The Radical Anion of Trimethyl Phosphite

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Summary Using e.s.r. spectroscopy it is shown that γ-irradiation of polycrystalline trimethyl phosphite generates the novel radical anion $\cdot P(OMe)_3^-$ which undergoes a structural rearrangement on annealing.

Although the tri-co-ordinated sulphuranyl radicals $\cdot S(OR)_3$ are well established,[1,2] the isoelectronic phosphorus radical anions $\cdot P(OR)_3^-$ have not been identified in previous work.[3,4] We present here an e.s.r. study of the first such species, $\cdot P(OMe)_3^-$.

Irradiation of polycrystalline trimethyl phosphite with ^{60}Co γ-rays (dose, 2·5 Mrad) at 77 K yielded spectrum (a) shown in the Figure. Apart from the features previously assigned to carbon-centred radicals and the dimer radical cation $(MeO)_3P\dot{-}P(OMe)_3^+$,[5] the spectrum consists primarily of an anisotropic doublet† ($A_{\parallel}(^{31}P) = 640$ G, $A_{\perp}(^{31}P) =$

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† The fine structure is probably due to site splitting which is also present in the spectrum of the dimer radical cation in this crystalline matrix (see also ref. 5).

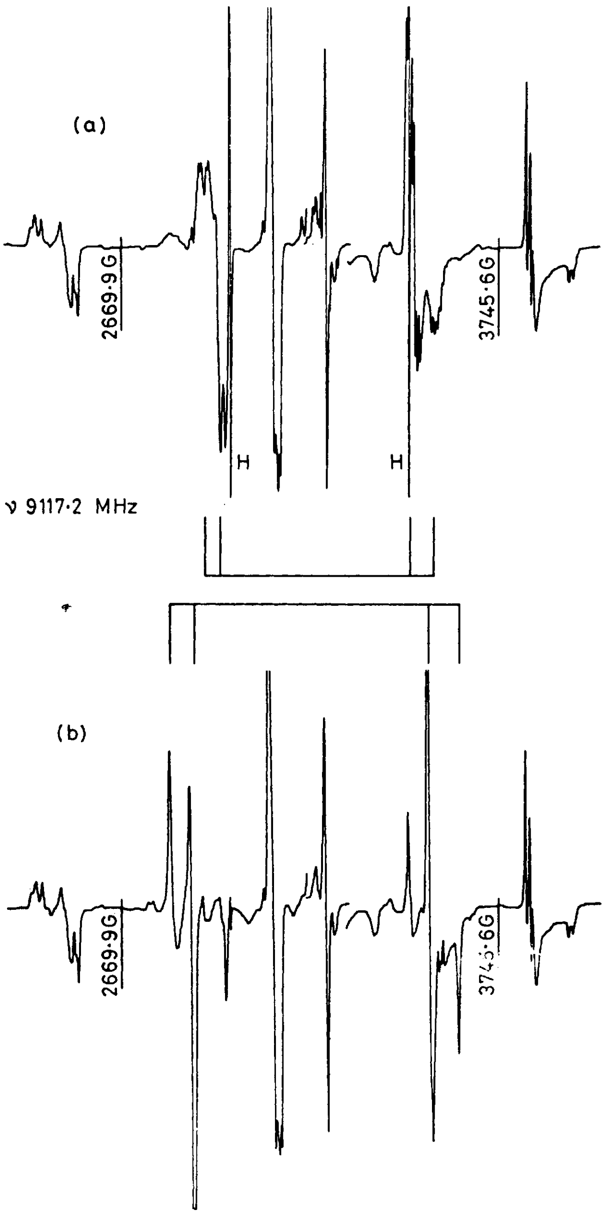
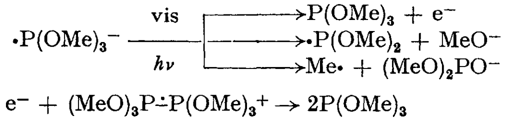


FIGURE. First-derivative e.s.r. spectra of γ-irradiated polycrystalline trimethyl phosphite at 92 K showing features assigned to $\cdot P(OMe)_3^-$. Spectra (a) and (b) were recorded, respectively, before and after annealing for 12 min at 126 K. For each spectrum, the gain was reduced by a factor of ten in recording the centre line.

523 G, $g_{\parallel} = 2{\cdot}002$, $g_{\perp} = 2{\cdot}003$) lying immediately outside the hydrogen-atom lines. Exposure of the sample to visible light removed this doublet and produced line components attributable to the $\cdot Me$ and $\cdot P(OMe)_2$[5] radicals. In addition, this photobleaching brought about a reduction in the intensity of the dimer radical cation spectrum. These changes are readily interpreted by the reactions in the Scheme, and the ^{31}P doublet is assigned to $\cdot P(OMe)_3^-$.



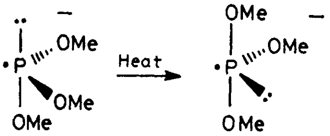
$$\cdot P(OMe)_3^- \xrightarrow[h\nu]{vis} \begin{cases} P(OMe)_3 + e^- \\ \cdot P(OMe)_2 + MeO^- \\ Me\cdot + (MeO)_2PO^- \end{cases}$$

$$e^- + (MeO)_3P\dot{-}P(OMe)_3^+ \rightarrow 2P(OMe)_3$$

SCHEME

When the sample was annealed prior to photobleaching, spectrum (b) in the Figure was obtained. As indicated by the line diagram, a new ^{31}P doublet ($A_{\parallel} = 812$ G, $A_{\perp} = 668$ G, $g_{\parallel} = 2{\cdot}001$, $g_{\perp}$ $2{\cdot}002$) was produced at the expense of the original $\cdot P(OMe)_3^-$ doublet. Since this new spectrum could also be photobleached by visible light with the same spectral changes as those observed for the unannealed sample, it is also assigned to the trimethyl phosphite radical anion.

The spectral change on annealing parallels the effects observed by Symons and his co-workers[6] for tetra-co-ordinated phosphorus radicals and attributed by them to pseudo-rotations within a trigonal-bipyramidal structure. Similarly, we propose that the present tri-co-ordinated radical anion is initially formed with one methoxy ligand and a 'lone pair' of electrons in the axial positions, and then rearranges to give two axial methoxy ligands on annealing, as depicted in reaction (1). Since the methoxy ligand can be considered to be more electronegative than a 'lone pair', the increase in the ^{31}P coupling constant is to be expected.[7,8]



(1)

We have also identified $\cdot P(OMe)_3^-$ in other γ-irradiated systems, including single crystals of $P(OMe)_3$ and in methyltetrahydrofuran glasses containing dissolved $P(OMe)_3$, where similar changes occurred on photobleaching and thermal annealing. However, the radical anion does not appear to be formed with an appreciable yield when pure trimethyl phosphite is γ-irradiated in the glassy state. These results will be reported in a future paper.

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