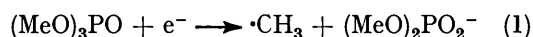


## Unstable Intermediates. Part 169.<sup>1</sup> Electron Capture Processes in Organic Phosphates: an Electron Spin Resonance Study

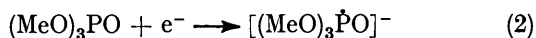
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A range of mono-, di-, and tri-alkyl phosphates have been exposed to <sup>60</sup>Co  $\gamma$ -rays at 77 K and at ambient temperature, together with their solutions in CD<sub>3</sub>OD at 77 K. Monoalkyl phosphates (as the sodium, potassium, magnesium, or calcium salts) gave alkyl radicals on electron capture at 77 K, but a low yield of  $\cdot\text{PO}_3^{2-}$  was detected after irradiation at ambient temperature. The major electron loss centre was formed by loss of  $\alpha$ -hydrogen ( $\text{R}_2\dot{\text{C}}\text{OPO}_3^{2-}$ ). In general, the <sup>31</sup>P hyperfine coupling for these radicals was in the range 0–10 G, but for the radical  $\text{Me}\dot{\text{C}}\text{HOPO}_3^{2-}$  in the calcium salt a coupling of 45 G indicated considerable hyperconjugative interaction. Dialkyl phosphates gave the phosphoryl radicals  $\text{RO}\dot{\text{P}}\text{O}_2^-$  on irradiation at 77 K, together with alkyl radicals. Some sodium and potassium salts also gave relatively low yields of the parent anions,  $(\text{RO})_2\dot{\text{P}}\text{O}_2^{2-}$  (phosphoranyl radicals). These were not obtained from CD<sub>3</sub>OD solutions, but the phosphoryl radicals and alkyl radicals were detected. Only phosphoryl radicals were obtained on irradiation at ambient temperature. The major electron-loss centres were again  $\text{R}_2\dot{\text{C}}\text{OPO}_2(\text{OR})^-$ . Trialkyl phosphates at 77 K gave predominant yields of the parent phosphoranyl anions,  $(\text{RO})_3\dot{\text{P}}\text{O}^-$ , although phosphoryl radicals were also detected. On annealing, there was no evidence for the conversion of phosphoranyl radicals into phosphoryl radicals. Solutions in CD<sub>3</sub>OD gave the same species, but the phosphoryl radicals were obtained in relatively greater yields. Again, the major electron-loss centres seemed to be  $\text{R}_2\dot{\text{C}}\text{OPO}(\text{OR})_2$  radicals. A doublet species having  $A_{\parallel}$  237 and  $A_{\perp}$  179 G was also obtained from  $\text{MeOPO}_3\text{Na}_2$ ,  $\text{MeOPO}_3\text{Mg}$ , and other methyl esters after irradiating at 77 K and slight annealing. In some cases, an extra 8 G splitting was observed on these features. Possible structures for this species are discussed.

THE first e.s.r. study of phosphate esters exposed to high energy radiation was for trimethyl phosphate,<sup>2</sup> and revealed the formation of  $\cdot\text{CH}_3$  and  $\text{H}_2\dot{\text{C}}\text{OPO}(\text{OMe})_2$  radicals. The former, formed by dissociative electron capture (1) was thought to be the sole radical product



from the excess of electrons, whilst the latter, which was characterised by a 4.0 G doublet splitting from <sup>31</sup>P, was identified as the major electron-loss centre.  $\text{R}_2\dot{\text{C}}\text{OPO}(\text{OR})_2$  radicals had previously been studied in the liquid phase.<sup>3,4</sup> Later, we found that direct electron capture at phosphorus to give a phosphoranyl radical competes with process (1) and also that an alternative dissociation can occur, to give a phosphoryl radical.<sup>5</sup>



Ezra and Bernard also detected the phosphoryl radical  $(\text{EtO})\dot{\text{P}}\text{O}_2^-$  in irradiated diethyl magnesium phosphate,<sup>6</sup>

<sup>1</sup> Part 168, S. P. Mishra and M. C. R. Symons, *J.C.S. Dalton*, 1976, 1622.

<sup>2</sup> A. Begum, S. Subramanian, and M. C. R. Symons, *J. Chem. Soc. (A)*, 1970, 1334.

<sup>3</sup> E. A. C. Lucken, *J. Chem. Soc. (A)*, 1966, 1354.

<sup>4</sup> A. R. Metcalfe and W. A. Waters, *J. Chem. Soc. (B)*, 1967, 340.

<sup>5</sup> I. S. Ginns, S. P. Mishra, and M. C. R. Symons, *J.C.S. Dalton*, 1973, 2509.

<sup>6</sup> F. S. Ezra and W. A. Bernard, *J. Phys. Chem.*, 1973, 59, 3543.

together with ethyl radicals,<sup>7</sup> and  $\text{CH}_3\dot{\text{C}}\text{HOPO}_2(\text{OEt})^-$  radicals.<sup>8</sup>

Phosphate esters are, of course, of fundamental importance in biology, and considerable attention has been paid to the effects of high energy radiation on biological phosphates and on model compounds. However, the possible involvement of phosphoranyl or phosphoryl radicals has not generally been considered. Some examples include that of Bernard and Snipes on irradiated 3'-cytidylic acid,<sup>7</sup> and of Hüttermann on adenosine 5'-monophosphate.<sup>8</sup> Several recent studies have been concerned with the mechanism of phosphate ion elimination in irradiated aqueous solutions.<sup>9–12</sup> It seems that splitting of the alkyl-phosphate bond follows attack by hydroxyl radicals,<sup>9,10,12</sup> as was proposed by Wilkinson and Williams.<sup>13</sup> A variety of mechanisms have been proposed, some of which involve abstraction of  $\alpha$ -hydrogen and others of  $\beta$ -hydrogen atoms by hydroxyl radicals.

<sup>7</sup> W. A. Bernard and W. Snipes, *Proc. Nat. Acad. Sci. U.S.A.*, 1968, 59, 1038.

<sup>8</sup> J. Hüttermann, *Z. Naturforsch.*, 1969, 24b, 1618.

<sup>9</sup> S. Steinken, G. Behrens, and D. Schulte-Frohlinde, *Internat. J. Radiation Biol.*, 1974, 25, 205.

<sup>10</sup> L. Stelter, C. von Sonntag, and D. Schulte-Frohlinde, *Internat. J. Radiation Biol.*, 1974, 25, 515.

<sup>11</sup> A. Van de Vorst, *Internat. J. Radiation Phys. Chem.*, 1974, 6, 143.

<sup>12</sup> N. K. Kochietkov, L. I. Kudrjashov, M. A. Chlenov, and L. P. Grineva, *Carbohydrate Res.*, 1974, 35, 235.

<sup>13</sup> R. W. Wilkinson and T. F. Williams, *J. Chem. Phys.*, 1955, 52, 600.

The aim of our study was to attempt to understand the factors that govern the various electron capture processes (1)–(3).

phosphoryl radicals have  $A_{iso}$  ( $^{31}\text{P}$ ) in the region of 700 G,<sup>16–18</sup> so they are usually clearly distinguishable from each other.<sup>5</sup>

E.s.r. parameters for various phosphoranyl and phosphoryl radicals derived from phosphate esters

| Ester   | Radical  | Irradiation temp. (K) | $^{31}\text{P}$ hyperfine coupling (G) <sup>a,b</sup> |                  |           | Other radicals   |
|---|--|-----------------------|---|------------------|-----------|--|
|   |  |                       | $A_{\parallel}$                                       | $A_{\perp}$      | $A_{iso}$ |  |
| Mono  |  |                       |   |                  |           |  |
| MeOPO <sub>3</sub> Na <sub>2</sub>  | ·PO <sub>3</sub> <sup>2-</sup>   | 313                   | 671   | 514              | 566       | $\dot{\text{C}}\text{H}_3 + \text{H}_2\dot{\text{C}}\text{OPO}_2^{2-}$   |
| CD <sub>3</sub> OPO <sub>3</sub> Na <sub>2</sub>                          | ·PO <sub>3</sub> <sup>2-</sup>   | 313                   | 675   | 517              | 570       | $\dot{\text{C}}\text{D}_3 + \text{D}_2\dot{\text{C}}\text{OPO}_2^{2-}$   |
| MeOPO <sub>3</sub> Mg   | ·PO <sub>3</sub> <sup>2-</sup>   | 313                   | 771   | 592              | 652       |  |
| C <sub>2</sub> H <sub>5</sub> OPO <sub>3</sub> Na <sub>2</sub>            | ·PO <sub>3</sub> <sup>2-</sup>   | 313                   | 690   | 520              | 577       | $\cdot\text{C}_2\text{H}_5 + \text{Me}\dot{\text{C}}\text{HOPO}_2^{2-}$  |
| C <sub>2</sub> H <sub>5</sub> OPO <sub>3</sub> Ca                         | ·PO <sub>3</sub> <sup>2-</sup>   | 313                   | 670   | 610 <sup>c</sup> | 630       |  |
| Di  |  |                       |   |                  |           |  |
| (MeO) <sub>2</sub> PO <sub>2</sub> Na                                     | (MeO) <sub>2</sub> ·P̄O <sub>2</sub> <sup>2-</sup> (i)                       | 77                    | 1 031   | 861              | 918       | $\dot{\text{C}}\text{H}_3 + \text{H}_2\dot{\text{C}}\text{OPO}_2(\text{OMe})^- +$<br>unknown species                   |
|   | (MeO) <sub>2</sub> ·P̄O <sub>2</sub> <sup>2-</sup> (ii)                      |                       | 936   | 786              | 836       |  |
|   | (MeO) <sub>2</sub> ·P̄O <sub>2</sub> <sup>-</sup>                            |                       | 709   | 579              | 622       |  |
| (MeO) <sub>2</sub> PO <sub>2</sub> Na in CD <sub>3</sub> OD               | (MeO) <sub>2</sub> ·P̄O <sub>2</sub> <sup>-</sup>                            | 77                    | 700   | 574              | 616       |  |
| (EtO) <sub>2</sub> PO <sub>2</sub> Na                                     | (EtO) <sub>2</sub> ·P̄O <sub>2</sub> <sup>2-</sup> (i)                       | 77                    | 1 043   | 883              | 936       | $\cdot\text{C}_2\text{H}_5 + \text{Me}\dot{\text{C}}\text{HOPO}_2(\text{OEt})$   |
|   | (EtO) <sub>2</sub> ·P̄O <sub>2</sub> <sup>2-</sup> (ii)                      |                       | 921   | 792              | 835       |  |
|   | (EtO) <sub>2</sub> ·P̄O <sub>2</sub> <sup>-</sup>                            | 77                    | 720   | 564              | 616       |  |
| (EtO) <sub>2</sub> PO <sub>2</sub> Na in CD <sub>3</sub> OD               | (EtO) <sub>2</sub> ·P̄O <sub>2</sub> <sup>-</sup>                            | 77                    | 725   | 565              | 618       |  |
| (Pr <sup>i</sup> O) <sub>2</sub> PO <sub>2</sub> Na                       | (Pr <sup>i</sup> ) <sub>2</sub> ·P̄O <sub>2</sub> <sup>2-</sup> <sup>d</sup> | 77                    | ca. 900–1 000   |                  |           | $\text{Me}_2\dot{\text{C}}\text{H} + \text{Me}_2\dot{\text{C}}\text{OPO}_2(\text{OPr}^i)$                              |
|   | (Pr <sup>i</sup> ) <sub>2</sub> ·P̄O <sub>2</sub> <sup>-</sup>               |                       | 705   | 550              | 602       |  |
| (Pr <sup>i</sup> O) <sub>2</sub> PO <sub>2</sub> Na in CD <sub>3</sub> OD | (Pr <sup>i</sup> ) <sub>2</sub> ·P̄O <sub>2</sub> <sup>-</sup>               | 77                    | 740   | 565              | 623       |  |
| (Me <sub>3</sub> CO) <sub>2</sub> PO <sub>2</sub> K                       | (Me <sub>3</sub> CO)·P̄O <sub>2</sub> <sup>-</sup>                           | 77                    | 715   | 550              | 605       | $\text{Me}_3\dot{\text{C}}$  |
| (Me <sub>3</sub> CO) <sub>2</sub> PO <sub>2</sub> K in CD <sub>3</sub> OD | (Me <sub>3</sub> CO)·P̄O <sub>2</sub> <sup>-</sup>                           | 77                    | 749   | 574              | 632       | $\text{H}_2\dot{\text{C}}\text{C}(\text{Me})_2\text{OPO}_2(\text{OBu})^-$  |
| (A)   | -OCH <sub>2</sub> CH <sub>2</sub> ·O·P̄O <sub>2</sub> <sup>-</sup>           | 77                    | 700   | 550              | 600       | $\text{H}_2\dot{\text{C}}\text{CH}_2\text{OPO}_2^-$  |
| (A) + CD <sub>3</sub> OD  | -OCH <sub>2</sub> CH <sub>2</sub> ·O·P̄O <sub>2</sub> <sup>-</sup>           | 77                    | 720   | 552              | 608       | (B)<br>$\text{H}_2\dot{\text{C}}\text{CH}_2\text{OPO}_2^-$   |
| Tri   |  |                       |   |                  |           |  |
| (MeO) <sub>3</sub> PO   | (MeO) <sub>3</sub> ·P̄O <sup>-</sup>   | 77                    | 936   | 791              | 839       | $\text{CH}_3 + \text{H}_2\dot{\text{C}}\text{OPO}(\text{OMe})$   |
|   | + (MeO) <sub>2</sub> ·P̄O  | 77                    | 780   | 613              | 669       |  |
| (MeO) <sub>3</sub> PO + CD <sub>3</sub> OD                                | (MeO) <sub>3</sub> ·P̄O <sup>-</sup>   | 77                    | 960   | 802              | 855       |  |
| (EtO) <sub>3</sub> PO   | (EtO) <sub>3</sub> ·P̄O <sup>-</sup>   | 77                    | 951   | 796              | 848       |  |
|   | + (EtO) <sub>2</sub> ·P̄O  |                       | 784   | 593              | 650       |  |
| (EtO) <sub>3</sub> PO + CD <sub>3</sub> OD                                | (EtO) <sub>3</sub> ·P̄O <sup>-</sup>   |                       | 960   | 800              | 853       |  |
|   | + (EtO) <sub>2</sub> ·P̄O  |                       | 770   | 608              | 662       |  |
| (Pr <sup>i</sup> O) <sub>3</sub> PO                                       | (Pr <sup>i</sup> ) <sub>3</sub> ·P̄O <sup>-</sup>                            | 77                    | 990   | 796              | 861       | $\text{Me}_2\dot{\text{C}}\text{H}$  |
|   | + (Pr <sup>i</sup> ) <sub>2</sub> ·P̄O                                       | 77                    | <sup>d</sup>  | 600              |           |  |
| (Pr <sup>i</sup> O) <sub>3</sub> PO + CD <sub>3</sub> OD                  | (Pr <sup>i</sup> ) <sub>3</sub> ·P̄O <sup>-</sup>                            | 77                    | 990   | <sup>d</sup>     |           | $\text{Me}_2\dot{\text{C}}\text{H}$  |
|   | + (Pr <sup>i</sup> ) <sub>2</sub> ·P̄O                                       | 77                    | 770   | 600              | 657       |  |
| (C)   | (D)  | 77                    | ca. 1 100   | ca. 960          | ca. 1 006 | $\text{R}\dot{\text{C}}\text{H}_2 + \text{R}\dot{\text{C}}\text{HOPR}_3$   |
|   | + (RO) <sub>2</sub> ·P̄O   | 77                    | 802   | 634              | 690       |  |
| (E)   | (F)  | 77                    | 1 007   | 932              | 990       | $\text{R}\dot{\text{C}}\text{H}_2 + \text{R}\dot{\text{C}}\text{HOPR}_3 + \text{H}_2\dot{\text{C}}\text{CH}_2\text{R}$ |
|   | + (RO) <sub>2</sub> ·P̄O   | 77                    | 792   | 637              | 689       |  |

<sup>a</sup>  $G = 10^{-4}$  T. <sup>b</sup> Calculated from the Breit–Rabi equation: the  $g$  values were invariably close to the free-spin value. <sup>c</sup> Small anisotropy suggests some libration at 77 K. <sup>d</sup> Species in low abundance with poorly defined features.

## RESULTS AND DISCUSSION

Our results are summarised in the Table and some typical e.s.r. spectra are given in Figures 1–5. We found that it was essential to use carefully purified materials since, otherwise, low yields of extraneous phosphoranyl or phosphoryl radicals were detected, which were lost on purification. (The purity of all materials was checked by  $^1\text{H}$  and  $^{31}\text{P}$  n.m.r. spectroscopy.)

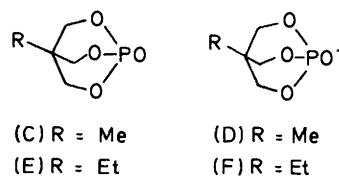
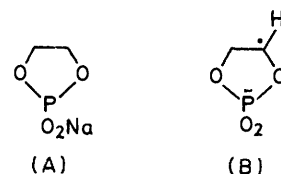
Phosphoranyl and phosphoryl radicals are characterised by large  $^{31}\text{P}$  doublet splittings which make them readily detectable despite the presence of far stronger signals in the central ( $g$  2) region. Phosphoranyl radicals of this type have  $A_{iso}$  ( $^{31}\text{P}$ ) coupling constants in the region of 1 000 G,<sup>14,15</sup> whilst  $\cdot\text{PO}_3^{2-}$  and related

<sup>14</sup> P. J. Krusic, W. Mahler, and J. K. Kochi, *J. Amer. Chem. Soc.*, 1972, **94**, 6033.

<sup>15</sup> A. G. Davies, D. Griller, and B. P. Roberts, *Angew. Chem. Internat. Edn.*, 1971, **10**, 738.

<sup>16</sup> A. Horsfield, J. R. Morton, and D. H. Whiffen, *Mol. Phys.*, 1961, **4**, 475.

*Electron Gain Centres.*—The wide range of results for phosphoranyl and phosphoryl radicals summarised in



<sup>17</sup> A. G. Davies, D. Griller, and B. P. Roberts, *J. Amer. Chem. Soc.*, 1972, **94**, 1782.

<sup>18</sup> C. M. L. Kerr, K. Webster, and F. Williams, *Mol. Phys.*, 1973, 1461.

the Table lead to certain generalisations. Monophosphate esters, irradiated at 77 K either pure or in

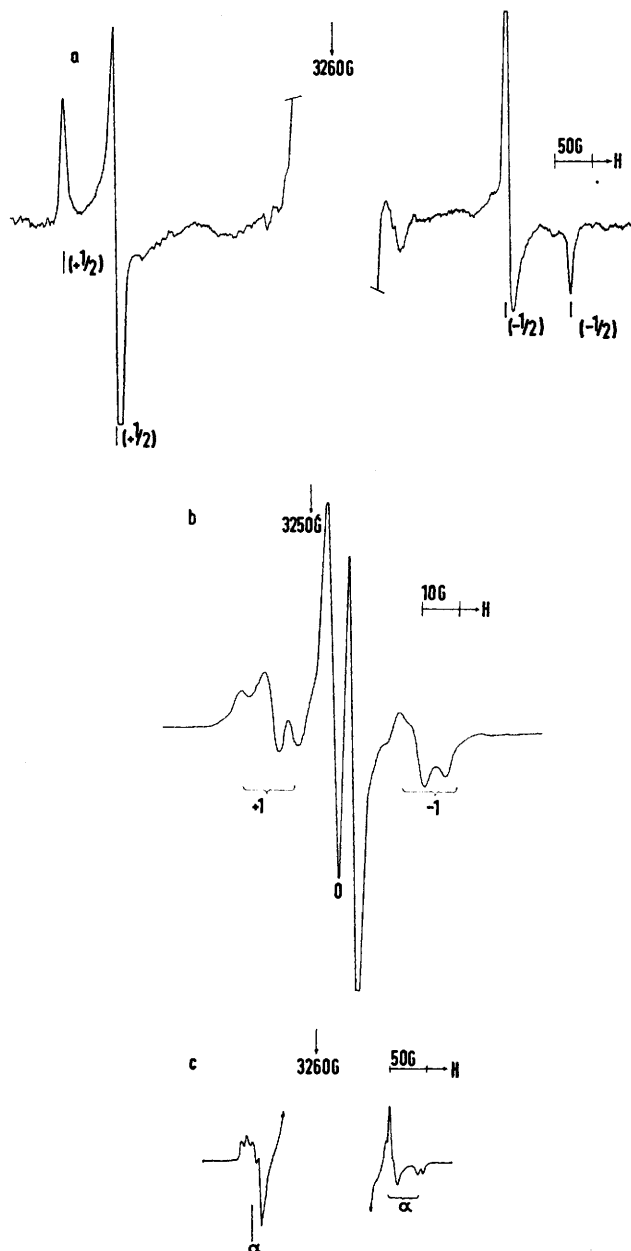


FIGURE 1 First derivative X-band e.s.r. spectra for  $\text{CH}_3\text{OPO}_3^{2-}$  (or  $\text{CD}_3\text{OPO}_3^{2-}$ ) ions after exposure to  $^{60}\text{Co}$   $\gamma$ -rays: a, showing features assigned to  $\text{PO}_3^{2-}$  radicals; b, showing features assigned to  $\text{H}_2\text{C(O)PO}_3^{2-}$  radicals; and c, the features ( $\alpha$ ) separated by *ca.* 200 G, discussed in the text

$\text{CD}_3\text{OD}$  glasses, gave no detectable yield of phosphoranyl or phosphoryl radicals. Nevertheless, solutions of the monophosphates in  $\text{CD}_3\text{OD}$  considerably suppressed the yield of trapped electrons, so that process (1) must be efficient.

However, in certain cases, notably the sodium salts, well defined features for  $\text{PO}_3^{2-}$  were obtained after irradiation at ambient temperatures (*ca.* 40 °C in the Vickrad cell) (Figure 1). We stress that similar features

were not obtained on irradiating at 77 K and then warming to ambient temperature.

All the diesters studied gave phosphoryl radicals,  $\text{RO}\dot{\text{P}}\text{O}_2^-$ , on irradiation at 77 K, together with alkyl radicals,  $\text{R}^\cdot$ . Sodium salts also gave the parent phosphoranyl radicals at 77 K (Figure 2). Solutions in  $\text{CD}_3\text{OD}$ , however, gave only the phosphoryl radicals and alkyl radicals, and only phosphoryl radicals were detected after irradiation at ambient temperature (Figure 2b).

Triesters, however, almost invariably gave both phosphoranyl and phosphoryl radicals at 77 K, with the former in greater abundance (Figure 3). However, alkyl radicals were also formed, so that all three electron capture processes (1)–(3) must occur simultaneously. Solutions in  $\text{CD}_3\text{OD}$  gave phosphoryl radicals in considerable excess of the phosphoranyl radicals and irradiation at room temperature again gave only the phosphoryl radicals,  $(\text{RO})_2\dot{\text{P}}\text{O}$ , as detectable trapped species.

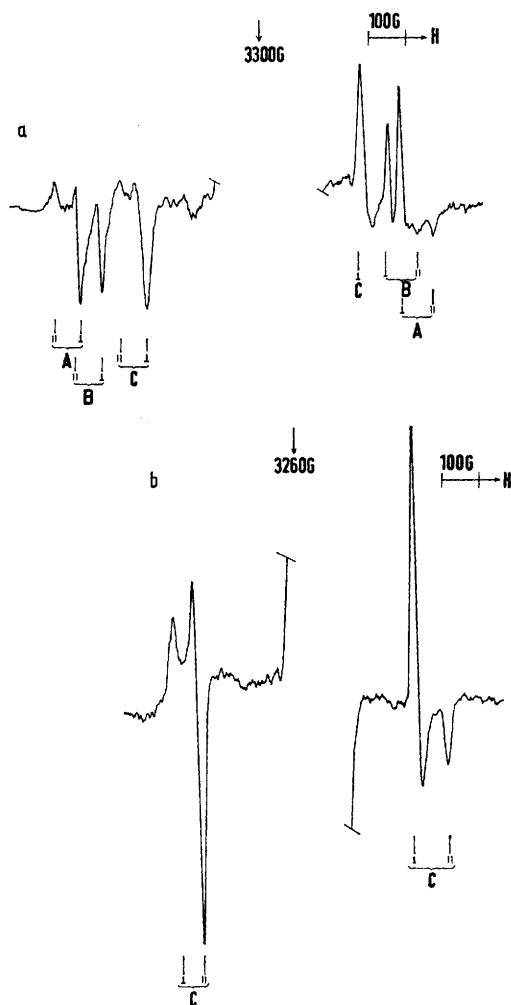


FIGURE 2 First derivative X-band e.s.r. spectra for  $(\text{MeO})_2\text{PO}_2\text{Na}$  after exposure to  $^{60}\text{Co}$   $\gamma$ -rays: a, at 77 K, showing features assigned to two types of  $(\text{MeO})_2\text{PO}_2^{2-}$  radicals (A and B) and  $(\text{MeO})\dot{\text{P}}\text{O}_2^-$  radicals, (C), and b, at room temperature, showing features assigned to  $(\text{MeO})\dot{\text{P}}\text{O}_2^-$  radicals (C)

For the triesters there was a clear trend favouring phosphoryl radicals relative to phosphoranyl radicals on going from Me through Et and Pr<sup>i</sup> to Bu<sup>t</sup> (Figure 3). This same trend, though less clearcut, was also found for the diesters.

These reactions with electrons are summarised in the Scheme. Since, for the pure esters there is no evidence for the formation of trapped electron centres,  $e_{tr}^-$ , we can assume that all these reactions involve mobile or 'dry' electrons. This is the major contrast between our studies and those of fluid aqueous solutions, since in the latter, aquated electrons,  $e_{aq}^-$ , are formed very rapidly and their reactivity is appreciably less than that of 'dry' electrons.

In the Scheme, the trimethyl ester has been arbitrarily selected for illustrative purposes. The central 'anion' is meant to represent a weakly bonding situation between the unrelaxed ester and an electron. Process *a* comprises a bond opening to give the phosphoranyl radical. The thermodynamically favoured structure is shown, having the two electronegative methoxy-groups in the apical sites. However, in several instances, we have either obtained two somewhat different phosphoranyl radicals (Figures 2a and 3d), detected at 77 K, or one has been converted into another with a larger hyperfine coupling on slight annealing (Table). We suggest that in these cases, process *b* has occurred initially, with subsequent inversion (*c*) to give the stable

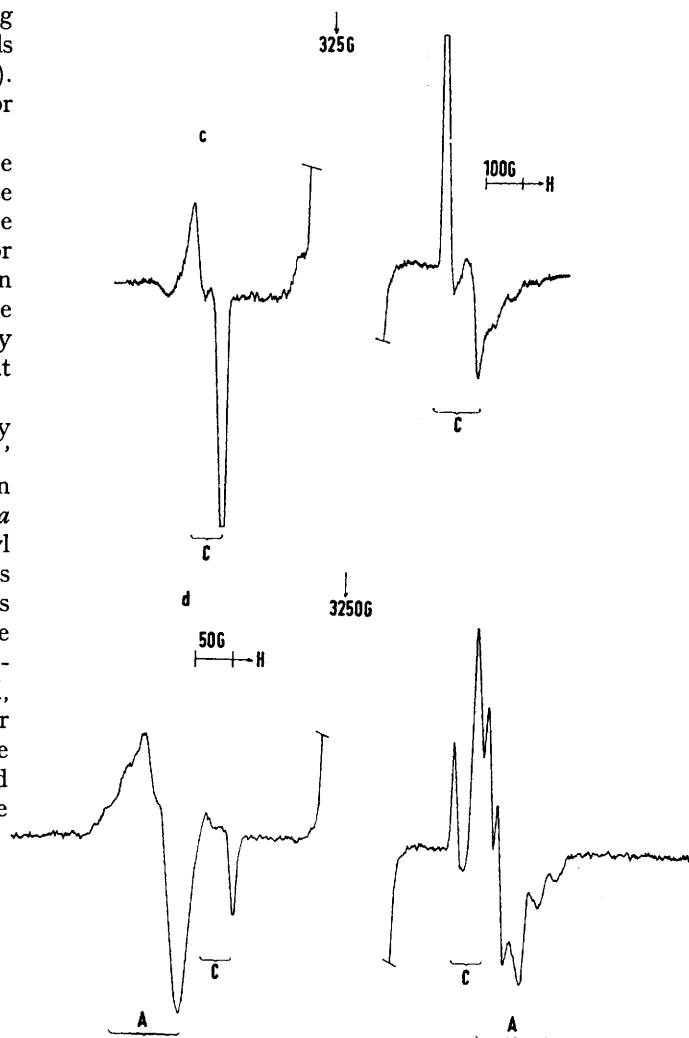
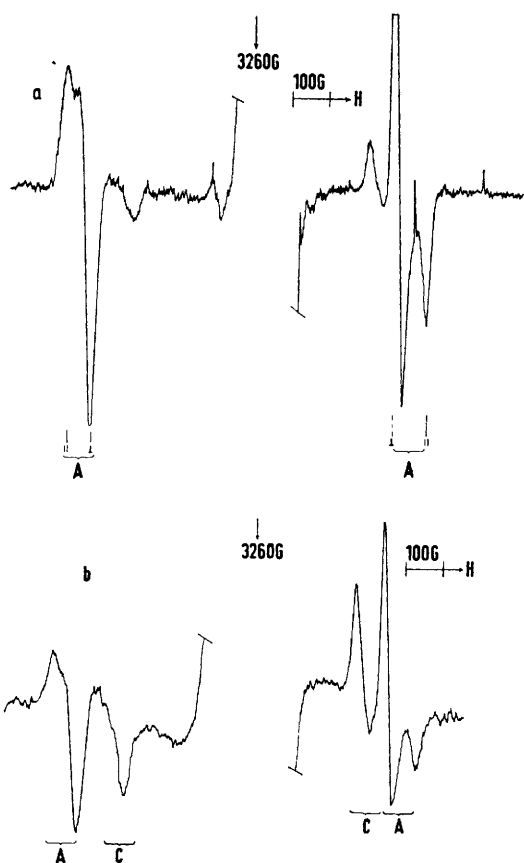
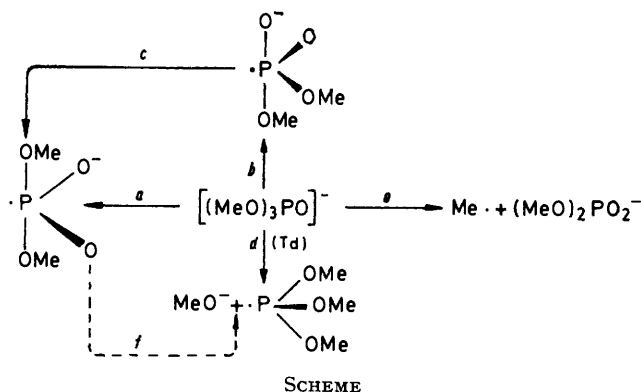


FIGURE 3 First derivative X-band e.s.r. spectra for various  $(RO)_2PO$  esters after exposure to  $^{60}Co$   $\gamma$ -rays at 77 K: a,  $(MeO)_3PO$  in  $CD_3OD$  showing mainly  $(MeO)_3\dot{P}O^-$  features (A); b,  $(EtO)_3PO$  in  $CD_3OD$  showing  $(EtO)_3\dot{P}O^-$  (A), and  $(EtO)_2\dot{P}O$  features (C); c,  $(Pr^iO)_3PO$  in  $CD_3OD$  showing mainly  $(Pr^iO)_2\dot{P}O$  features; and d,  $(Pr^iO)_3PO$  showing three types of phosphoranyl radicals (A)

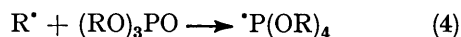
form. We suggest that *b* is sometimes kinetically preferred because of the smaller bulk of the oxide ligand which can move more freely. Just this behaviour has



been observed for hydride ligands, which seem invariably to move initially into an apical site in preference to other ligands.<sup>19,20</sup>

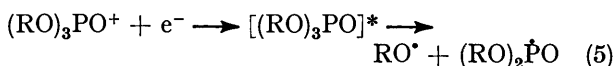
Instead of undergoing a bending distortion, the initially tetrahedral anion can undergo a bond stretching, leading either to the loss of methoxide ions (*d*) or of methyl radicals (*e*). Apparently, both these processes compete with *a* and *b* at 77 K. It seems that phosphoryl radicals are formed by *d* rather than by *f*, since on annealing, there was no evidence for *f*: generally, the signals for both radicals decayed simultaneously, but when the phosphoryl radical signal was lost preferentially there was no growth in the phosphoryl radical signal.

Although the reactions of the Scheme seem to be most probable, there are alternatives which should be considered. Thus, phosphoryl radicals could be formed by alkyl radical attack, for example reaction (4). We



expect that  $A_{iso}$  (<sup>31</sup>P) should increase on going from  $ROPO_3^{3-}$  through  $(RO)_2\dot{P}O_2^{2-}$  and  $(RO)_3\dot{P}O^{-}$  to  $(RO)_4\dot{P}$ , but the crystal field of the cations can play a significant part in governing the magnitude of  $A_{iso}$ <sup>21</sup> and, hence, no clear conclusions can be drawn from comparisons of  $A$  values (see below). However, we can argue that reactions such as (4) are generally less probable for dilute solutions in  $CD_3OD$  and, hence, processes *a* and *b* would seem to be favoured.

Again, phosphoryl radicals could be formed by a direct excitation process, or following electron return [reaction (5)]. We would not expect to be able to



detect  $RO^{\cdot}$  radicals under these conditions,<sup>22</sup> but might have expected to find evidence for pair-wise trapping to give 'triplet-state' species. Careful searches at high gain gave no evidence for this, but we cannot rule out (5) completely.

Accepting the Scheme we can attempt to understand the different behaviour patterns for mono-, di-, and tri-esters. The marked tendency for di- and, especially, tri-esters to form phosphoryl radicals may arise because structures with two apical alkoxy-groups are more stable. There may also be a charge effect. The negative charges for the anionic esters are rather strongly located on the oxide ligands and their interaction with neighbouring cations may tend to inhibit ligand movement. It is significant that metal phosphates show no tendency to add electrons.<sup>5</sup>

Cations with a high charge-density and the hydrogen-bonding solvent,  $CD_3OD$ , favour *d* over *a*, probably because they help to stabilise the ejected alkoxide ions. Process *e* seems to recur in all cases, but is particularly favoured for stabilised alkyl radicals such as  $Me_2\dot{C}H$

and  $Me_3C^{\cdot}$  radicals. The interesting trend in which increasing the bulk of the alkyl groups favours *d* over *a* may again be linked to the difficulty of moving bulky alkoxy-groups through the solid in the direction required to form the stable phosphoryl radical. It may also be linked to the greater stability of the ejected  $RO^{-}$  anions as the bulk of R increases.

The magnitude of the dipolar hyperfine coupling is reasonably constant for the phosphoryl radicals listed in the Table ( $2B$  ca. 100 G). Variations are small and are not thought to have significant structural implications. They probably stem from errors in measurement and from limited librations in the crystalline solids. Similarly, the average  $2B$  value for the phosphoryl

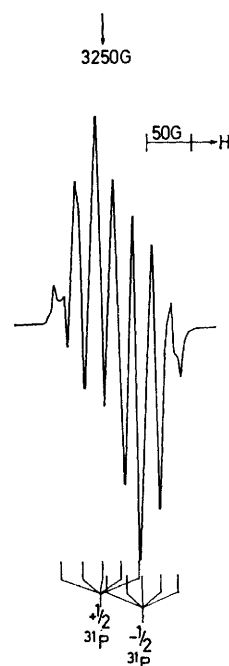


FIGURE 4 First derivative X-band e.s.r. spectrum for  $EtOPO_3Ca$  after exposure to  $^{60}Co$   $\gamma$ -rays at 77 K, showing features assigned to  $CH_3\dot{C}HOPO_2^{2-}$  radicals exhibiting a large coupling to  $^{31}P$

radicals is also ca. 100 G and, again, variations through the series are not large. These values can be roughly converted into  $3p_z$  orbital populations in the usual way,<sup>23</sup> giving  $a_p^2$  ca. 0.49, which is quite normal for such radicals.

There are, however, significant trends in  $A_{iso}$  ( $^{31}P$ ). The average for the triesters is 851 G. This can be compared with the value of ca. 890 G observed for  $(RO)_4\dot{P}$  radicals in solution.<sup>14,15</sup> The drop of ca. 39 G corresponds to the expected decrease on going from an OR ligand to  $O^{-}$ . However, for the diesters there are two sets of results, one giving ca. 927 and the other ca. 835 G. The latter accords with the trend noted above on loss of an alkyl group. However, the former value of 927 G is seen to be abnormally high even for an  $(RO)_4\dot{P}$  radical. We have suggested above that the

<sup>21</sup> M. C. R. Symons, *J. Chem. Soc. (A)*, 1970, 1998.

<sup>22</sup> M. C. R. Symons, *J. Amer. Chem. Soc.*, 1969, **91**, 5924.

<sup>23</sup> P. W. Atkins and M. C. R. Symons, 'The Structure of Inorganic Radicals,' Elsevier, Amsterdam, 1967.

<sup>19</sup> M. C. R. Symons, *Mol. Phys.*, 1972, **14**, 885.

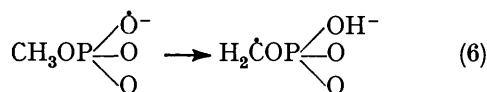
<sup>20</sup> S. P. Mishra and M. C. R. Symons, *Internat. J. Radiation Phys. Chem.*, 1976, **8**, 449.

difference between these species is one of conformation, but these comparisons throw some doubt on this conclusion. We suggest, however, that the downward trend has been fortuitously reversed by the crystal-field effect of neighbouring cations. That this can be large is clearly shown by the results for  $\text{PO}_4^{4-}$  formed in silicate ion sites in phenacite crystals.<sup>24</sup> Here,  $A_{\text{iso}} = 1\,156$  G which is again greater than the value for  $(\text{RO})_4\dot{\text{P}}$  radicals.

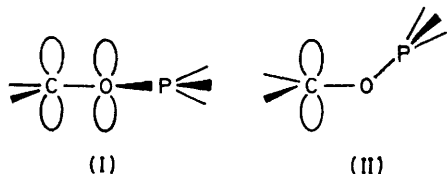
The trends for the phosphoryl radicals are more clear-cut, falling from an average value of 660 for  $(\text{RO})_2\dot{\text{P}}\text{O}$  radicals to 614 G for  $(\text{RO})\dot{\text{P}}\text{O}_2^-$ , and to 599 for  $\text{PO}_3^{2-}$ . However, the results for  $\text{PO}_3^{2-}$  show a clear trend to higher  $A_{\text{iso}}$  values as the charge:radius ratio for the cations increases, reaching 652 G for the magnesium salt. Such trends, which have been previously noted,<sup>21</sup> arise for the same electronegativity reasons as the trends caused by alkylation.

**Electron Loss Centres.**—The other major radical species detected in these experiments seems to be the  $\text{R}_2\dot{\text{C}}\text{OP}\leq$  centre. The primary centre is expected to form by loss of an electron from the oxide ligands to give centres analogous to  $\text{PO}_4^{2-}$ .<sup>25</sup> Here the electron is confined to a non-bonding orbital on oxygen and for the esters this is expected to be primarily on the oxide ligands. The characteristic features are expected to be a doublet in the 20–40 G region from hyperfine coupling to  $^{31}\text{P}$ , together with marked  $g$  anisotropy.<sup>25</sup> Since  $\text{PO}_4^{2-}$  radicals absorb in the 540 nm region, we would expect a similar absorption for the esters of this radical. In most cases, a weak, broad underlying e.s.r. absorption could be due to such radicals, but they were never major products. However, most samples were a pale violet colour after irradiation at 77 K, and we suggest that this is due to these hole centres.

The  $\text{R}_2\dot{\text{C}}\text{OP}\leq$  radicals may be formed, therefore, by proton loss, or by a tautomeric change, for example reaction (6). The most interesting aspect of the e.s.r.



spectra for these radicals was the variable value for the  $^{31}\text{P}$  isotropic hyperfine coupling, which ranged from ca. 0 to ca. 45 G (Figure 4). There are two distinct processes whereby the phosphorus atom can acquire



spin-density. These are illustrated in structures (I) and (II). In (I), the  $\text{PL}_3$  group lies in the radical plane,

$\pi$ -delocalisation onto the bridging oxygen is maximised, and the phosphorus atom acquires negative spin density *via* spin polarisation of the P–O  $\sigma$ -bonding electrons. This will result in a small, fairly isotropic coupling, and ca. 4 G, previously observed for the  $\text{H}_2\dot{\text{C}}\text{OPO}(\text{OMe})_2$  radical<sup>2</sup> is quite reasonable for structure (I). As the  $\text{PL}_3$  group moves out of the radical plane, this mechanism will fall off, reaching zero for (II), in which the  $\text{PL}_3$  group has moved through  $90^\circ$ . However, this is now the optimum structure for hyperconjugative delocalisation and spin polarisation, which confers a relatively large positive spin-density onto the phosphorus atom. The maximum coupling to  $^{31}\text{P}$  for such structures is ca. 100 G for radicals of the type  $\text{R}_2\dot{\text{C}}-\text{C}(\text{PL}_3)\text{R}_2$  or ca. 250 G for  $\text{R}_2\dot{\text{C}}-\text{C}(\text{PL}_2)\text{M}_2$ .<sup>26</sup> (In the latter case, some homoconjugation *via* the phosphorus lone-pair probably occurs,<sup>27</sup> so this is not a good analogy.)

The maximum of ca. 45 G detected for the ester radicals (specifically, for  $\text{C}_2\text{H}_5\text{POP}_3^{2-}$ ; cf. Figure 4) may be low because  $\theta < 90^\circ$ , which is most probable but, also, the anionic oxide ligands may make hyperconjugative delocalisation less effective. We suggest that structure (I) is the thermodynamically most stable species and that structures closer to (II) are formed because these are the original conformations dictated by crystal forces. If this is so, then the energy difference between (I) and (II) cannot be very large. However, we have not been able to observe the expected change from (II)  $\rightarrow$  (I) during annealing studies.

**The 200 G Species.**—In the particular case of methyl esters, an unknown radical was detected, having outer features separated by ca. 200 G (Figure 1d). (If the spectrum is treated as a doublet, then  $A_{\parallel} = 237$ , and  $A_{\perp} = 179$  G.) This was not detected for the corresponding  $\text{CD}_3$  derivatives and, hence, we conclude that there must be a contribution from one or more protons of ca.  $\leq 60$  G. In addition, a small splitting in the 6–10 G region on the outer parallel and perpendicular features was sometimes observed. One possibility would be species (II), with  $A(^{31}\text{P})$  ca. 160 G, with the small proton coupling originating from the OH group [equation (6)]. However, the total proton coupling cannot be  $> \text{ca. } 60$  G, in which case, features for the  $\text{D}_2\dot{\text{C}}$  derivative should have been detected. Also, radical (I) was invariably detected and it seems improbable that both (I) and (II) should be formed in the same samples. Again, the form of the (corrected)  $g$  tensor components, with an unusually low  $g_{\parallel}$  value of ca. 1.996 would not accord with this structure.

We recall that the radical  $\text{H}\dot{\text{C}}\text{O}$  is detected during the radiolysis of methanol at 77 K.<sup>28</sup> We do not wish to discuss the mechanism of this process, but suggest that a similar reaction for the methyl esters might lead to a species  $\text{HC}\dot{\text{O}}-\text{O}^+\text{P}\leq$  which could be the '200 G' species.

<sup>24</sup> M. C. R. Symons, *J. Chem. Phys.*, 1970, **53**, 857; H. Lozykowski, R. G. Wilson, and F. Holuj, *J. Chem. Phys.*, 1969, **51**, 7309.

<sup>25</sup> S. Subramanian, M. C. R. Symons, and H. W. Wardale, *J. Chem. Soc. (A)*, 1970, 1239.

<sup>26</sup> A. R. Lyons and M. C. R. Symons, *J.C.S. Faraday II*, 1972, **68**, 622.

<sup>27</sup> M. C. R. Symons, *Chem. Phys. Letters*, 1973, **19**, 61.

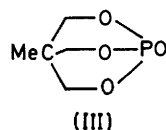
<sup>28</sup> J. A. Brivati, N. Keen, and M. C. R. Symons, *J. Chem. Soc.*, 1962, 237.

HCO has  $A(^1\text{H})$  ca. 125 G,<sup>28</sup> and apparent  $g$  tensor components equal to those for the '200 G' radical ( $g_{\parallel}$  1.996,  $g_{\perp}$  2.0031). If, by analogy, we assign the proton coupling for HCO to the present radical, then the derived coupling to  $^{31}\text{P}$  of  $A_{\parallel}$  ca. 92 G and  $A_{\perp}$  46 G is obtained, leading to  $A_{\text{iso}}(^{31}\text{P})$  63 and  $2B(^{31}\text{P})$  30.7 G. These values can be converted into approximate orbital populations by dividing by the calculated atomic values for unit occupancy,<sup>23</sup> giving  $a_{3s}^2$  ca. 0.017 and  $a_{3p}^2$  ca. 0.148. The half occupied orbital for HCO lies in the radical plane: if the  $\text{PL}_3$  group is also in this plane, then a form of  $\pi$ - $\sigma$  (hyperconjugative) overlap could give rise to the deduced coupling.

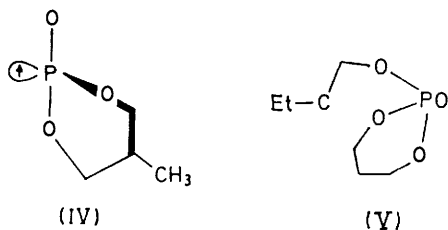
This suggestion is not proven, but we have been unable to devise other reasonable structures that accommodate the results.

**Cyclic Esters.**—The formation of phosphoranyl radicals from  $(\text{CH}_2\text{O})_2\text{POEt}$  by addition of  $\text{RO}^{\cdot}$  radicals has been studied by Davies *et al.*,<sup>29</sup> and from a range of spiro-phosphites by Griller and Roberts.<sup>30</sup> No unusual properties were observed. Our results for  $(\text{CH}_2\text{O})_2\text{PO}_2^-$  indicate that electron addition is unfavourable compared with dissociative electron capture  $d$  to give the phosphoryl radical  $-\text{OCH}_2\text{CH}_2\text{O}\dot{\text{P}}\text{O}_2^-$ , which has normal e.s.r. parameters (Table). Process  $e$  also occurred, giving the radical  $\text{H}_2\dot{\text{C}}\text{CH}_2\text{OPO}_2^-$ . This had an e.s.r. spectrum similar to that for  $\text{H}_2\dot{\text{C}}\text{CH}_2\text{OPO}(\text{OEt})$  radicals which has been discussed in depth by Ezra and Bernard.<sup>31</sup>

Our results for (III) and the ethyl derivative are curious. Rather surprisingly, these compounds formed



phosphoranyl radicals at 77 K, although in relatively low yield (Figure 5a). These must surely have structure (IV), in which case, according to our arguments above, a



reduced isotropic  $^{31}\text{P}$  coupling is expected. In fact, however,  $A_{\text{iso}}$  is considerably greater than that for  $(\text{MeO})_3\text{PO}^{\cdot-}$ , for example (Table). This result suggests that the formalised trigonal-bipyramidal structure implied in (IV) is incorrect and that the real structure in this case favours a higher spin density on phosphorus.

The central features were dominated by a radical having two equivalent  $\alpha$ -protons,  $\text{R}\dot{\text{C}}\text{H}_2$ . This is presumably  $\text{H}_2\dot{\text{C}}-\text{C}(\text{Me})\text{CH}_2\text{O}_2\text{PO}_2^-$  formed by process  $e$

<sup>29</sup> A. G. Davies, D. Griller, and B. P. Roberts, *J.C.S. Perkin II*, 1972, 2224.

in the Scheme. Features for  $\text{R}\dot{\text{C}}\text{HOPR}_3$  type radicals, formed by loss of  $\alpha$ -hydrogen, were also observed. One unusual result was that, for the ethyl derivative, the

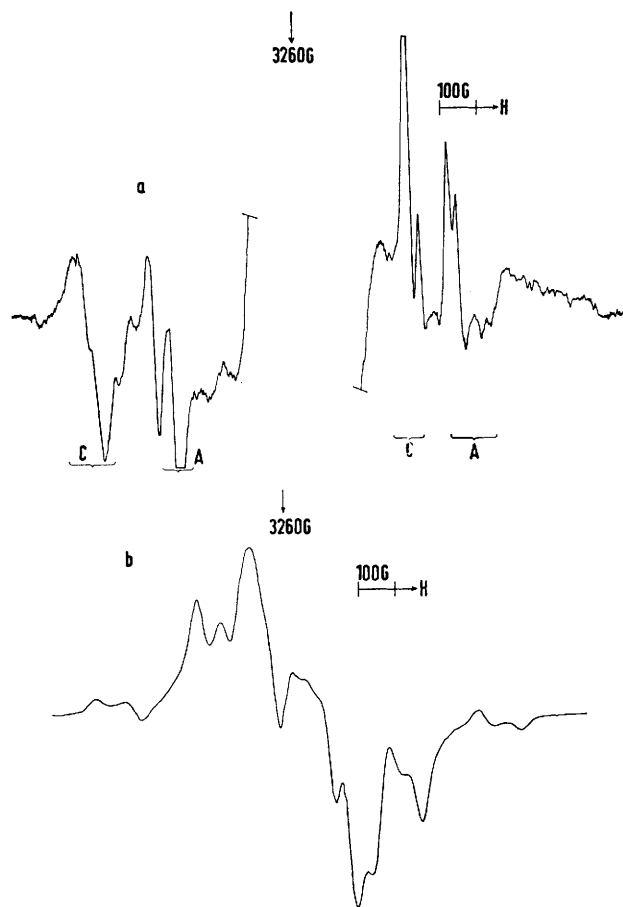
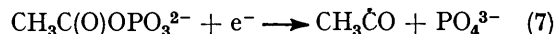


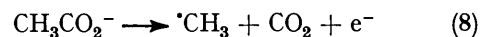
FIGURE 5 First derivative X-band spectra for (V) after exposure to  $^{60}\text{Co}$   $\gamma$ -rays at 77 K: a, showing features assigned to phosphoranyl (A) and phosphoryl (C) radicals and b, showing features assigned to  $\text{H}_2\dot{\text{C}}\text{CH}_2\text{R}$  radicals

radical  $\text{H}_2\dot{\text{C}}\text{CH}_2\text{R}$  was also detected (Figure 5b). We are not clear why the terminal methyl group should have lost a hydrogen atom specifically in this case.

**Irradiated Acetyl Phosphate.**—This compound [as the lithium salt  $\text{CH}_3\text{C}(\text{O})\text{OPO}_3\text{Li}_2$ ] was studied because of its key role in biochemistry. No species with large  $^{31}\text{P}$  coupling constants were detected, the dominant identifiable species being  $\text{CH}_3\dot{\text{C}}\text{O}$ ,<sup>32</sup>  $^{\cdot}\text{CH}_3$ , and  $\text{H}_2\dot{\text{C}}\text{C}(\text{O})\text{POP}_3^{2-}$ . The radical  $\text{CH}_3\dot{\text{C}}\text{O}$  is probably the major electron-gain centre [reaction (7)] and  $\text{H}_2\dot{\text{C}}\text{C}(\text{O})\text{OPO}_3^{2-}$  may be an



electron-loss centre, or formed by a secondary hydrogen atom abstraction. Although alkyl radicals are the normal electron loss centres for carboxylic acids and carboxylate ions [reaction (8)] it is not clear why they

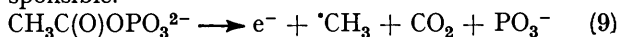


<sup>30</sup> D. Griller and B. P. Roberts, *J.C.S. Perkin II*, 1973, 1416.

<sup>31</sup> W. A. Bernard and F. S. Ezra, *J. Phys. Chem.*, 1974, **78**, 958.

<sup>32</sup> J. E. Bennett, B. Mile, and B. Ward, *Chem. Comm.*, 1969, 13.

are formed in this case. Possibly reaction (9) is responsible.



#### EXPERIMENTAL

Trimethyl and triethyl phosphate were obtained commercially (B.D.H.) and purified by distillation. Tri-isopropyl phosphate was prepared using established procedures and showed physical properties identical with those reported in the literature. Modification of the preparative method of Neunhoeffer and Maiwald<sup>33</sup> resulted in improved yield of 4-methyl- and 4-ethyl-1-oxo-2,4,7-trioxa-1-phosphabicyclo[2.2.2]octane.

Dialkyl metal phosphates were obtained by hydrolysis of the corresponding dialkyl phosphorochloridates with silver oxide followed by neutralization.<sup>34</sup> Metal monoalkyl

<sup>33</sup> O. Neunhoeffer and W. Maiwald, *Chem. Ber.*, 1962, **95**, 108.

<sup>34</sup> A. Zwierzak and M. Kluba, *Tetrahedron*, 1971, **27**, 3163.

phosphates resulted from hydrolysis of alkyl phosphorodichloridates with silver oxide followed by neutralization.<sup>35</sup> The physical properties were in agreement with those described in the literature.

Glassy beads, prepared by pipetting freshly distilled material, neat or in solution, directly into liquid nitrogen, were irradiated in the dark at 77 K in a <sup>60</sup>Co Vickrad source for up to 1 h at a dose rate of 4 Mrad h<sup>-1</sup>. Solid samples were finely pulverized before irradiation. X-Band e.s.r. spectra were recorded at 77 K and higher temperatures on a Varian E3 spectrometer.

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<sup>35</sup> 'Methoden der Organischen Chemie,' ed. K. Sasse, Georg Thieme Verlag, Stuttgart, 1964, vol. 12(2).