Unstable Intermediates

Part 122.[1]—Electron Spin Resonance Studies of Radicals from Irradiated Trimethylphosphine Oxide: the $Me_2\dot{P}O$ Radical

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Exposure of trimethylphosphine oxide to γ-rays at 77 K gave, after slight annealing, e.s.r. spectra with separate features assigned to $Me_3\dot{P}O^-$ (or $Me_3\dot{P}OR$), $Me_2\dot{P}O$ and $H_2\dot{C}PO(Me)_2$ radicals. At *ca.* 140 K the spectrum assigned to $Me_3\dot{P}O^-$ radicals was lost irreversibly, whilst that assigned to $Me_2\dot{P}O$ radicals changed reversibly to reveal well resolved proton hyperfine structure, with $a(H) = 5.6$ G. This temperature effect is explained in terms of extensive librations of the radicals, coupled with concerted restricted rotation of the methyl groups.

In alcohol media, only $Me_3\dot{P}O$ or $Me_3\dot{P}OH$ radicals were detected, whilst in sulphuric acid the main phosphorus radicals were Me_3P^+ and $H_2\dot{C}—P(OH)Me_2^+$.

Continuing our studies of various phosphorus centred radicals,[2-7] we have turned our attention to mixed alkyl-oxy radicals. The radical $\dot{P}O_3^{2-}$ is well established magnetically,[8] and various alkyl-phosphine cations, $R_3P^{+\bullet}$, have recently been studied in the solid-state.[3] Although several tetra-coordinated alkyl-alkoxy derivatives, $R_nP(OR)_{4-n}$ are now known in the liquid state,[9, 10] the only ter-coordinated species detected in fluid solution, to our knowledge, are the dialkoxy-radicals $O\dot{P}(OR)_2$.[11] These are simply alkyl derivatives of $\dot{P}O_3^{2-}$, and the results [11] show that alkylation has only a minor effect on the magnetic properties, having the same form as environmental effects.[12]

EXPERIMENTAL

Purified trimethylphosphine oxide was kindly supplied by Dr. D. J. H. Smith. Methanol, ethanol and sulphuric acid were reagent grades. Small spherical beads were prepared by rapidly freezing the oxide in liquid nitrogen, prior to exposure to ^{60}Co γ-rays at 77 K in a Vickrad cell for up to 2 h at a nominal dose rate of 4 Mrad h^{-1}.

E.s.r. spectra were obtained using a Varian E3 spectrometer, either at 77 K using a quartz dewar insert, or between *ca.* 85 K and the softening point of the solid using a Varian variable temperature accessory. *Q*-band spectra were run on a superheterodyne spectrometer constructed in these laboratories.

RESULTS AND DISCUSSION

Typical e.s.r. spectra obtained from γ-irradiated trimethyl-phosphine oxide are illustrated in the figures.

The central features at 77 K were characteristic of radicals of type $H_2\dot{C}PR_3$,[2] (fig. 1(*a*)) and the derived parameters (table 1) are in accord with expectation.[2, 13] On annealing to *ca.* 140 K, better resolution was achieved (fig. 1(*b*)), but extra lines appeared in the wings which were barely discernible at 77 K. These were selectively broadened again on cooling; we can offer no clear identification of the species responsible for these extra features.

The features assigned to $Me_2\dot{P}O$ radicals varied markedly with temperature, as exemplified in fig. 2(*a*) and 2(*b*). These changes, which were completely reversible, involve the apparent ^1H hyperfine coupling as well as the ^{31}P and g-tensors (table 1). These radicals, which were very much more stable than those associated with the

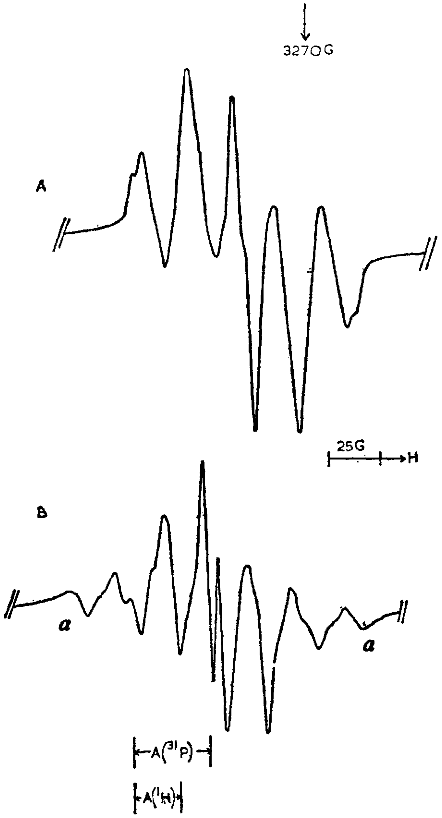


FIG. 1.—First derivative e.s.r. spectrum of trimethylphosphine oxide after exposure to γ-rays at 77 K, showing features assigned to $H_2\dot{C}P(O)Me_2$ radicals; *A*, at 77 K; *B*, at *ca.* 140 K showing extra lines (*a*).

TABLE 1.—E.S.R. DATA FOR RADICALS IN IRRADIATED TRIMETHYLPHOSPHINE OXIDE

radicals	proton coupling/G	^{31}P coupling/G A_x	A_y	A_z	g-values $g_\parallel$	$g_\perp$
$H_2\dot{C}P(O)Me_2$	*ca.* 21	*ca.* 38			*ca.* 2.003	
$H_2\dot{C}P(OH)Me_2^+$	20	40			2.003	
$Me_2\dot{P}O$ (77 K)	20(∥) 17.5(⊥)[a]	295	295	535	1.997	2.009
(140 K)	5.6	310	375	433		
Me_3PO^- or	not resolved					
Me_3POH (in EtOH)	not resolved	738	548	548[b]	1.997	2.015
Me_3P^+ (in H_2SO_4)	not resolved	600	290	290	2.002	2.01
PO_3^{2-}[c] (in Na_2HPO_3)		706.5	540.2	540.2	1.992	2.007

[a] apparent coupling only (see text); [b] error *ca.* ±10 G because of broad lines.; [c] ref. (12).

outermost features, were only lost when the glasses became soft. Their identification as $Me_2\dot{P}O$ follows from the following observations: (i) they contain only one strongly coupled phosphorus nucleus; (ii) they contain at least two equally coupled methyl groups; (iii) the isotropic hyperfine coupling to ^{31}P (375 G) is far too small for the only other reasonable species, namely $Me_3\dot{P}O^-$ or $Me_3\dot{P}OR$. (iv) the derived orbital populations (table 2) show a clear gradation in the values for $Me_3\dot{P}^{+\bullet}$, $Me_2\dot{P}O$ and PO_3^{2-}, both with respect to the fall in total spin-density on phosphorus with increase in the number of oxygen ligands, and the fall in *p*/*s* ratio, and hence increase in pyramidal character, as methyl ligands are replaced by oxygen ligands.

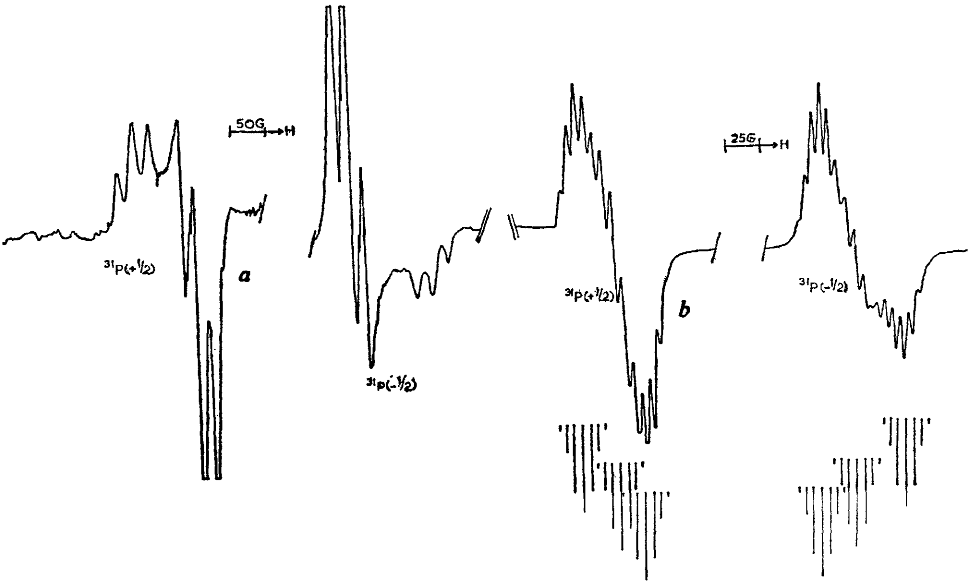


FIG. 2.—First derivative e.s.r. spectrum of trimethylphosphine oxide after exposure to γ-rays at 77 K and annealing to remove features assigned to Me_3PO^- and related species. *a*, At 77 K; *b*, at *ca.* 140 K.

TABLE 2.—DERIVED ORBITAL POPULATIONS

	$a_s^2(\%)$	$a_p(\%)$	$a_s^2+a_p^2(\%)$	p/s
Me_3P^+	10.8	100	110.8	9.3
Me_2PO	10.3	78	88.3	7.6
PO_3^{2-}	16.4	53.8	71.2	3.3
$Me_3PO^-(H^+)$	17	61.5	78.5	3.6

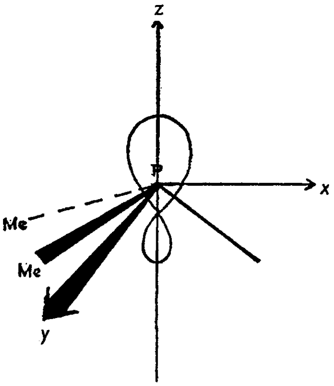
The changes in the proton features on cooling to 77 K almost certainly reflect some form of restricted rotation of the methyl groups. We suggest that this takes the form of slow, coupled rotations such that the sum of the coupling constants for all six protons remains constant.[14] This would leave the $M_I = \pm 3$ lines independent of time, whilst the remainder would change continuously with time, except for one component of the $M_I = 0$ line. If, at 77 K, this motion is at such a frequency as to result in a major broadening of the ±2 and ±1 lines, then only the ±3 and 0 lines would be detected, and the intensity of the $M_I = 0$ line would tend to equal those of the $M_I = \pm 3$ lines.

It is interesting that for the radicals $Me_2\dot{C}OH$ or $Me_2\dot{C}O^-$, the methyl groups are rotating rapidly on an e.s.r. time-scale at 77 K.[15, 16] This suggests that the two methyl groups are forced together by the tendency for Me_2PO radicals to have a locally pyramidal structure at the phosphorus atom.

No proton hyperfine coupling was detected for $Me_3P^{+}\cdot$ and related ions,[3, 17] but the lines were broad, possibly reflecting the absence of free rotation. However, for the isoelectronic $R_3Si\cdot$ radicals, ^1H hyperfine coupling constants of *ca.* 6.3 G were observed,[18] which is very close to the value now assigned to Me_2PO radicals. Since the magnitude of the coupling to β protons clearly falls as the deviation from planarity increases, we would argue that Me_2PO radicals have about the same pyramidal character as $R_3Si\cdot$ radicals. Since we have previously concluded that $R_3P^{+}\cdot$ radicals are more nearly planar than $R_3Si\cdot$ radicals, this means that replacing an alkyl ligand by O^- has slightly increased the degree of bending at the phosphorus atom.

That this is indeed the case can be judged more conclusively from the changes in the ^{31}P tensor components on going from $R_3P^{+}\cdot$ to Me_2PO and then to $\cdot PO_3^{2-}$ radicals (table 1). (There is only slight delocalisation onto oxygen in $Me_2\dot{P}O$ radicals, and the consequent reduction in coupling to the methyl protons is small. When allowance is made for this, the coupling (6.3 G) remains close to that for $Me_3Si\cdot$ radicals (6.3 G).)

The temperature dependence of the ^{31}P hyperfine components is best understood in terms of librations about the x and y axes, as arbitrarily defined in the insert. We suggest that libration about one axis (say x) is greater than that about the other (y). Thus a partial averaging of 80 G by libration about x gives $A'_y = 375$ G and $A'_z = 455$ G which, taken together with a smaller partial averaging of *ca.* 17 G about y, gives $A_x = 312$ G, $A'_y = 375$ G and $A'_z = 438$ G, the new experimental values being 310, 375 and 433 G respectively.



Identification of the species responsible for the outermost features is less compelling, since only the ^{31}P coupling was detected. However, the fact that a very similar species was formed in alcohol glasses containing the phosphine oxide, whilst the concurrent formation of e_t^--centres in the alcohol was suppressed, leads us to suggest the radical anion $Me_3\dot{P}O^-$ or its conjugate acid, $Me_3\dot{P}OH$, as the most probable species. The calculated isotropic coupling to phosphorus of *ca.* 610 G is very close to those observed by others [9, 10] for R_3POR radicals (*ca.* 618 G), thus strongly supporting our identification. (The significance of these results will be discussed more fully in conjunction with our solid-state results for other radicals of this class.) The species formed in the pure material could also be $Me_3\dot{P}OMe$, if reaction (4) given below is correct, since methyl radicals were not detected.

Curiously, sulphuric acid solutions, which probably contain mainly Me_3POH^+ ions, had e.s.r. spectra, after exposure to ^{60}Co γ-rays at 77 K, quite different from those discussed above. The major phosphorus centred radical (fig. 3) had parameters closely similar to those for $R_3P^{+\bullet}$ radicals [3] and we therefore assign these features to $Me_3P^{+\bullet}$ radicals. The central portion of the spectrum was very similar to that in fig. 1 and we therefore identify the species responsible as $H_2\dot{C}P(OH)Me_2^+$. Broad features with a marked g-value variation (confirmed by Q-band studies) may well be due to $Me_3\dot{P}O^+$ radicals, but further studies are needed to check this suggestion.

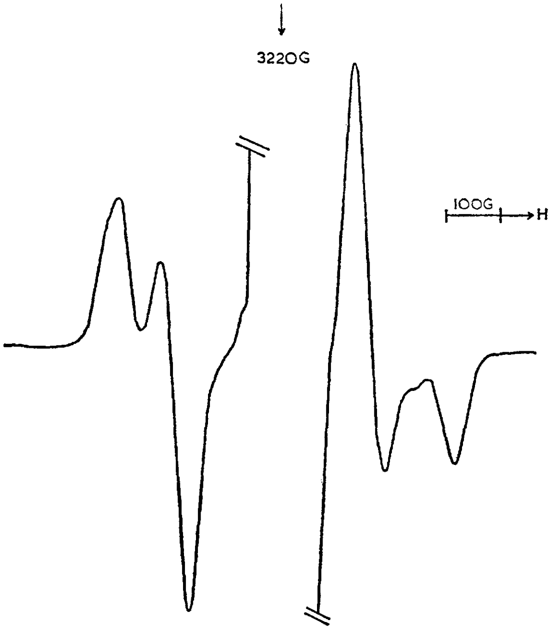


FIG. 3.—First derivative e.s.r. spectrum of trimethylphosphine oxide in sulphuric acid after exposure to γ-rays at 77 K, showing features assigned to Me_3P^+ radicals.

POSSIBLE MECHANISMS

In accord with our previous analyses,[2-7] we suggest an initial ionization and electron trapping for the pure material:

$$2Me_3P\dot{O} \rightarrow Me_3P\dot{O}^+ + Me_3\dot{P}O^- \tag{1}$$

followed by

$$Me_3P\dot{O}^+ \rightarrow H_2\dot{C}P(O)Me_2(+H^+) \tag{2}$$

$$Me_3P\dot{O}^+ + Me_3\dot{P}O^- \rightarrow 2Me_3PO^* \tag{3}$$

$$Me_3PO^* \rightarrow Me + Me_2\dot{P}O \tag{4}$$

$$Me_3PO + Me \rightarrow Me_3POMe. \tag{5}$$

In alcoholic solutions, we may also have

$$Me_3\dot{P}O^- + ROH \rightarrow Me_3\dot{P}OH + RO^- \tag{6}$$

and in sulphuric acid

$$\mathrm{Me_3POH^+ + e \rightarrow Me_3\dot{P}OH} \tag{7}$$

$$\mathrm{Me_3POH + 2H_2SO_4 \rightarrow Me_3P^{+\bullet} + H_3O^+ + 2HSO_4^-}. \tag{8}$$

We do not usually find it necessary to postulate homolytic fission, as in (4), but the formation of $\mathrm{Me_2PO}$ radicals in good yield is difficult to explain in terms of ionic processes.

We thank the S.R.C. for a grant to A. B. and Mr. J. A. Brivati for experimental assistance.

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