Electron Spin Resonance Studies of the Photolysis and Radiolysis of *O,O'*-Dialkyl Hydrogen Phosphorodithioates [$(RO)_2P(S)SH$], their Salts, Corresponding Disulphides, and Related Compounds: Formation of Thio and Dithio Radicals, Radical Ions, and Phosphorus-centred Radicals

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Isotropic and anisotropic e.s.r. parameters are reported for some dialkoxy(thiophosphoryl)thio radicals [$(RO)_2P(S)S^{\cdot}$] generated by photolysis of some *O,O'*-dialkyl hydrogen phosphorodithioates, their salts, and corresponding disulphides [in some cases in the presence of $(Bu^tO)_2$]. The unpaired electron in these radicals is evidently shared equally between the two sulphur atoms in an in-plane orbital; the variation of the linewidth with viscosity and temperature is interpreted in terms of spin-rotation interaction. The radicals are very short-lived (with $2k_t$ *ca.* 10^9 dm^3 mol^{-1} s^{-1}); though they are apparently unreactive towards either aliphatic alkenes or oxygen, they react rapidly to give peroxyl radicals in the presence of both.

The analogous oxygen-substituted radicals $(RO)_2P(O)S^{\cdot}$ possess the unpaired electron localized on sulphur: though they prove undetectable in fluid solution (presumably on account of marked line-broadening) their rapid reaction with the corresponding anion to give the σ^*-species $[(RO)_2P(O)S]_2^{-\cdot}$ could be monitored. Solid-state spectra from photochemically generated dithio radicals $(RO)_2P(X)S_2^{\cdot}$ (X = O or S) are also reported.

Finally, radiolysis of solid samples of these compounds leads to the characterization of anisotropic spectra from the appropriate thio and dithio radicals as well as those from electron-loss species ($RSSR^{+\cdot}$) and electron-gain radicals [both of σ^*-type $(RSSR)^{-\cdot}$ and phosphoranyl-type structure $^{-\cdot}P(OR)_2(X)$-$SSP(X)(OR)_2$]; structural aspects, matrix effects, and further reactions [*e.g.* to give phosphoryl radicals $^{\cdot}PL_3$ and alkyl radicals] are discussed.

E.s.r. spectroscopy has recently been employed to characterize a variety of different types of sulphur-centred radical formed in fluid solution and the solid state. For example, in the reaction between thiols and $^{\cdot}OH$ radicals in aqueous solution signals from sulphinyl ($RSO^{\cdot}$) and sulphonyl ($RSO_2^{\cdot}$) radicals as well as disulphide radical anions ($RSSR^{-\cdot}$) have been detected;[1] these species result from further reactions of first-formed thio radicals which, though not directly detectable on account of the large anisotropy in their *g* values,[2] can nevertheless be trapped and recognized *via* their adducts with, *e.g.*, $CH_2{=}NO_2^-$.[1] Sulphuranyl radicals $(RO)_3S^{\cdot}$ and $R\dot{S}(OR)_2$ have been detected in photolytic experiments with sulphoxylates[3] and sulphenates,[3,4] respectively, and the 'dimer' radical cations $R_2SSR_2^{+\cdot}$ have been identified as key intermediates in the oxidation of thioethers, *e.g.* with the hydroxyl radical[5] or *via* electrochemical or photolytic methods.[6] Radiation damage of these substrates in the solid state provides crucial information on the structure of dimer radical cations (see *e.g.* refs. 7 and 8) as well as evidence for, *e.g.*, $MeSSMe^{+\cdot}$ from dimethyl disulphide;[7] the very different types of anisotropic spectra assigned to thio ($RS^{\cdot}$) and dithio ($RS_2^{\cdot}$) radicals from thiols and disulphides can also be distinguished[9,10] (see also ref. 11).

Sulphur-centred radicals have been proposed as possible intermediates in the decomposition of more complex sulphur-containing compounds which are used as antioxidants;[12,13] for example it has been suggested[14,15] that the reaction of zinc bis(dialkyl phosphorodithioates), $[(RO)_2P(S)S]_2Zn$, with peroxyl radicals involves the formation of radicals of the type $(RO)_2P(S)S^{\cdot}$. Anisotropic spectra attributed[16] to such species have been detected after u.v. irradiation of some *O,O'*-dialkyl hydrogen phosphorodithioates, and a simple doublet with *a* 2.5 mT that has been detected[14-17] in fluid solution may be the analogous isotropic spectrum. On the other hand, these radicals could not be detected directly during the photolysis of the acids and in the reaction of $^{\cdot}OH$ (from Ti^{III} and H_2O_2) with $(RO)_2P(S)S^-$,[18] although their presence was demonstrated *via* spin-trapping experiments.

We here report the results of a series of experiments in which we set out to characterize the e.s.r. parameters as well as the kinetic and structural properties of radicals of the type $(RO)_2P(S)S^{\cdot}$ and analogous species including $(RO)_2P(O)S^{\cdot}$. Our approach involved firstly the study of the photochemical decomposition of the relevant acids and disulphides; subsequent experiments entailed u.v.-photolytic and radiolytic reactions in the solid state, with the intention of providing both confirmation of structural assignments from solution spectra and information on the radiation damage inflicted upon these classes of compound.

Results and Discussion

Photolytic Reactions in Fluid Solution.—(a) *Bis(dialkoxythiophosphoryl) disulphides*, $(RO)_2P(S)SSP(S)(OR)_2$, (1) *and related compounds.* The majority of our experiments with fluid solutions involved direct *in situ* photolysis, with the focussed but unfiltered radiation from a 1 kW mercury–xenon lamp, of deoxygenated samples containing the substrate (typically *ca.* 0.1 mol dm^{-3}) in inert solvents in the temperature range 190—300 K.

The spectra obtained are typified by those shown for $(Pr^iO)_2P(S)SSP(S)(Pr^iO)_2$ in Figure 1; spectroscopic parameters for the radicals from a variety of substrates studied are collected in Table 1. For each disulphide studied the spectrum

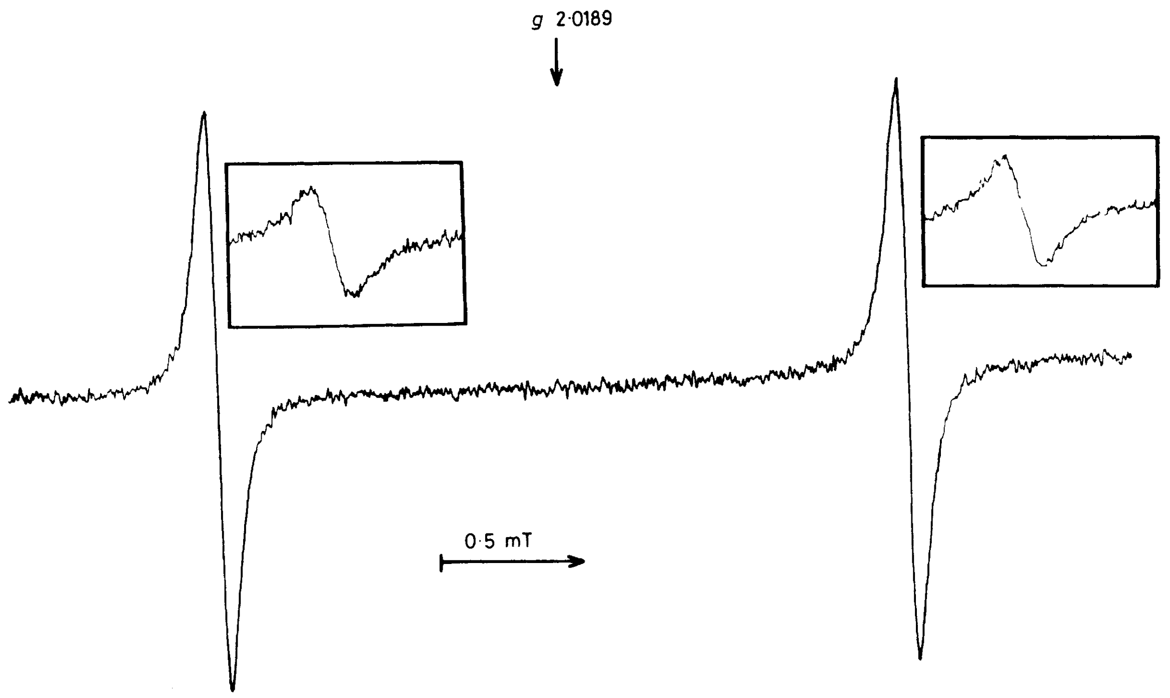


Figure 1. Isotropic spectrum of $(Pr^iO)_2P(S)S^{\cdot}$ (2; R = Pr^i) obtained by photolysis of $[(Pr^iO)_2P(S)S]_2$ in isopentane at 207 K, with (inset) signals recorded at 253 K

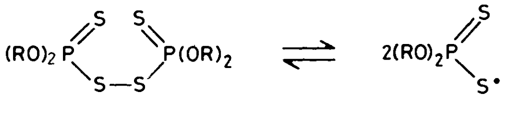
Table 1. E.s.r. parameters for dialkoxy(aryloxy)thiophosphorylthio radicals $(RO)_2P(S)S^{\cdot}$

	Method of generation[a]	Solvent[b]	T/K	a(P)/mT[c]	g[d]	ΔB/mT[e]
R = Et	$[(RO)_2P(S)]_2S_2$	P	191	2.460	2.0188	0.10
			205	2.490	2.0188	0.13
R = Pr^n	$[(RO)_2P(S)S]_2Zn/(Bu^tO)_2$	P	191	2.460	2.0188	0.09
R = Pr^i	$[(RO)_2P(S)]_2S_2$	P	191	2.445	2.0189	0.06
			207	2.450	2.0189	0.07
			232	2.465	2.0189	0.10
		T	202	2.420	2.0189	0.14
	$[(RO)_2P(S)S]_2Zn$	T	202	2.430	2.0189	0.14
R = Bu^i	$[(RO)_2P(S)S]_2Zn/(Bu^tO)_2$	T	202	2.460	2.0184	0.23
R = Bu^s	$[(RO)_2P(S)S]_2$	T	191	2.470	2.0185	0.16
R = Me_3CCH_2	$[(RO)_2P(S)S]_2Zn/(Bu^tO)_2$	P	191	2.480	2.0190	0.07
		T	202	2.460	2.0190	0.15
R = MeC_6H_4	$[(ArO)_2P(S)S]_2Zn/(Bu^tO)_2$	T	202	2.460	2.0203	0.18
$(RO)_2$ = $[CH_2]_3O_2$	$(RO)_2P(S)SH/(Bu^tO)_2$	T	202	2.460	2.0188	0.23

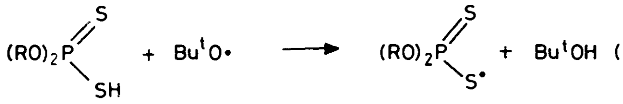
[a] *in situ* photolysis; see text. [b] P, isopentane; T, toluene. [c] ±0.005. [d] ±0.0001. [e] ±0.02.

comprised solely a doublet [attributed to a phosphorus splitting, a(P) typically *ca.* 2.45 mT, g *ca.* 2.0188] which was quite intense at low temperatures and which decayed rapidly when the light beam was interrupted (kinetics of decay are discussed later). The following features are notable. Firstly, the phosphorus splittings and g values are relatively insensitive to the structure of the alkyl group, the temperature, and the solvent (those employed included isopentane and toluene). Secondly, the isotropic e.s.r. parameters (which are similar to those previously reported[14,17] in related systems) are approximately equal to the average of the anisotropic parameters of the species formed in u.v.-irradiated *O,O'*-dialkyl hydrogen phosphorodithioates (see ref. 16 and later); justification for assignment to $(RO)_2P(S)S^{\cdot}$ (2) and comments on the structure are presented subsequently. Thirdly, the spectra did not alter significantly with time during photolysis (even after several hours or repeated irradiation) which suggests that the only significant photoproduct is the starting material, formed by the reverse of reaction (i). Fourthly, though in a given spectrum there was no difference between the widths of the two components of the doublet, the widths of the lines increased significantly with temperature (see *e.g.* Figure 1), so that the signal height decreased dramatically as room temperature was approached. The implications of this are described in the next section.

Under a given set of conditions, the intensity of the signals from a variety of different substrates (1) were in the order R = Pr^i > MeC_6H_4 ~ Me_3CCH_2 > Et ~ Pr^n; we interpret this in terms of the relative linewidths of the signals (and possibly the decay kinetics) rather than changes in the rates of formation of the different species. Despite several detailed examinations, especially involving highly amplified signals with the sharpest lines [*e.g.* from (2; R = Pr^i) at *ca.* 190 K in isopentane] we were unable to detect ^{33}S satellite lines (^{33}S has



(1) (2) (i)



(2) (ii)

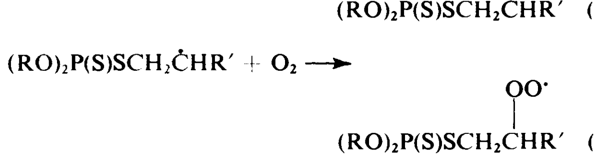
$I = \frac{3}{2}$, with a natural abundance of 0.76%:[19] our failure to detect sulphur splittings may indicate either that the splitting is significantly less than the linewidth or that the ^{33}S lines are somewhat broader than the main peaks, *e.g.* because of quadrupolar or anisotropic relaxation).

Identical but weaker spectra were obtained *via* direct photolysis of the corresponding acids $(RO)_2P(S)SH$ and their zinc salts $[(RO)_2PS_2]_2Zn$ under similar conditions; in each case addition of di-t-butyl peroxide considerably enhanced the intensity of the signal from (2) [evidently *via* reaction (ii) for the acids] though the signal intensity decreased with the photolysis time (see also ref. 17).

Irradiation of the appropriate disulphides was employed to generate a series of radicals (2) in solution in isopentane in the presence of various additives. The signals from (2) were not significantly depleted in the presence of either oxygen or any one of the alkenes oct-1-ene, isobutene, or 4-methylpent-2-ene (at concentrations of up to *ca.* 0.5 mol dm^{-3}); * depletion did however occur in the presence of styrene (0.1 mol dm^{-3}) or 2,4,6-tri-t-butylphenol (0.01 mol dm^{-3}) and for the latter new signals (from the appropriate phenoxyl radical[20]) were detected (for the former a weak, complex, and unanalysed signal was obtained). These observations suggest, perhaps unexpectedly, that radicals (2) are unreactive in their separate reactions with oxygen and aliphatic alkenes. However, in a series of experiments in which oxygen and an alkene (or styrene) were present, signals from (2) were rapidly replaced by those attributed a peroxyl radical structure, with g 2.015.[21] The signals from styrene, oct-1-ene, and 4-methylpent-2-ene possessed a single hydrogen splitting (*ca.* 0.2 mT), characteristic of a secondary-alkyl peroxyl,[21] whereas that from isobutene had no further splitting.

These results are interpreted in terms of the rapid (but, at least for aliphatic alkenes, reversible) addition of (2) to the alkene [*e.g.* reaction (iii), R' = n-C_6H_{13}] followed by rapid trapping of the first-formed radicals when oxygen is present [reaction (iv)]. This is consistent with the suggestion (see ref. 22 and refs. therein) that radicals $(RO)_2P(S)S^{\bullet}$ can act as chain carriers in alkene autoxidation [*via* ready addition to the double bond and subsequent addition of oxygen (see also ref. 15)] and with the readiness of β-sulphur-substituted carbon radicals to undergo β-fission [see *e.g.* ref. 23].

$$(RO)_2P(S)S^{\bullet} + CH_2{=}CHR' \rightleftharpoons (RO)_2P(S)SCH_2\dot{C}HR' \quad \text{(iii)}$$



$$(RO)_2P(S)SCH_2\dot{C}HR' + O_2 \longrightarrow (RO)_2P(S)SCH_2CH(OO^{\bullet})R' \quad \text{(iv)}$$

$$\left.\begin{array}{l} g\ \ 2.0152 \\ a(\mathrm{H})\ 0.240\ \ \mathrm{mT}\end{array}\right\}\text{for } R' = \text{n-}C_6H_{13}$$

We also extended a previous study[18] and examined the reaction of $^{\bullet}OH$ (generated from Ti^{III}–H_2O_2 in aqueous solution) with a variety of substrates, including $(EtO)_2P(S)S^-NH_4^+$. In no case could signals from radicals (2) be directly detected (and photolytic experiments with H_2O_2 in water were similarly unsuccessful); however, on addition of the *aci*-anion of nitromethane as a spin trap in the flow-system studies, detection of signals unambiguously assignable to adducts $(RO)_2P(S)SCH_2NO_2^{-\bullet}$ [*e.g.* for R = Et, a(N) 2.287, a(2H) 0.500, a(P) 0.125 mT, g 2.0055] clearly characterize the formation of these radicals during the oxidation (see later).

(b) *Linewidth variations for* $(RO)_2P(S)S^{\bullet}$. The lack of a discernible difference between the widths of the two individual lines in the spectra of $(RO)_2P(S)S^{\bullet}$ under given conditions suggests that the anisotropy in the phosphorus splitting is very small, as confirmed by the solid-state spectra (see later). The general increase of linewidth with temperature is behaviour opposite of that expected from the 'normal' dependence of the linewidth from anisotropic contributions (in A or g) on the rotational correlation time and hence on η/T, where η is the solvent viscosity and T is the absolute temperature.[24] Instead, the predominance of a different and comparatively rare form of relaxation (probably spin-rotational in origin) is suggested.[25] This relaxation mechanism, which has been proposed to account for the anomalous linewidths observed for peroxyl radicals[26] (g *ca.* 2.015) and some selenium-containing radicals[27] (*e.g.* phenoselenazine$^{+\bullet}$, g 2.0161) in solution, is expected to be significant for radicals with a large average g-shift; a linewidth contribution to ΔB proportional to T/η is predicted. T_2^{-1} is given by equation (v)[25] for a hydrodynamically spherical molecule of cylindrical magnetic symmetry and radius a [with ΔB (in mT) $1/(2.8\,\pi\sqrt{3} \times 10^7 T_2)$]: if we make the simplifying assumptions here that radicals (2) have the appropriate symmetry and that $\Delta g_{\perp} \ll \Delta g_{\parallel}$ (see later) then equations (vi) and (vii), where τ is the rotational correlation time, result:

$$T_2^{-1} = \frac{kT}{12\pi a^3\eta}(\Delta g_{\parallel}^2 + 2\Delta g_{\perp}^2) \quad \text{(v)}$$

$$\simeq \frac{3kT}{4\pi a^3\eta}(\Delta g_{\mathrm{iso}})^2 \quad \text{(vi)}$$

$$\simeq \frac{(\Delta g_{\mathrm{iso}})^2}{\tau} \quad \text{(vii)}$$

Figure 2 shows the variation in ΔB (which is proportional to T_2^{-1}) for $(Pr^iO)_2P(S)S^{\bullet}$ as a function of T/η for pentane and isopentane in the temperature range 193—296 K (viscosities were calculated[28] using the Bingham equation); the linear dependence expected on the basis of spin-rotation interaction is confirmed. From equations (vi) and (vii) we can derive values of a and τ_c for $(Pr^iO)_2P(S)S^{\bullet}$ in isopentane as 0.1 nm and 3×10^{-11} s (at 191 K), respectively. These values are of the magnitude anticipated for such parameters (see *e.g.* ref. 29), which suggests that the model is appropriate.

The order of linewidths in isopentane at 191 K (R = Et > Pr^n > CH_2CMe_3 > Pr^i) is also broadly consistent with this mechanism since the rate of tumbling should also decrease in this order. On the other hand, there appears to be no such structural correlation for data in toluene [and the linewidths for this solvent are somewhat higher than might be anticipated

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* Unanalysed signals built up at higher temperatures after prolonged photolysis, suggesting the occurrence of secondary reactions (*e.g.* subsequent decomposition of photoproducts): this behaviour was not investigated further.

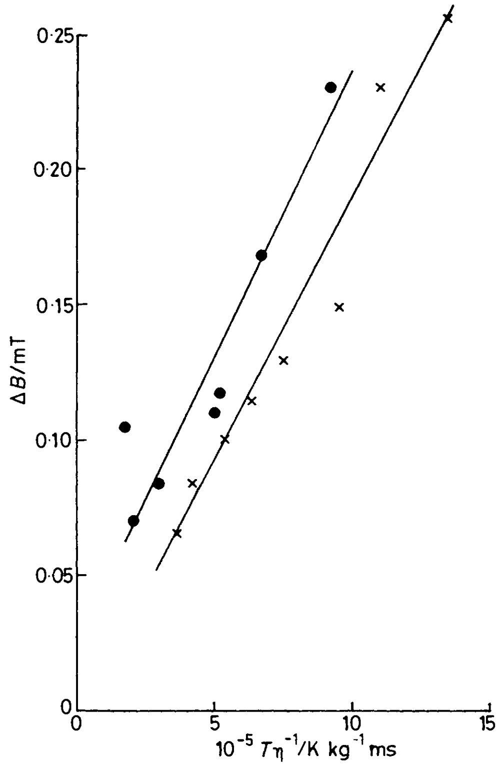

Figure 2. Variation of ΔB (mT) for (2; R = Pr^i) with T/η for pentane and 2-isopentane in the temperature range 193—296 K [● n-pentane; × isopentane]

on the basis of equations (v)—(vii)]. This may reflect the occurrence of specific radical–solvent interactions in this case, but further speculation appears unjustified.

Our failure to detect $(RO)_2P(S)S^{\cdot}$ in aqueous solution may be due to marked line-broadening of this type: although this would be expected on the basis of the relatively high temperatures at which the experiments were conducted (*ca.* 295 K), the viscosity of water is significantly greater than those of the other solvents employed under comparable conditions, and the calculated value of ΔB should hence be lower (we estimate *ca.* 0.06 mT in H_2O at 300 K). An alternative possibility is that the radicals are removed *via* rapid reaction with *e.g.* H_2O_2.

Finally, we contrast the lack of detection of thio radicals in fluid solution by e.s.r. with the relative ease of detection of $(RO)_2P(S)S^{\cdot}$ (with, generally, narrow lines). This implies that the thiophosphorylthio radical does not possess all the spin density located on a single sulphur atom (as is also indicated by the relatively low g_{av} value). Further evidence is provided by the anisotropic spectrum.

(c) *Kinetics of decay of* $(RO)_2P(S)S^{\cdot}$. Decay kinetics were obtained for the diethoxy- and di-isopropoxy-(thiophosphoryl)thio radicals in toluene in the temperature range 188—238 K;* these experiments were performed with the parent disulphides by following the rates of disappearance of the signals when the light beam was interrupted with either a shutter or a rotating sector (data collection over a series of cycles was achieved with a Datalab DL4000B microcomputer: full details of the experimental procedure will be published elsewhere [30]).

Table 2. Termination rate constants ($2k_t$) for some dialkoxy-(thiophosphoryl)thio radicals [$(RO)_2P(S)S^{\cdot}$] [a,b]

R	T/K	$10^{-9} \times 2k_t$/dm^3 mol^{-1} s^{-1}
Et	183	1.2
	202	2.7
Pr^i	198	0.7
	208	1.0
	218	1.35
	228	1.6
	238	2.35

[a] In toluene. [b] Estimated error ±20%.

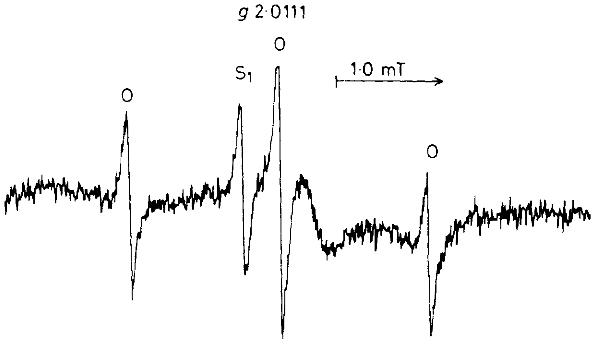

Figure 3. Isotropic e.s.r. spectrum (O) of the σ*-anion $(EtO)_2P(O)SSP(O)(OEt)_2^{-\cdot}$ (4) obtained from reaction of $(EtO)_2P(O)S^-$ with $^{\cdot}OH$ (from Ti^{III}–H_2O_2) in an aqueous flow system at room temperature. The singlet S$_1$ is from a Ti^{IV}–$HO_2^{\cdot}$ complex

In all experiments the decay traces were satisfactorily analysed in terms of second-order kinetics: examples of the resulting rate constants are collected in Table 2. These values are typical of diffusion-controlled reactions (*cf.* values of $2k_t$ of *ca.* 10^9 dm^3 mol^{-1} s^{-1} for simple aliphatic radicals under similar conditions [31]) and consistent with this is the finding that the activation energy for dimerization of (2; R = Pr^i) (calculated from an Arrhenius plot of the results in Table 2) is *ca.* 12 kJ mol^{-1}. This is as expected if its magnitude is largely governed by diffusion through the solvent (as found, for instance, by Schuh and Fischer [32] for the t-butyl radical in a variety of solvents: in benzene, for example, [32] E_{kin} = 10.16 kJ mol^{-1}); the value of A of *ca.* 1×10^{12} dm^3 mol^{-1} s^{-1} is also reasonable for this type of reaction.

(d) *Reactions of* O,O′-*diethyl hydrogen phosphorothioate* $(EtO)_2P(O)SH$ *and related species.* No isotropic e.s.r. signal assignable to $(EtO)_2P(O)S^{\cdot}$ (3) (for which a doublet with high g value would be expected) was detectable either in experiments in which samples of $(EtO)_2P(O)SH$ [alone or with $(Bu^tO)_2$] in toluene were photolysed [exactly as for the generation of $(RO)_2P(S)S^{\cdot}$] or in flow-system studies of the reaction of $^{\cdot}OH$ with $(RO)_2P(O)S^-$ (as its sodium salt). This may reflect the extreme broadening which would accompany the localization of the spin on sulphur (rather than oxygen) (*cf.* the failure to detect $RS^{\cdot}$ in fluid solution). On the other hand, in both sets of experiments a signal was obtained [enhanced in the photolysis experiments when $(Bu^tO)_2$ was also added] which comprised a triplet (evidently associated with two equivalent phosphorus nuclei), with parameters a(2P) 1.48 mT, g 2.0112 (in toluene at 208 K); and a(2P) 1.41 mT, g 2.0111 in aqueous solution (see Figure 3). The g value is close to those reported (see *e.g.* ref. 33) for disulphide radical anions ($RSSR^{-\cdot}$) and this, together with the observation of two equivalent phosphorus splittings (and crucial radiolysis results; see later) enables us to characterize the signal as being

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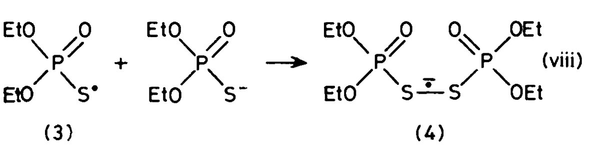
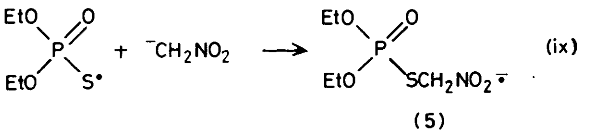
* At temperatures above *ca.* 240 K the relatively large linewidths involved rendered the signal-to-noise ratios too low for reliable kinetic experiments to be performed.





from the anion radical (4). This presumably arises *via* addition of (3) to the appropriate anion in the aqueous solution experiments [reaction (viii)], or in the photolytic experiments *via* reaction of (3) with the parent acid. The fact that this reaction is observed for (3) and not the analogous radical (2) presumably reflects both the extra stability of the latter and the necessity to localize the unpaired electron in the σ^*-orbital on forming the dimer.*

Although a detailed kinetic study of the behaviour of (4) was not attempted, experiments with a rotating sector (see before) established that decay is rapid and *apparently* second order (with $2k_t$ as expected for a diffusion-controlled process: *e.g.* 7.5×10^9 dm^3 mol^{-1} s^{-1} at 204 K in toluene).† We attempted to generate ' mixed ' anion radicals akin to (4) in photolytic experiments in which both $(EtO)_2P(S)SH$ and $(EtO)_2P(O)SH$ were oxidised together with $Bu^tO^\bullet$; however, the only signals detected were those of (4) and (2; R = Et), as described for the separate experiments. In the oxidation of $(EtO)_2P(O)S^-$ with $^\bullet OH$ in the Ti^{III}—H_2O_2 system, addition of the *aci*-anion of nitromethane as a spin trap led to the detection of the adduct (5), with parameters *a*(N) 2.275, *a*(2H) 0.475, *a*(P) 0.125 mT, *g* 2.0055; these clearly establish the structure of the adduct as sulphur-bonded and indicate that the first-formed radical (presumably with the spin essentially localized on sulphur) can be intercepted.

Photolysis of Solid Samples.—Dialkyl hydrogen phosphorodithioates and related compounds. Figure 4 shows the anisotropic spectrum obtained when a pure sample of $(EtO)_2P(S)SH$ (as a glass at 140 K) was u.v.-irradiated in the cavity of the spectrometer. The signal intensity built up to a maximum after about 10 min and then levelled off, remaining unchanged for some time after the light was switched off. Similar spectra were recorded for this substrate over the temperature range 133—173 K [and similarly for $(RO)_2P(S)SH$, R = Pr^n, Pr^i, or Bu^s] and were also obtained almost immediately when fluid solutions of the same substrates undergoing *in situ* photolysis were rapidly frozen.

The anisotropic e.s.r. spectrum shown in Figure 4 has parameters A_1(P) 2.36, A_2(P) 2.56, A_3(P) 2.51 mT, with g_1 2.0025, g_2 2.0147, g_3 2.037. These clearly correspond to the isotropic spectrum attributed to (2; R = Et) above [*a*(P) 2.49 mT, g_{iso} 2.0188] (*cf.* also refs. 14 and 16) and provide supporting evidence for the correct identification of this species. Data for the analogous species are collected in Table 3.

The following points are notable. Firstly, the spread of *g* values is considerably smaller than that normally associated

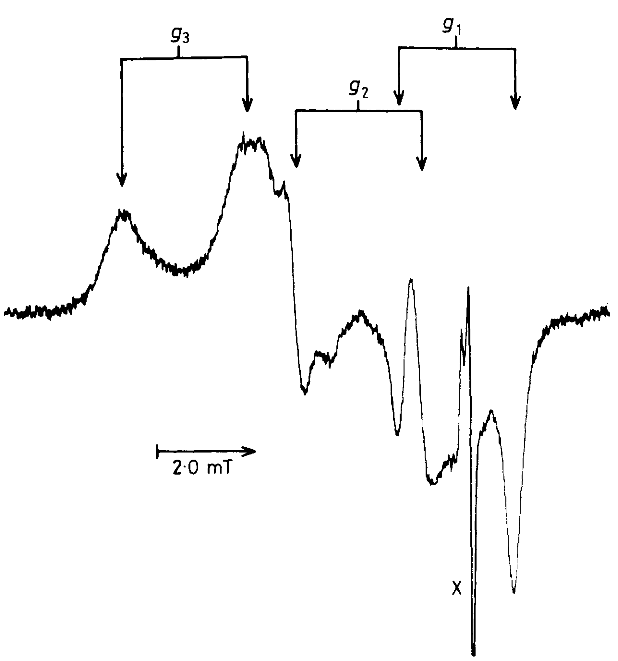
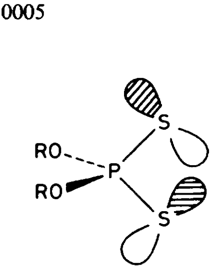


Figure 4. Anisotropic e.s.r. spectrum of $(EtO)_2P(S)S^\bullet$ (2; R = Et) from a u.v.-irradiated polycrystalline sample of $(EtO)_2P(S)SH$ at 140 K; the signal from the paramagnetic impurity in the cell (×) has *g* 2.0005



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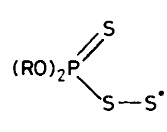

(7)

with a thio radical in which the unpaired electron is localized upon sulphur (typical examples have $g_{\parallel} \sim 2.2$, $g_{\perp} \sim 2.0$ ^{9,10}); this is entirely consistent with the ready detection of the isotropic spectrum (unlike $RS^\bullet$) and with a structure in which the two sulphur atoms share the unpaired electron. Secondly, the degree of anisotropy in the phosphorus splitting is remarkably low and indicates that the small phosphorus splitting observed (which corresponds to a percentage *s*-orbital occupancy of the unpaired electron on phosphorus of *ca.* 0.7%) probably arises *via* spin-polarization of the S–P bond from unpaired electron density in sulphur *p*-orbitals. Of the two most likely structures for the radical we favour that [(6)] which places the odd electron in the ' in-plane ' sulphur *p*-orbital (*cf. e.g.*^{34} $ArCO_2^\bullet$) rather than those at right angles to the SPS plane.

When the corresponding disulphide $[(Pr^iO)_2P(S)S]_2$ was photolysed as a glass in propan-2-ol in the range 130—230 K the signal from (2; R = Pr^i) was also observed. A second signal present with three broad lines (g_1 2.0022, g_2 2.0251, g_3 2.039) was also detectable, being most intense at the lower end of the temperature range employed; ‡ signals similar to the latter were observed for samples of disulphides $[(RO)_2P(S)S]_2$, R = Et, Bu^s, or Pr^i, as glasses in toluene at *ca.* 130 K

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* Their simple organic equivalents $RSSR^-$ are known to have the unpaired electron localized in the S–S antibonding σ-orbital and are hence often referred to as σ^*-anions.

† However, this value is greater than expected for the self-reaction of a large anion in toluene; as pointed out by a referee, an alternative first-order decay process may be involved.

‡ A weak unassigned doublet, *g* 2.085, *A* ~ 0.8 mT, was also discerned.

Table 3. Anisotropic e.s.r. data for thio and dithio radicals from photolysed samples of *O,O'*-dialkyl hydrogen phosphorodithioates and related compounds

(a) Thio radicals

Substrate	Conditions	R$^\cdot$	g_1 [a]	g_2 [a]	g_3 [a]	A_1(P) [b]	A_2(P) [b]	A_3(P) [b]
$(EtO)_2P(S)SH$	140 K, neat	(2; R = Et)	2.0025	2.0147	2.037	2.36	2.56	2.51
$(Pr^1O)_2P(S)SH$	140 K, neat	(2; R = Pr^i)	2.0017	2.0149	2.036	2.32	2.58	2.61
$[(Pr^1O)_2P(S)S]_2$	140 K, Pr^iOH	(2; P = Pr^1)	obscured	2.0153	2.035	—	2.38	2.44
$(Bu^sO)_2P(S)SH$	140 K, neat	(2; R = Bu^s)	2.0017	2.0146	2.036	2.34	2.59	2.38
$(Pr^nO)_2P(S)SH$	140 K, neat	(2; R = Pr^n)	2.0029	2.0151	2.036	2.38	2.55	2.50

(b) Dithio radicals

Substrate	Conditions	R$^\cdot$	g_1	g_2	g_3 [a]
$[(EtO)_2P(O)S]_2$	130 K, neat	(8)	2.0025	2.0254	2.040
$[(EtO)_2P(S)S]_2$	130 K, toluene	(7; R = Et)	2.0024	2.0259	2.041
$[(Pr^iO)_2P(S)S]_2$	140 K, Pr^iOH	(7; R = Pr^i)	2.0022	2.0251	2.039
$[(Pr^iO)_2P(S)S]_2$	140 K, toluene	(7; R = Pr^i)	2.0022	2.0257	2.040
$[(Bu^sO)_2P(S)S]_2$	130 K, toluene	(7; R = Bu^s)	2.0023	2.0260	2.041

[a] ±0.0005 except for g_3 (±0.001). [b] in mT, ±0.05.

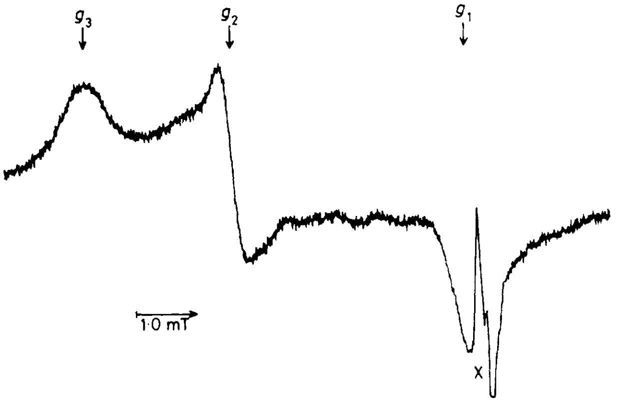
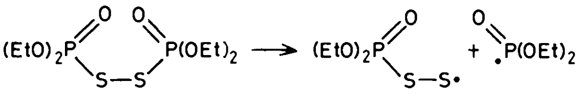


Figure 5. Anisotropic e.s.r. spectrum of $(EtO)_2P(O)SS^\cdot$ (8) obtained by photolysis of a polycrystalline sample of $[(EtO)_2P(O)S]_2$ at 140 K. (The signal marked × is from a paramagnetic impurity in the cell, with g 2.0005)

(see Table 3) [and also for some samples of acids $(RO)_2P(S)SH$, R = Pr^n or Bu^s, which had been photolysed (as pure samples rather than in a solvent) for a considerable period of time and in which disulphide may be formed *via* reaction of (2)]. Photolysis of solid samples of the disulphide $[(EtO)_2P(O)S]_2$, either as a glass of the pure liquid or in toluene, also gave rise to a similar and particularly strong broad spectrum with principal g values 2.0022, 2.0254, and 2.040 (see Figure 5). This type of signal somewhat resembles those detected (along with $RS^\cdot$) in irradiated samples of disulphides and related compounds and which has been previously attributed both to dithio ($RS_2^\cdot$) [10,11] and adduct [9] [$RS\dot{S}R_2$] species [the anisotropic spectrum assigned to $Bu^tSS^\cdot$ has principal g values 2.001, 2.026, and 2.059, with g_{av} 2.029]. We here favour the former structure [*i.e.* (7), (8)] and note that any phosphorus splitting would be expected to be small. We were unable to detect signals from either the phosphoryl radicals which would be expected to accompany such simple cleavage [reaction (x)] (though parallel radiolytic experiments were successful) or (3), which might be expected to resemble spectra from simple thio radicals.

In contrast, photolysis of $(EtO)_2P(O)SH$ as a pure sample at 130 K led to the detection of a signal with $g_\perp$ 2.0023, $g_\parallel$ 2.0172, and $A(2P)_\perp$ 1.36, $A(2P)_\parallel$ 1.65 mT, which is attributed



(x)

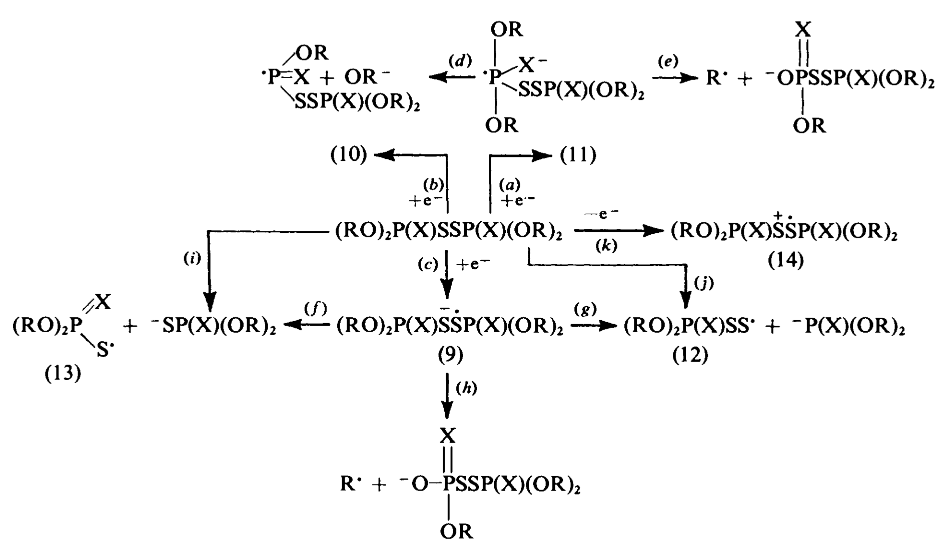
(8)

to the solid-state spectrum of the σ*-anion. This presumably arises *via* addition of the first-formed (undetected) thio radical $(EtO)_2P(O)S^\cdot$ to the parent molecule.

The solid-state photolysis experiments appear to confirm the ready occurrence of S–H and, for the disulphides $[(RO)_2P(S)S]_2$, S–S fission; however, particularly for $[(EtO)_2P(O)S]_2$ and for $[(RO)_2P(S)S]_2$ at lower temperatures, S–P cleavage can clearly also result.

Radiolysis of Solid Samples.—In an attempt to obtain corroboration for assignments made on the basis of photolytic studies (and, in particular, to establish parameters for 'electron-loss' and 'electron-gain' species derived from $[(RO)_2P(S)S]_2$ and related compounds) solid samples [powders, or solid solutions in solvents of differing type, namely 2-methyltetrahydrofuran (MeTHF), CD_3OD, and Freon ($CFCl_3$)] were γ-irradiated at 77 K. Spectra were also recorded for samples which had been annealed (typically to *ca.* 140 K) and re-cooled to 77 K. An initial description of the individual spectra is followed by general mechanistic comments and more detailed structural points.

(a) *Bis(di-isopropoxythiophosphoryl) disulphide.* Radicals of several different types could be clearly identified from a γ-irradiated powder sample of $[(Pr^iO)_2P(S)S]_2$. For example Figure 6 shows the central portion of the spectrum attributed to the σ*-anion (9; R = Pr^i, X = S) (see Scheme 1 for identification of the range of radical structures detected from this and related compounds). This species is characterized by the g values and the magnitude of the splitting from two equivalent phosphorus nuclei [see Table 4; *cf.* isotropic data for $RSSR^{-\cdot}$ and $(RO)_2P(O)SSP(O)(OR)_2^{-\cdot}$ (before)]; the satellite lines accompanying each of the peaks in Figure 6 are due to spin-flip transitions of neighbouring protons. This spectrum was also accompanied by two large doublets attributed to phosphoryl (10; R = Pr^i, X = S) and phosphoranyl (11; R = Pr^i, X = S) radicals. The assignments (see Table 4) are based on the typical parameters obtained for such species [*cf.* ref. 35 for e.s.r. parameters of dialkoxyphosphoryl radicals $(RO)_2\dot{P}{=}O$ and refs. 36—38 for results for



Scheme 1. Radicals identified in γ-irradiated bis(dialkoxythiophosphoryl) and bis(dialkoxyphosphoryl) disulphides

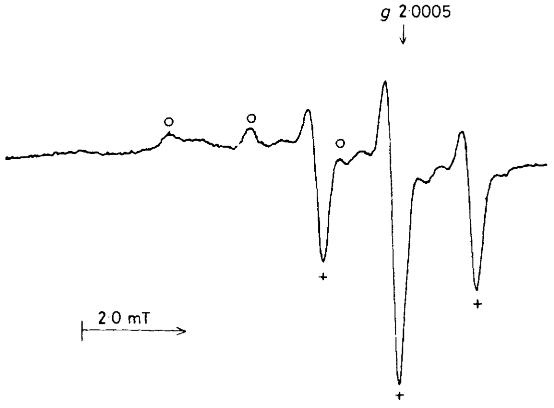


Figure 6. Anisotropic e.s.r. spectrum of the σ^*-anion (9; $R = Pr^i$, $X = S$) showing parallel (○) and perpendicular features (+): this is the central portion of the spectrum obtained by γ-irradiation of a powder sample of $[(Pr^iO)_2P(S)S]_2$

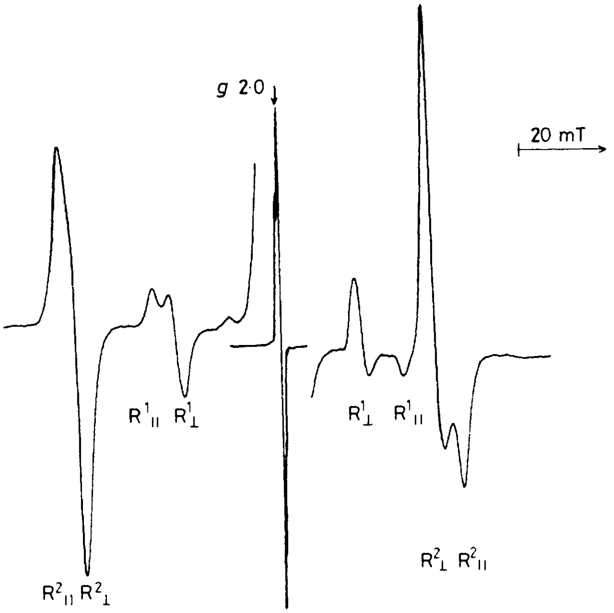


Figure 7. Anisotropic spectra of the phosphoryl radical $EtO\dot{P}(S)$-S^- (R^1) and the phosphoranyl radical $(EtO)_2\dot{P}(S^-)S^-$ (R^2) obtained by γ-irradiation of a solid sample of $(EtO)_2P(S)S^-NH_4^+$ in CD_3OD

phosphoranyl radicals [*e.g.* $(EtO)_3\dot{P}SMe$], $Cl_2(OR)PO^{-\cdot}$, and $(MeO)_2\dot{P}(S^-)Br$, respectively] and on the similar but clearer spectra obtained from analogous salts (see *e.g.* Figure 7): radicals of type (10) and (11) are subsequently referred to as of $\cdot PL_3$ and $\cdot PL_4^-$ type for brevity. Further structural and mechanistic details are discussed in a later section.

On annealing the irradiated powder samples several changes were observed, but most notably the appearance of a signal in the centre of the spectrum attributed to the dithio radical (12) [with parameters similar to that from (8) characterized in the photolysis of $(EtO)_2P(O)SSP(O)(OEt)_2$].

The particularly complex spectra obtained from samples in MeTHF were analysed, on the basis of the powder result, in terms of overlapping signals from the σ^*-anion (9), the dithio radical (12), and a trace of the appropriate phosphoranyl radical $\cdot PL_4^-$ [(11)]; no $\cdot PL_3$ could be detected. On annealing, a signal assigned to (13; $R = Pr^i$, $X = S$) could be discerned (with anisotropic parameters close to those obtained from the photolysis experiment illustrated in Figure 4). Data are summarized in Tables 4 and 5. In CD_3OD, signals detected included those of the σ^*-anion, $\cdot PL_4^-$, and $\cdot PL_3$ (the latter giving ' doublets ' of *ca.* 5 mT on annealing, probably from radicals in different conformations) as well as that assigned to $\cdot CMe_2OP(OPr^i)(S)SSP(S)(OPr^i)_2$ [with little anisotropy, and a(6H) 1.9 mT, g 2.002]; signals from the σ^*-anion and the last radical were most pronounced on annealing.

Lastly, irradiation of samples in $CFCl_3$ gave, in general, poorly defined spectra; however, it was possible to recognize features believed to be associated with the parent's radical cation (14; $R = Pr^i$, $X = S$). The parameters (see Table 4) are typical of the π-type radical cations from simple disulphides.

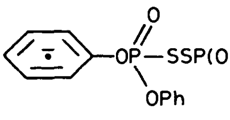
(b) *Bis(diethoxyphosphoryl) and bis(diphenoxyphosphoryl) disulphides.* γ-Irradiation of a powder sample of $[(EtO)_2P(O)S]_2$ led to the detection of a complex spectrum dominated by signals attributed to $\cdot Et$, $\cdot PL_3$, and $\cdot PL_4$ (see Table 4) as well as the dithio radical (12; $R = Et$, $X = O$) (see Scheme 1 and Table 4). Although features from the appropriate σ^*-anion (9; $R = Et$, $X = O$) were generally poorly defined for powder samples, significantly stronger spectra from this

Table 4. E.s.r. parameters of sulphur-centred radicals obtained from radiolysis of solid samples [a]

Compound	$(RO)_2P(S)\overset{-\cdot}{S}SP(S)(OR)_2$ or $(RO)_2P(O)\overset{-\cdot}{S}SP(O)(OR)_2$				$(RO)_2P(S)\overset{+\cdot}{S}SP(S)(OR)_2$					
	$A_{\parallel}$(2P)	$A_{\perp}$(2P)	$g_{\parallel}$	$g_{\perp}$	A_1	A_2	A_3	g_1	g_2	g_3
					(each 2P)					
$[(Pr^iO)_2P(S)S]_2$	1.54	1.46	2.021	2.0025 (powder)	1.3	1.5	1.2	2.002	2.014	2.035 (Freon)
	1.55	1.60	2.021	2.0025 (MeTHF)						
$[(Pr^iO)_2P(S)S]_2Zn$		1.52	2.021	2.0025 (MeTHF)						
$(Pr^iO)_2P(S)S^-NH_4^+$	1.5	1.5	2.021	2.003 (MeTHF)						
$[(EtO)_2P(O)S]_2$		1.35		2.0025 (MeTHF)						
		1.35		2.0025 (CD_3OD)						

Compound	$(RO)_2P(S)S^{\cdot}$ or $(RO)_2P(O)S^{\cdot}$						$(RO)_2P(S)SS^{\cdot}$ or $(RO)_2P(O)SS^{\cdot}$			
	A_1	A_2	A_3	g_1	g_2	g_3	g_1	g_2	g_3	$[A(^{31}P) \sim 0]$
	(each 1P)									
$[(Pr^iO)_2P(S)S]_2$							2.003	2.026	2.042	(powder)
									2.043	(MeTHF)
$[(Pr^iO)_2P(S)S]_2Zn$									2.038	(MeTHF)
$(Pr^iO)_2P(S)S^-NH_4^+$	2.35	2.35	2.54	2.002	2.018	2.041 (powder)			2.048	(MeTHF)
$[(EtO)_2P(O)S]_2$							1.998	2.022	2.037	(powder)
							1.998	2.023	2.0385	(MeTHF)
		1.8	2.0		2.0268	2.053 (CD_3OD)	1.999	2.0255	2.041	(CD_3OD)
$[(PhO)_2P(O)S]_2$							2.009	2.026	2.0475	(powder)
							2.000	2.025	2.039	(MeTHF)
								2.026		(CD_3OD)

[a] Splittings typically ±0.04 mT; g typically ±0.001.



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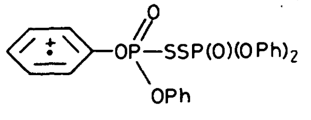
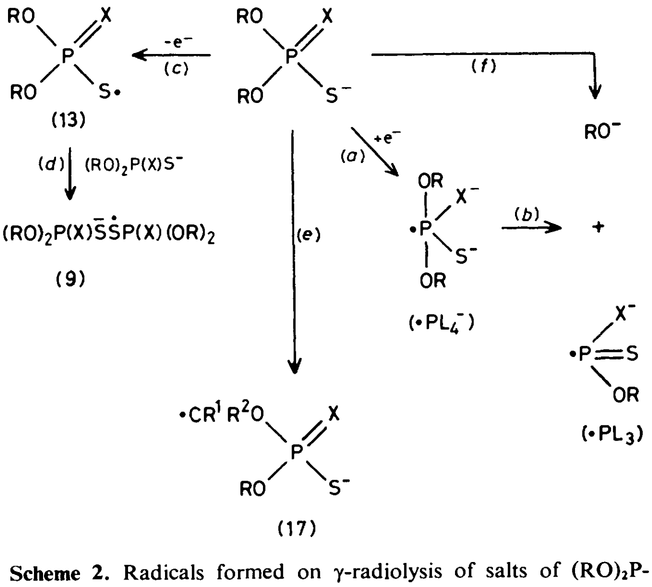


(16)

species were obtained, together with those from $^{\cdot}$Et and the dithio radical, in experiments employing glasses in MeTHF. In CD_3OD signals were obtained from $^{\cdot}$Et, the dithio radical, the σ^*-anion, and phosphorus-centred radicals, as well as extra doublet features (apparent on annealing) assigned to the thio radical (13; R = Et, X = O) (see Table 4); it is interesting that, as expected, the highest g value (2.053) is significantly greater than that for $(RO)_2P(S)S^{\cdot}$ but nevertheless considerably less than that associated with thio radicals with all the spin on a single sulphur (for example g *ca.* 2.158). The very low solubility of the substrate in Freon precluded the detection of analysable signals from this medium.

γ-Irradiation of $[(PhO)_2P(O)S]_2$, as the powder and in electron-donating solvents, led to the detection of signals attributed to $^{\cdot}PL_4^-$, $^{\cdot}PL_3$, and dithio radicals (see Tables 4 and 5), as well as to the ligand (phenyl) π^*-radical anion (15) in the powder [*cf.*[36] $Bu^tO\dot{P}Ph_3$]. The spectrum from the corresponding aromatic radical cation (16) [rather than the π^*-cation (14; R = Ph, X = O)] was identified from samples dissolved in Freon.

(c) *Salts of* $(RO)_2P(X)S^-$ (X = S *or* O). Spectra obtained from polycrystalline samples of $[(Pr^iO)_2P(S)S]_2]Zn$ were generally ill defined, though clear signals from $^{\cdot}PL_4^-$ (but not $^{\cdot}PL_3$) could be recognized (see Table 5). In contrast, in MeTHF signals were detected from the phosphoranyl and phosphoryl radicals (with $[^{\cdot}PL_4^-] > [^{\cdot}PL_3]$), as were both the di-isopropoxy(thiophosphoryl)thio radicals (13; R = Pr^i, X = S) and the σ^*-anion (9; R = Pr^i, X = S) on annealing (the latter



Scheme 2. Radicals formed on γ-radiolysis of salts of $(RO)_2P(X)S^-$ (X = O or S)

Table 5. E.s.r. parameters for phosphorus-centred radicals obtained by γ-radiolysis of solid samples ^{a}

Substrate	Matrix	$\cdot\mathrm{PL_3}$ ^{b}			$\cdot\mathrm{PL_4^-}$ ^{c}						
		$A_{\parallel}$	$A_{\perp}$	A_{iso}	$A_{\parallel}$	$A_{\perp}$	A_{iso}	$2B$ ^{d}	$\%s$ ^{d}	$\%p$ ^{d}	$p:s$ ratio
		(or A_1, A_2, A_3)									
$[(\mathrm{Pr^iO})_2\mathrm{P(S)S}]_2$	Powder		48.4^{e} 34.7^{e}		90.7	76.5	81.3	9.48	22	47	2.1 : 1
	$\mathrm{CD_3OD}$		49.8^{e} 38.0^{e}		90.5	76.2	81.0	9.50	22	47	2.1 : 1
	MeTHF				86.2	66.4	73.0	13.10	20	65	3.3 : 1
$[(\mathrm{Pr^iO})_2\mathrm{P(S)S}]_2\mathrm{Zn}$	Powder										
	$\mathrm{CD_3OD}$	57.5	39.3	45.4	89.1	75.5	80.0	9.10	22	45	2.1 : 1
			39.1^{e} 48.1^{e}								
	MeTHF	56.0	43.0	47.3	89.3	77.2	81.3	8.00	22	40	1.8 : 1
			39.1^{e} 49.0^{e}								
$(\mathrm{EtO})_2\mathrm{P(S)S^-NH_4^+}$	Powder	56.5	40.0	45.5	91.4	77.1	81.8	9.50	22	47	2.1 : 1
		58.8 55.9	$41.3, 41.1^{e,f}$ $38.9, 39.0^{e,f}$	47.1 44.6							
	$\mathrm{CD_3OD}$	56.4	38.4	44.4	91.3	77.0	81.8	9.50	22	47	2.1 : 1
	MeTHF				88.9	75.0	79.6	9.30	21	46	2.1 : 1
					84.2	65.5	71.8	12.4	20	62	$3.1:1^{i}$
$(\mathrm{Pr^iO})_2\mathrm{P(S)S^-NH_4^+}$	Powder	58.7	$41.5, 41.0^{f}$	47.1	90.7	77.0	81.9	9.1	22	45	2.0 : 1
	$\mathrm{CD_3OD}$	56.3	38.2	44.2	89.6	75.5	80.2	9.4	22	47	2.1 : 1
			37.5^{e} 47.8^{e}								
	MeTHF				87.9	75.4	79.5	8.3	22	41	1.9 : 1
					82.7	65.5	71.2	11.5	19	57	$2.1:1^{i}$
$(\mathrm{EtO})_2\mathrm{P(O)S^-Na^+}$	Powder		47.0^{g}		90.7	76.9	81.5	9.2	22	46	2.1 : 1
		76.7	58.1^{h}	64.2							
	$\mathrm{CD_3OD}$		47.3		90.8	75.6	80.8	10.0	22	50	2.3 : 1
		79.0	58.8	65.5							
$[(\mathrm{PhO})_2\mathrm{P(O)S}]_2$	Powder		49.1		90.8	75.8	80.8	10.0	22	50	2.3 : 1
	$\mathrm{CD_3OD}$		49.0		92.2	76.4	81.7	10.5	22	52	2.3 : 1
	MeTHF		$40\text{—}50^{e}$ 40—50		97.9	79.8	85.9	12.1	23	60	2.6 : 1
$[(\mathrm{EtO})_2\mathrm{P(O)S}]_2$	Powder		49.3		82.6	70.8	74.8	7.8	20	39	1.9 : 1
	$\mathrm{CD_3OD}$		48.7		83.2	70.8	74.9	8.2	20	41	2.0 : 1
	MeTHF		46.6		87.6	67.3	74.1	13.5	20	67	3.3 : 1

[a] A(P) (in mT) ±0.4 mT. [b] *g ca.* 2.0; phosphoryl radical (for structural assignment, see text and Schemes 1 and 2). [c] *g ca.* 2.0; phosphoranyl radical anion (for structural assignment, see text and Schemes 1 and 2). [d] For calculation of $\%s$ and $\%p$ contribution to the orbital of the unpaired electron see *e.g.* ref. 13. [e] Doublet feature seen on annealing: see text. [f] Axial anisotropy. [g] Weak; becomes sharp on annealing. [h] Very strong. [i] Major phosphoranyl radical.

presumably arises *via* addition of the thio radical to the appropriate anion). Similar results were obtained in $\mathrm{CD_3OD}$, together with the appearance on annealing of signals from (17; $R^1 = R^2 = \mathrm{Me}$, $X = \mathrm{S}$) (see Scheme 2). Lack of solubility prevented the recording of spectra from this or the other salts in Freon matrices.

For $(\mathrm{Pr^iO})_2\mathrm{P(S)S^-NH_4^+}$ in the polycrystalline state, strong signals were obtained from $(\mathrm{Pr^iO})_2\mathrm{P(S)S^{\cdot}}$ and $\cdot\mathrm{Pr^i}$ as well as $\cdot\mathrm{PL_4^-}$ and $\cdot\mathrm{PL_3}$ (with the former less intense than the latter) and, on annealing, the σ*-anion (9; $R = \mathrm{Pr^i}$, $X = \mathrm{S}$). In MeTHF two $\cdot\mathrm{PL_4^-}$ species were detected (see later), at lower concentrations than $[\cdot\mathrm{PL_3}]$, and traces of the thio radical and σ*-radical were recognized after annealing. In $\mathrm{CD_3OD}$, signals from $\cdot\mathrm{PL_4^-}$ and $\cdot\mathrm{PL_3}$ were accompanied by those from $\cdot\mathrm{Pr^i}$ and (17; $R^1 = R^2 = \mathrm{Me}$, $X = \mathrm{S}$). In contrast, for ammonium diethyl phosphorodithioate, $^{+\cdot}\mathrm{NH_3}$ was seen as the dominant signal from powder samples (with $[\cdot\mathrm{PL_4}]^- > [\cdot\mathrm{PL_3}]$); annealing gave (17; $R^1 = \mathrm{H}$, $R^2 = \mathrm{Me}$, $X = \mathrm{S}$) but no thio radicals. For MeTHF only $\cdot\mathrm{PL_4^-}$ (again in two variations) and $\cdot\mathrm{PL_3}$ were detected (with the former in higher concentrations), but there were no detectable signals from substrate-derived radicals in the central portion of the spectrum. In $\mathrm{CD_3OD}$, the phosphorus-centred species were detected along with (17; $R^1 = \mathrm{H}$, $R^2 = \mathrm{Me}$, $X = \mathrm{S}$).

Finally, irradiation of $(\mathrm{EtO})_2\mathrm{P(O)S^-Na^+}$ in polycrystalline form led to the detection of $\cdot\mathrm{Et}$, (17; $R^1 = \mathrm{H}$, $R^2 = \mathrm{Me}$, $X = \mathrm{O}$), $\cdot\mathrm{PL_4^-}$, and $\cdot\mathrm{PL_3}$ but not the thio radical (13; $R = \mathrm{Et}$, $X = \mathrm{O}$). Spectra from experiments with MeTHF and $\mathrm{CD_3OD}$ were dominated by signals from $\cdot\mathrm{Et}$ and, in the latter case, $\cdot\mathrm{PL_4^-}$ and $\cdot\mathrm{PL_3}$; no sign of the thio radical or σ*-anion could be discerned.

(d) *Aspects of mechanism and structure*. Radiolysis of the pure compounds is expected to give electron-gain and electron-loss radicals as well as possible products of bond homolyses.[39] However, dilute solutions in solvents such as $\mathrm{CD_3OD}$ or MeTHF, which trap ' holes ' readily but do not react efficiently with electrons, strongly favour electron capture by solute molecules. In contrast, solvents such as $\mathrm{CFCl_3}$, which capture electrons readily and irreversibly, favour ' hole ' migration to give solute electron-loss centres.[39]

The reactions proposed for the disulphides are summarized in Scheme 1; our results reveal that a variety of electron-capture processes occur. For example, initial electron capture at phosphorus can give a phosphoranyl radical (11) with the

SOMO localized on phosphorus and the two axial ligands [pathway (*a*)]. This radical may break down either by loss of alkoxide ions [reaction (*d*)] (favoured in the good anion-solvating medium CD_3OD) or by loss of an alkyl radical [reaction (*e*)]. Alternatively, the S–S σ-bond can stretch to accommodate the electron in the localized S–S σ*-orbital [pathway (*c*)]. This is the most probable mode of addition for these compounds. Again, the parent anion can evidently react as indicated in pathways (*f*), (*g*), and (*h*) but we suggest that the route to R˙ is probably (*e*) rather than (*h*) since the R–O bond in (9) is remote from the localized σ*-orbital.

We stress that dissociative electron capture may not occur after initial formation of the anion (9) or (11) but may proceed directly as in pathway (*b*), (*i*), or (*j*) (see also ref. 39).

The apical site in (11) may be occupied by sulphur rather than oxygen; although it is not possible to judge from our data, we note that Giles and Roberts suggest [36] that the apicophilicity of sulphur is greater than that of oxygen. It is also possible that some of the phosphoranyl radicals (at least) might possess an alternative, σ*-structure, with the unpaired electron in a localized, stretched $\dot{P}$–S bond [*cf.* ref. 40 and the σ*-structure assigned [36] to $RS\dot{P}(Ph)_3$]. This structure might be expected to be the precursor to reactions (*g*) and (*j*) (see Scheme 1). However, we do not think that it is a reasonable structure for the $^{\bullet}PL_4^-$ species detected from disulphides since electron migration into the S–S σ* orbital [to give the (observed) σ*-anion] should take place readily at all temperatures.

Electron loss (*k*) is expected to give the sulphur π-cation (14), and, as expected on this basis, this was the only species clearly detected in Freon matrices.

The reactions of $(RO)_2P(X)S^-$ salts on radiolysis are summarized in Scheme 2. The major electron-gain processes are pathway (*a*), giving the phosphoranyl anions, and dissociative electron capture to give phosphoryl radicals, either directly [(*f*)] or indirectly [(*b*)]. Alkyl radicals were not detected directly, but they may be responsible for the detection of the radicals (17), formed by subsequent hydrogen-atom abstraction reactions.

Electron-loss gives $(RO)_2P(X)S^{\bullet}$ centres, as expected [pathway (*c*)], and these readily react with the salts to give the σ*-dimer anions [reaction (*d*)].

The results for $(RO)_2P(S)S^{\bullet}$ [(13; X = S)] confirm the photolytic results. We stress that the small *g*-shifts clearly establish the delocalized nature of the orbital containing the unpaired electron. This type of radical has smaller *g*-shifts than those for the oxy-derivative $(RO)_2P(O)S^{\bullet}$ for two reasons. One is that the *g*-tensor direction must lie along the symmetry axes for the (13; X = S) radicals [see structure (6)] but the parallel axis will be close to the P–S bond direction for (13; X = O) (with consequent maximum orbital angular momentum in this direction and hence a large *g*-shift). In addition, the relatively strong in-plane bonding for (6) will lift the degeneracy of the combined sulphur orbitals which are coupled by the magnetic field far more than the weaker O ··· S interaction in (13; X = O). It is the greater spread of *g* values for (13; X = O) which gives rise to more efficient spin–lattice relaxation and hence undetectably broad lines for these radicals in the liquid phase.

Experimental

E.s.r. spectra in photochemical and flow experiments were recorded with a Varian E104 spectrometer, with 100 kHz modulation and an *X*-band Klystron. Hyperfine splittings were measured directly from the field-scan, itself calibrated with an aqueous solution of Fremy's salt [*a*(N) 1.3091 mT [41]]; *g* values were usually measured by reference to the paramagnetic impurity in the photolysis cell (*g* 2.0005), or by comparison with Fremy's salt (*g* 2.0055 [42]). Absolute radical concentrations in the kinetic experiments were measured by comparison of doubly integrated spectra with those from standard solutions of DPPH in benzene. Samples were photolysed *in situ* with the unfiltered but focused radiation from an Hanovia 977B-1 1 kW mercury–xenon lamp; the temperature was controlled with a Varian Variable Temperature accessory and was monitored to within ±1 K with a Comark 5 000 digital thermometer. Intermittent irradiation was achieved with either a Rofin Frequency Programmable Light Chopper Mk. II or a Compur Electronic M shutter and successive decay curves were accumulated with a Datalab DL4000 microcomputer.[30] Solutions were deoxygenated by purging with nitrogen or standard vacuum freeze–thaw techniques.

A three-way flow system was employed for the Ti^{III}–H_2O_2 studies: the reagent concentrations and details of uses of the *aci*-anion of nitromethane as a spin trap were as previously described.[43]

In the radiolysis experiments, samples were frozen as small beads or powders to 77 K and exposed to ^{60}Co γ-rays in a Vickrad cell for up to 1 Mrad. E.s.r. spectra were measured at 77 K for samples in a liquid nitrogen Dewar flask with a Varian E109 spectrometer; samples were annealed either using a variable-temperature accessory or by decanting the liquid nitrogen from the Dewar flask and allowing the sample to warm up in the cavity (with continuous e.s.r. monitoring and recooling to 77 K when significant changes were noticed).

The *O,O′*-dialkyl hydrogen phosphorothioates and their ammonium salts were prepared according to the method of Wystrach *et al.*,[44] except for the ethyl salt which was commercially available (Aldrich) and which was recrystallized from ethanol prior to use. The appropriate zinc salts were prepared by metathetical exchange reactions from the ammonium salts using zinc sulphate.[18,45] The appropriate disulphides were prepared by oxidation of the ammonium salts with aqueous iodine–potassium iodide.[46] Sodium *O,O′*-diethyl phosphorothioate was prepared by the method of Pesin and Khaletskii [47] and the disulphide and that of diphenyl hydrogen phosphorothioate were prepared according to the method of Krawczyk and Skowronska.[48] All solvents were commercially available (AnalaR grade) and used as supplied.

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