CO_2^-$	1·96	2·11 (2H) [f]	5·59		
$\cdot PO_3^{2-}$	$MeCH{:}CH{\cdot}CO_2^-$	$X{\cdot}CHMe{\cdot}\dot{C}H{\cdot}CO_2^-$ [b]	1·97	0·54 (1H)	4·98		0·08 (3H)
$\cdot PO_3^{2-}$	$CH_2{:}CH{\cdot}OAc$	$X{\cdot}CH_2{\cdot}\dot{C}H{\cdot}OAc$ [c]	1·90	2·05 (2H)	6·59		0·16 (3H)
$\cdot PO_3^{2-}$	$CH_2{:}CH{\cdot}CN$	$X{\cdot}CH_2{\cdot}\dot{C}H{\cdot}CN$ [c]	1·95	1·61 (2H)	6·20		0·34 (1N)
$\cdot PO_3^{2-}$	$^-O_2C{\cdot}CH{:}CH{\cdot}CO_2^-$ [e]	$X{\cdot}CH(CO_2^-){\cdot}\dot{C}H{\cdot}CO_2^-$	1·94	0·43 (1H)	5·47		
$HPO_2^{\cdot-}$	$CH_2{:}CH{\cdot}CO_2^-$	$X{\cdot}CH_2{\cdot}\dot{C}H{\cdot}CO_2^-$	2·00	1·76 (2H)	7·54	0·17	
$HPO_2^{\cdot-}$	$MeCH{:}CH{\cdot}CO_2^-$	$X{\cdot}CHMe{\cdot}\dot{C}H{\cdot}CO_2^-$	1·98	1·01 (1H)	7·56	0·16	
$HPO_2^{\cdot-}$	$CH_2{:}CH{\cdot}CN$	$X{\cdot}CH_2{\cdot}\dot{C}H{\cdot}CN$ [d]	2·00	1·60 (2H)	6·56	0·25	0·34 (1N)
$HPO_2^{\cdot-}$	$^-O_2C{\cdot}CH{:}CH{\cdot}CO_2^-$ [e]	$X{\cdot}CH(CO_2^-){\cdot}\dot{C}H{\cdot}CO_2^-$	1·98	0·60 (1H)	6·40	0·30	

[a] *g* 2·0034 except where stated. [b] *g* 2·0035. [c] *g* 2·0030. [d] *g* 2·0029. [e] Maleate ion. [f] The centre line of the 1 : 2 : 1 triplet (ΔH 0·030 mT) was broadened with respect to the wing lines (ΔH 0·015 mT).

TABLE 2

Hyperfine splitting constants (mT) for adducts from phosphorus-containing radicals and oximes [a]

Phosphorus radical, X·	Oxime	Adduct	$a_N = a_{H(N)}$	$a_{\beta\text{-H}}$	a_P	$a_{H(P)}$
$\cdot PO_3^{2-}$	$MeCH{:}NOH$	$X{\cdot}CHMe{\cdot}NHO{\cdot}$	1·44	1·21 (1H)	2·85	
$\cdot PO_3^{2-}$	$EtCH{:}NOH$	$X{\cdot}CHEt{\cdot}NHO{\cdot}$ [b]	1·44	0·60 (1H)	3·53	
$HPO_2^{\cdot-}$	$CH_2{:}NOH$	$X{\cdot}CH_2{\cdot}NHO{\cdot}$ [c]	1·39	1·07 (2H)	3·86	0·23
$HPO_2^{\cdot-}$	$MeCH{:}NOH$	$X{\cdot}CHMe{\cdot}NHO{\cdot}$ [c]	1·39	1·02 (1H)	3·71	0·24
$HPO_2^{\cdot-}$	$EtCH{:}NOH$	$X{\cdot}CHEt{\cdot}NHO{\cdot}$ [c]	1·39	0·72 (1H)	3·87	0·24
$PhPO_2^{\cdot-}$	$MeCH{:}NOH$	$X{\cdot}CHMe{\cdot}NHO{\cdot}$	1·39	0·91 (1H)	4·06	
$PhPO_2^{\cdot-}$	$EtCH{:}NOH$	$X{\cdot}CHEt{\cdot}NHO{\cdot}$	1·39	0·59 (1H)	4·18	

[a] *g* 2·0057 except where stated. [b] *g* 2·0056. [c] *g* 2·0058.

TABLE 3

Hyperfine splitting constants (mT) for adducts from phosphorus-containing radicals and nitroalkane *aci*-anions (*g* 2·0050)

Phosphorus radical, X·	Nitroalkane	Adduct	$a_{\beta\text{-H}}$	$a_{\gamma\text{-H}}$	a_N	a_P	$a_{H(P)}$
$\cdot PO_3^{2-}$	$MeNO_2$	$X{\cdot}CH_2{\cdot}NO_2^{\cdot-}$	1·07 (2H)		2·49	3·14	
$\cdot PO_3^{2-}$	$EtNO_2$	$X{\cdot}CHMe{\cdot}NO_2^{\cdot-}$	0·32 (1H)	0·03 (3H)	2·56	2·70	
$\cdot PO_3^{2-}$	$PrNO_2$ [a]	$X{\cdot}CHEt{\cdot}NO_2^{\cdot-}$	0·22 (1H)	0·085 (1H) 0·025 (1H)	2·38	3·68	
$\cdot PO_3^{2-}$	Pr^iNO_2	$X{\cdot}CMe_2{\cdot}NO_2H$ [b]			2·76	1·09	
$HPO_2^{\cdot-}$	$MeNO_2$	$X{\cdot}CH_2{\cdot}NO_2^{\cdot-}$	1·01 (2H)		2·51	2·92	0·15
$HPO_2^{\cdot-}$	$EtNO_2$	$X{\cdot}CHMe{\cdot}NO_2^{\cdot-}$	0·61 (1H)	0·04 (3H)	2·55	2·68	0·14
$HPO_2^{\cdot-}$	$PrNO_2$	$X{\cdot}CHEt{\cdot}NO_2^{\cdot-}$	0·27 (1H)	0·05 (1H)	2·43	3·47	0·20
$HPO_2^{\cdot-}$	Pr^iNO_2	$X{\cdot}CMe_2{\cdot}NO_2^{\cdot-}$		0·03 (6H)	2·62	1·69	0·10
$PhPO_2^{\cdot-}$	$MeNO_2$	$X{\cdot}CH_2{\cdot}NO_2^{\cdot-}$	1·01 (2H)		2·45	3·34	
$PhPO_2^{\cdot-}$	$EtNO_2$	$X{\cdot}CHMe{\cdot}NO_2^{\cdot-}$	0·37 (1H)	0·03 (3H)	2·48	3·04	
$PhPO_2^{\cdot-}$	$PrNO_2$	$X{\cdot}CHEt{\cdot}NO_2^{\cdot-}$	0·22 (1H)	0·09 (1H)	2·33	3·87	

[a] $a_{\delta\text{-H}}$ 0·025 mT (3H). [b] a_{OH} 0·31 mT; see text.

Two general features of the data are noteworthy. First, it is apparent that the phosphorus anions compete very effectively with the olefinic compounds for the hydroxyl radical, for there was no trace of the adducts formed by the hydroxyl radical with the latter compounds. No doubt the high reactivity of the phosphorus anions can be associated with the relatively weak P–H bonds [20] from which abstraction occurs. Secondly, the compounds with which the radicals $\cdot PO_3^{2-}$ and $HPO_2^{\cdot-}$ give adducts also yield adducts with $SO_3^{\cdot-}$, and likewise acrolein, acrylamide, and the 3,3-dimethylacrylate ion are relatively unreactive towards both the phosphorus and the sulphur radicals; [10] we infer closely similar characteristics for the two types of species.[10]

Addition to Oximes.—When generated at pH 9 in the presence of formaldoxime (from formaldehyde and hydroxylamine *in situ*), acetaldoxime, or propionaldoxime, the phosphorus-containing radicals gave species of which the e.s.r. parameters are in Table 2. The spectra are assigned to radicals of the type $CR^1R^2X{\cdot}NHO{\cdot}$ (R^1, R^2 = H or alkyl, X = PO_3^{2-}, HPO_2^-, or $PhPO_2^-$) on the basis of arguments set out previously for adducts formed by oximes with other radicals [21,22] [reaction (4) is illustrative]; the large doublet splitting is assigned to

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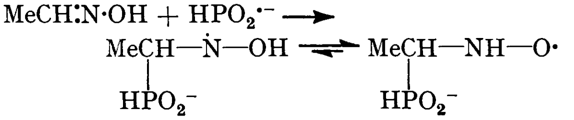
[20] J. R. Van Wazer, 'Phosphorus and its Compounds,' vol. 1, Interscience, New York, 1958, p. 887.

[21] D. J. Edge and R. O. C. Norman, *J. Chem. Soc.* (*B*), 1969, 182.

[22] D. J. Edge and R. O. C. Norman, *J. Chem. Soc.* (*B*), 1970, 1083.

the ^{31}P nucleus, and the extra small doublet splitting in adducts from the radical $HPO_2^{\cdot -}$ is attributed to the P–H proton.



$$\mathrm{MeCH{:}N{\cdot}OH + HPO_2^{\cdot -} \longrightarrow \underset{HPO_2^-}{MeCH}\text{—}\dot{N}\text{—}OH \rightleftharpoons \underset{HPO_2^-}{MeCH}\text{—}NH\text{—}O{\cdot}} \qquad (4)$$

Addition to Nitroalkane aci-*Anions*.—The spectra of which the hyperfine splitting constants are in Table 3 were observed during reaction of the phosphorus-containing radicals with some aliphatic nitro-compounds. Their ascription to species of the type $CR^1R^2X{\cdot}NO_2^{\cdot -}$ (R^1, R^2 = H or alkyl, X = PO_3^{2-}, HPO_2^-, or $PhPO_2^-$) formed from the corresponding *aci*-anion, and the assignments of splitting constants, follow principles which have been discussed for other adducts from *aci*-anions,[1,10] together with the following specific points. First, the doublet splitting in the range 0·10 to 0·20 mT in the radicals formed from $HPO_2^{\cdot -}$ is assigned to the P–H proton. Secondly, different splittings (0·085 and 0·025 mT) in the adduct $MeCH_2CH(PO_3^{2-}){\cdot}NO_2^{\cdot -}$ from 1-nitropropane and $\cdot PO_3^{2-}$ are attributed to the two γ-protons, the magnetic non-equivalence of which is ascribed to the chirality of the adjacent carbon atom; * in the adducts from this nitro-compound and the other two phosphorus radicals only one splitting attributable to a γ-proton was observed, possibly because the other (again unequal to the first) was small enough to be masked by the line-widths (*ca.* 0·03 mT). Finally, the adduct from 2-nitropropane and $\cdot PO_3^{2-}$ contained a doublet splitting not expected for the species $^{2-}O_3P{\cdot}CMe_2{\cdot}NO_2^{\cdot -}$ but of the same order of magnitude as found for the OH proton in some adducts of the type $R{\cdot}NO_2H$,[22] and the nitrogen splitting is also typical of such adducts;[22] evidently the radical anion in this case is protonated, its greater basicity compared with the related radicals in Table 3 no doubt being associated with the combined effect of the dianionic phosphorus group and two methyl substituents. There was no change in the spectrum at pH 10, and attempts to make observations at higher pH were unsuccessful because of the complex spectra then observed.

Finally, the spectra in Table 3 were accompanied by very weak signals from the radical anion corresponding to the parent nitroalkane[23] except that, with 2-nitropropane and $PhPO_2^{\cdot -}$, only this radical anion ($Me_2CH{\cdot}NO_2^{\cdot -}$) was observed.

Conformational Preferences and Magnitude of a_P.—We sought information about the preferred conformations of some of the radicals in Tables 1—3, and about the dependence of a_P upon conformation, both by comparing the splitting constants for groups of related radicals and by examining the variation of the splitting constants for a particular radical with temperature (Table 4).

TABLE 4

Variation with temperature of the hyperfine splitting constants (mT) of some of the species in Tables 1—3 [a]

Radical	Temp.	$a_{\alpha\text{-H}}$	$a_{\beta\text{-H}}$	a_N	a_P
$^{2-}O_3P{\cdot}CH_2{\cdot}\dot{C}H{\cdot}CO_2^-$	8°	1·97	2·10 [b]		5·64
	21	1·96	2·11 [b]		5·59
	38	1·95	2·12 [b]		5·56
$^-O_2PH{\cdot}CH_2{\cdot}\dot{C}H{\cdot}CO_2^-$	8	2·02	1·73		7·64
	20	2·00	1·76		7·54
	40	2·00	1·78		7·43
$^{2-}O_3P{\cdot}CHMe{\cdot}\dot{C}H{\cdot}CO_2^-$	9	1·97	0·52		5·01
	21	1·97	0·54		4·98
	39	1·97	0·56		4·95
$^-O_2PH{\cdot}CHMe{\cdot}\dot{C}H{\cdot}CO_2^-$	7	1·98	1·0 [c]		7·69
	22	1·98	1·0 [c]		7·56
	42	1·97	1·01		7·37
$^-O_2PH{\cdot}CH_2{\cdot}NHO{\cdot}$	8	1·39	1·07	1·39	3·92
	19	1·39	1·07	1·39	3·86
	38	1·39	1·09	1·39	3·79
$^-O_2PH{\cdot}CHMe{\cdot}NHO{\cdot}$	9	1·39	1·02	1·39	3·79
	21	1·39	1·02	1·39	3·71
	38	1·39	1·02	1·39	3·68
$^-O_2PH{\cdot}CH_2{\cdot}NO_2^{\cdot -}$	8		1·015	2·52	2·90
	23		1·01	2·51	2·92
	40		1·01	2·505	2·92
$^{2-}O_3P{\cdot}CHMe{\cdot}NO_2^{\cdot -}$	8		0·295	2·57	2·63
	25		0·32	2·56	2·70
	40		0·335	2·53	2·72
$^-O_2PH{\cdot}CHMe{\cdot}NO_2^{\cdot -}$	9		0·585	2·565	2·65
	23		0·605	2·545	2·68
	39		0·605	2·545	2·70

[a] Splittings for nuclei in Tables 1 and 2 which are not quoted here did not vary detectably with temperature. There was no detectable variation for any of the nuclei in the radical $^{2-}O_3P{\cdot}CH_2{\cdot}NO_2^{\cdot -}$. [b] For line-width variation, see text. [c] The relatively broad lines limited the accuracy of the measurement.

Consider the adduct from acrylate ion and $\cdot PO_3^{2-}$. The α-proton splitting constant is slightly less than that for $\cdot CHMe{\cdot}CO_2^-$ (2·02 mT[19]) but not by so significant an amount as would suggest a strong interaction with the phosphorus nucleus; moreover, a_P, though large, corresponds to only *ca.* 0·015 of an unpaired spin in the outermost populated *s*-orbital (since A_0 for that orbital is 364·0 mT[14]). Thus, $a_{\beta\text{-H}}$ can justifiably be compared for the two radicals; the fact that it is significantly less for the phosphorus-containing species than for the radical $\cdot CHMe{\cdot}CO_2^-$ (2·49 mT[19]) shows[16] that the average value of $\cos^2 \theta_H$ is less than for a freely rotating methyl group (1/2), and that therefore $\cos^2 \theta_P$ is greater than 1/2. Consequently, the preferred conformations are of the type (1) and (2) ($\theta_P < 45°$; $\theta_{H^1} \neq \theta_{H^2}$) rather than (3), with interconversion between (1) and (2) occurring at a rate comparable with the frequency interval between the splittings for the two β-protons (to account for the broadening of the central line of the 1 : 2 : 1 triplet with respect to the wing lines; see Table 1). This is in accord with the increase in $a_{\beta\text{-H}}$ with temperature (since $\cos^2 \theta_H$ should tend to 1/2 in the limit); as expected, the width of the central line of the triplet became progressively narrower as the temperature was raised (ΔH 0·035, 0·03, 0·025 mT at 8, 21,

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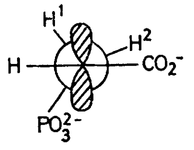
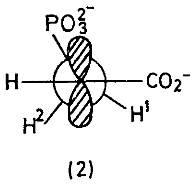
* We have previously inferred that the non-equivalence of β-protons in some radicals of the type $CXYZ{\cdot}CH_2{\cdot}NO_2^{\cdot -}$ results from the presence of the adjacent chiral carbon atom.[1]

[23] M. McMillan and R. O. C. Norman, *J. Chem. Soc.* (*B*), 1968, 590.

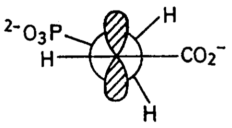
and 38°, respectively) with respect to the wing lines (0·015 mT at all three temperatures). Now, a_P decreases with rise in temperature, while the average value of $\cos^2\theta_P$ should decrease towards 1/2; that is, the results are consistent with the view that a_P decreases as θ_P increases. (This does not imply that the relationship is necessarily of the $\cos^2\theta$ type; moreover, our results do not enable us to distinguish between interactions of hyperconjugative or *p–d* type.)



(1)



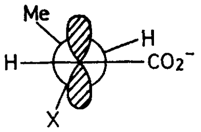
(2)



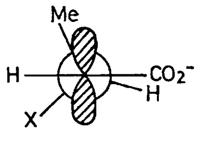
(3)

The results for the adduct from acrylate ion and $HPO_2^{\bullet -}$ can be understood similarly, except that there was no evidence that the interconversion between rotamers was slow in terms of the e.s.r. time-scale.

The relatively small values of $a_{\beta\text{-H}}$ for the adducts formed by crotonate ion with $\cdot PO_3^{2-}$ and $HPO_2^{\bullet -}$ indicate that $\cos^2\theta_H$ is much less than 1/2; in accord with this, $a_{\beta\text{-H}}$ increases with temperature for the former adduct (the rather broad lines in the spectrum of the latter adduct prevented us from discerning a possible small variation with temperature). Thus, the preferred conformation should be of the type (4 or 5; $X = PO_3^{2-}$ or HPO_2^-), in which θ_X is $<45°$ or $\geqslant 45°$, respectively. For the adduct with $HPO_2^{\bullet -}$, the similar value of a_P to that for the adduct from acrylate ion and $HPO_2^{\bullet -}$ suggests that $\cos^2\theta_P$ is very similar in the two cases and therefore $>1/2$ for the adduct from crotonate ion; that is, the preferred conformation is of the type (4) rather than (5), so that the decrease in a_P with increase in temperature is again consistent with decrease in a_P with increase in θ_P. For the adduct of crotonate ion with $\cdot PO_3^{2-}$, the somewhat smaller value of a_P than for the corresponding adduct with acrylate ion then suggests that $\cos^2\theta_P$ is somewhat smaller in the former; however, it may still be $>1/2$, so that the decrease in a_P with increase in temperature is unexceptional.

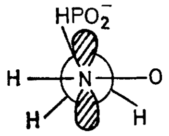


(4)

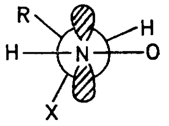


(5)

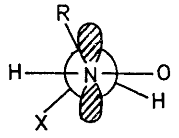
The conformational preferences for the nitroxide radicals obtained by the addition of phosphorus radicals to oximes appear to be similar to those for radicals formed from olefinic compounds. Thus, the lower value of $a_{\beta\text{-H}}$ for $^-O_2PH{\cdot}CH_2{\cdot}NHO{\cdot}$ than for $CH_3{\cdot}NHO{\cdot}$ ($a_{\beta\text{-H}}$ 1·38 mT [24]), coupled with the close similarity in $a_{H(N)}$ and in a_N (1·38 mT [24] for $CH_3{\cdot}NHO{\cdot}$), indicate that preferred conformations have $\theta_P < 45°$ [*e.g.* (6)]; the temperature dependences of $a_{\beta\text{-H}}$ and a_P for $^-O_2PH{\cdot}CH_2{\cdot}NHO{\cdot}$ are consistent with this view and the hypothesis that a_P decreases as θ_P increases. Similarly, the low values of $a_{\beta\text{-H}}$ in $RCHX{\cdot}NHO{\cdot}$ (R = Me or Et, $X = PO_3^{2-}$, HPO_2^-, or $PhPO_2^-$) suggest that conformations of the types (7) or (8) are favoured for these radicals. For $^-O_2PH{\cdot}CHMe{\cdot}NHO{\cdot}$ the phosphorus splitting decreases as the temperature rises (no other significant changes were detected), so that, given that a_P decreases as θ_P increases, conformation (7) is preferred to (8).



(6)

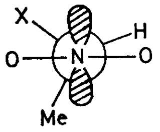


(7)

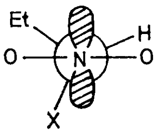


(8)

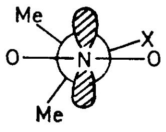
In some respects the results for the radicals from nitro-*aci*-anions parallel those from the olefinic compounds and oximes and might be interpreted in an analogous manner. For example, the smaller values of $a_{\beta\text{-H}}$ for the adducts $X{\cdot}CH_2{\cdot}NO_2^{\bullet -}$ when $X = PO_3^{2-}$, HPO_2^-, or $PhPO_2^-$ compared with X = H (1·2 mT [23]) suggest that the average values of $\cos^2\theta_H$ and $\cos^2\theta_P$ are, respectively, $<$ and $>1/2$, corresponding to preferred conformations analogous to (1) and (2). The very small values of $a_{\beta\text{-H}}$ for the adducts from nitroethane and 1-nitropropane, coupled with the relatively small and large values of a_P for the former and latter groups of adducts, respectively, could be interpreted—given, as we should expect from our previous discussion, that a_P decreases as θ_P increases—in terms of preferential conformations (9) and (10) in which $\theta_H \gg 45°$, and θ_X (X = P-containing group) is much greater in (9) than in (10); this difference between the methyl- and ethyl-containing radical is unexpected, but a parallel situation occurs for the adducts from acetaldoxime and propionaldoxime. For the adduct from 2-nitropropane and $HPO_2^{\bullet -}$, the low value of a_P suggests that a conformation of the type (11) is favoured.



(9)



(10)



(11)

Other observations illustrate the difficulty of carrying out a full analysis of the nitro-radical anions. First, we should expect that, if $\cos^2\theta_P$ were $>1/2$ for the adducts from nitromethane, then a_P would decrease as the temperature is raised, whereas for the adduct formed by $\cdot PO_3^{2-}$ it remains essentially unchanged and with that from $HPO_2^{\bullet -}$ it increases slightly but significantly. Secondly, in addition to the large difference in a_P between adducts from nitroethane and 1-nitropropane, there is an appreciable difference in a_N; moreover, there

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[24] C. J. W. Gutch and W. A. Waters, *J. Chem. Soc.*, 1965, 751.

are also significant differences in a_N between adducts formed by various phosphorus radicals with a particular nitro-compound.

We suggest that an additional factor, namely the geometry at the nitrogen atom, is important. Thus, whereas the radicals from olefinic compounds which we have considered are probably coplanar at the tervalent carbon atom,[19] those from the *aci*-anions are expected to be bent at nitrogen.[1,19] It may be that the degree of bending is sensitive not only to temperature but also to the nature of the substituents on the adjacent carbon atom, so that both $a_{\beta\text{-H}}$ and a_P vary as a result of changes in geometry in nitrogen as well as conformation. For example, the decrease in a_N on replacement of methyl by ethyl in a radical of the type $X{\cdot}CHMe{\cdot}NO_2{}^{\cdot -}$ (X = a phosphorus substituent) could be associated largely with a greater tendency towards coplanarity at nitrogen (hence decreased *s*-character in the unfilled nitrogen orbital) resulting from increased compressional forces (*cf.* our argument[1] concerning, *e.g.*, the smaller value of a_N in $Me_3C{\cdot}CH_2{\cdot}NO_2{}^{\cdot -}$ compared with $Me{\cdot}CH_2{\cdot}NO_2{}^{\cdot -}$); further, the corresponding increase in *p*-character in the unfilled nitrogen orbital could result in a more efficient transmission of spin to phosphorus and hence the observed increase in a_P. It is notable that, for the adducts from each phosphorus radical and the nitroalkanes $MeNO_2$, $EtNO_2$, and $PrNO_2$, a_P increases as a_N falls; in contrast, in the nitroxide series, where we should expect the radicals to be essentially coplanar at nitrogen, not only is there no detectable variation of a_N with temperature but also substitution of, *e.g.*, an ethyl for a methyl substituent affects a_P markedly but a_N not at all. Thus, we conclude that it is inappropriate to consider the conformational preferences of the nitro-radical anions until the importance of hybridisation has been elucidated.

EXPERIMENTAL

A Varian E-3 e.s.r. spectrometer, with 100 kHz modulation and an *X*-band klystron, was used. Splitting constants and *g*-factors were measured by comparison with Fremy's salt (a_N 1·3091 mT,[25] *g* 2·0055[26]). Relative concentrations of radicals were measured by comparison of the peak-to-peak heights of the first derivatives of appropriate resonances; no differences in line-widths were observed. Temperatures reported were constant to ±1°; other data were obtained at room temperature.

pH Measurements were made to within ±0·1 with an Electronic Instruments model 23A pH meter and a phthalate buffer as standard. A mixing chamber was employed which allowed three reagents to be mixed simultaneously about 0·02 seconds before passage of the combined solution through the cavity of the spectrometer, with a flow rate of 150 ml min^{-1} for each solution. All solutions were deaerated by the passage of nitrogen. For reactions at pH 9, the first solution contained titanium(III) chloride (0·008M), EDTA (6 g/l), and the phosphorus-containing anion (0·1M), the second contained hydrogen peroxide (0·05M), and the third was either closed or contained an organic substrate [0·1M for olefinic compounds, acetaldoxime, and propionaldoxime; 0·1M in each of hydroxylamine hydrochloride and formaldehyde (for formaldoxime); 0·05M for nitroalkanes]; ammonia (*d* 0·880) was added to the first and third solutions to give pH 9. For the reactions in acid solution, the concentrations were as above but with the organic compound in the titanium(III) stream and the phosphorus compound in the third stream. Sulphuric acid was added to the solutions to give the required pH.

All chemicals were of laboratory reagent grade. The sodium hypophosphite did not reduce iodine in neutral solution, excluding the presence of phosphite impurity.[27]

The tenure of an I.C.I. Fellowship (by J. P. L.) is gratefully acknowledged.

Note added in proof: Professor A. L. J. Beckwith, University of Adelaide, has informed us of his work on phosphorus-containing radicals which he has submitted to *Austral. J. Chem.* Some of the results reported here are similar to those he has obtained. We thank him for communicating his results before publication.

[2/488 *Received*, 6*th March*, 1972]

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[25] R. J. Faber and G. K. Fraenkel, *J. Chem. Phys.*, 1967, **47**, 2462.

[26] J. Q. Adams, S. W. Nicksic, and J. R. Thomas, *J. Chem. Phys.*, 1966, **45**, 654.

[27] A. I. Vogel, 'A Textbook of Quantitative Inorganic Analysis,' 3rd edn., Longmans, 1961.