

## Electron addition to triethylphosphite induced by ionising radiation : An ESR study

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With a view to obtain  $[\text{P}(\text{OEt})_3]^-$  radical anions and to establish their preferred structure, solutions of triethylphosphite in different solvents have been exposed to  $^{60}\text{Co}$   $\gamma$ -rays at 77K and studied by ESR spectroscopy. Two phosphorus centred radicals suggested are parent radical anion and  $\cdot\text{P}(\text{OEt})_2$  formed by dissociative electron capture. In methyltetrahydrofuran an electron adduct with  $A = 264\text{G}$  and small value of  $A$  is assigned to the primary radical anion having a planar T structure with SOMO on  $3p$  of phosphorus, normal to the radical plane. In a methanolic solution, the same radical anion with extensive protonation having a phosphoranyl type radical with large  $^1\text{H}$  and  $^{31}\text{P}$  hyperfine splitting is formed. The well defined triplets due to  $^2\text{H}$  adduct, obtained in  $\text{CD}_3\text{OD}$  glasses, confirm this assignment. Other phosphorus centred radicals detected are  $\text{MeO-P}(\text{OEt})_3$  and the cation dimer  $(\text{EtO})_3\text{P-P}(\text{OEt})_3^+$ .

ESR spectroscopy has been extensively used to study electron addition to  $\text{PL}_4$  units<sup>1-3</sup>. In general, phosphoryl radicals are formed by dissociative electron capture according to the equation,



The configuration of  $\text{PL}_4$  and  $\cdot\text{PL}_3$  are given in inserts I and II, respectively. Structure III is an intermediate step for Eq. (1). It is indeed a subject of immense interest that the electron addition to tervalent phosphorus derivatives to give  $\cdot\text{PL}_3^-$  radical anions having an extra loan-pair of electron has not been extensively studied. An attempt was made by Symons<sup>4</sup> to add electron to trimethylphosphite,  $\text{P}(\text{OMe})_3$ , using solutions in methanol. He reported the presence of three types of radicals. The first one was the dimer radical cation IV,  $[(\text{MeO})_3\text{P-P}(\text{OMe})_3]^+$ , formed only in concentrated solutions. The phosphoranyl type radical I,  $\cdot\text{P}(\text{OMe})_2$  formed by addition of methoxy radicals to  $\text{P}(\text{OMe})_3$  or by methanol to  $\cdot\text{P}(\text{OMe})_3^+$  cations was the other species observed by him. The third radical was phosphinyl radical (V) giving two intense parallel features separated by *ca.* 284G. This was very well studied by Kerr *et al.*<sup>5</sup>. At that time it was assumed by Symons that all the parent radical anions were either protonated, or had undergone dissociative electron capture. Due to this, no parent radical anions could be detected. Later, Hudson and Williams<sup>6</sup> postulated two alternative structures for this radical anion. One is given as structure VI in which the loan pair of electrons has occupied axial position. On warming above 77K, this structure is changed to VII in which the loan pair of electrons is present in equatorial position.

In the light of close similarity between  $\text{P}(\text{OMe})_3$  and  $\text{P}(\text{OEt})_3$ —it was considered desirable to give an unambiguous evidence to show the formation of triethyl phosphite radical anion and to establish its structure by studying solutions of triethylphosphite in methanol, deuterated methanol and methyltetrahydrofuran using electron spin resonance technique at low temperature.

### Materials and Methods

Triethylphosphite, *E.*, 2-methyltetrahydrofuran, methyl- $d_3$  alcohol- $d$  ( $\text{CD}_3\text{OD}$ ) and methylalcohol of AR grade were obtained from Aldrich Chemical Company and used as such. Dilute solutions

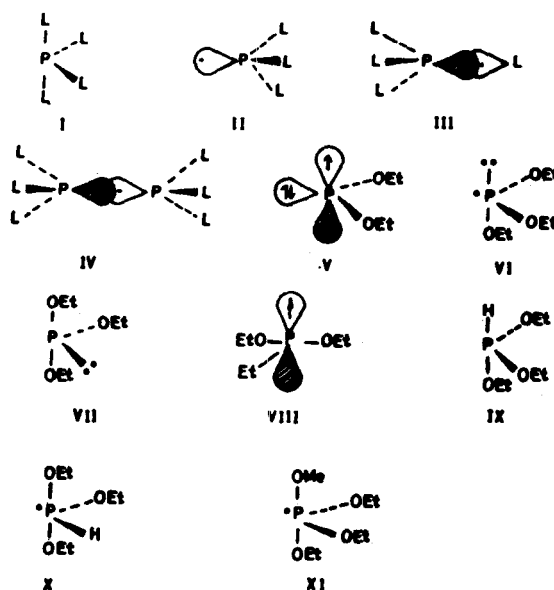
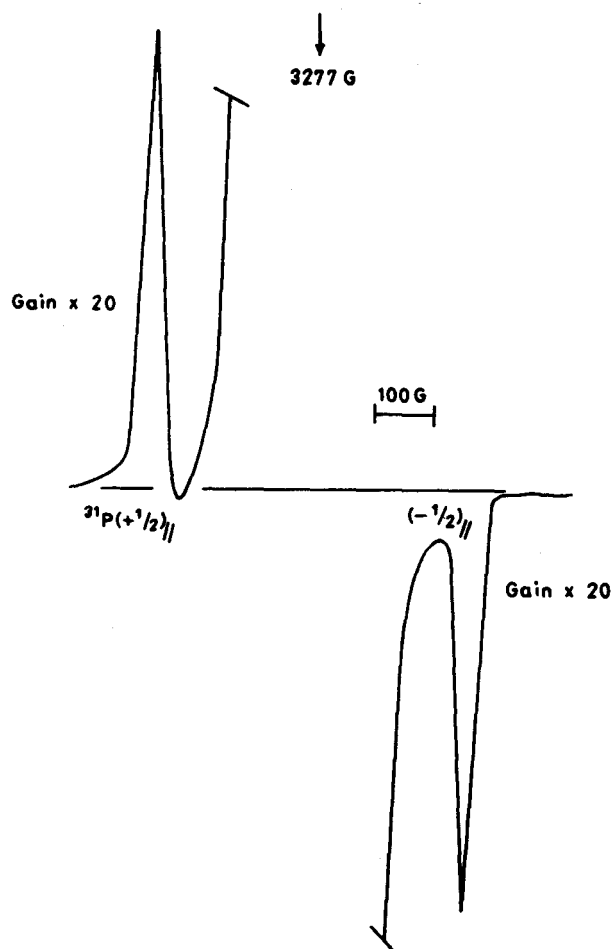
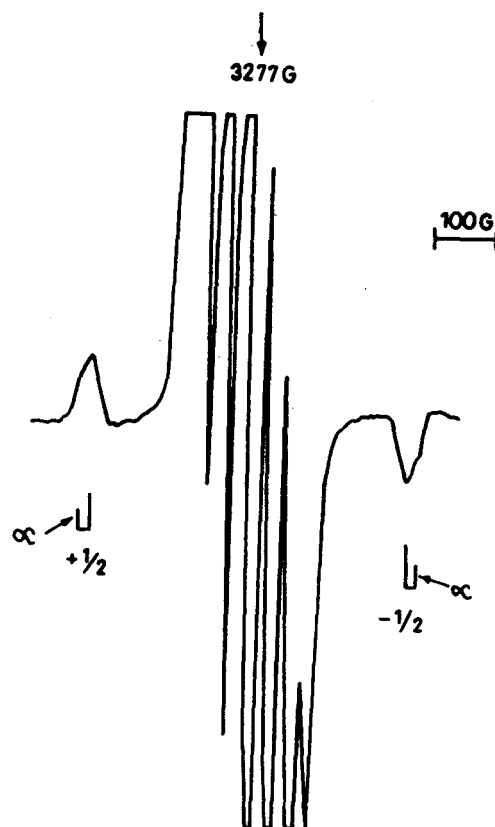


Table 1—ESR parameters for phosphorus centred radicals

| Radical                                                        | Structure | $^{31}\text{P } A$<br>(G) | $^{31}\text{P } A$<br>(G) | $^{31}\text{P } A_{iso}$<br>(G) |
|----------------------------------------------------------------|-----------|---------------------------|---------------------------|---------------------------------|
| $\cdot\text{P}(\text{OEt})_2$                                  | V         | 284                       | small                     | 95                              |
| $\cdot\text{P}(\text{OEt})_3$                                  | VIII      | 264                       | small                     | 88                              |
| $\text{H } \dot{\text{P}}(\text{OEt})_3$                       | IX        | 690                       | 550                       | 596                             |
| $\text{MeO } \dot{\text{P}}(\text{OEt})_3$                     | 1H        | 150                       | 150                       |                                 |
| $(\text{EtO})_3\text{P}^{\cdot-}$                              | XI        | 980                       | 840                       | 886                             |
| $(\text{EtO})_3\text{P}^{\cdot-} \cdot \text{P}(\text{OEt})_3$ | IV        | 725                       | 620                       | 655                             |

Fig. 1a— $\text{P}(\text{OEt})_3$  in methyltetrahydrofuran showing  $^{31}\text{P} \pm \frac{1}{2}$  parallel features assigned to radical anion.

( $\sim 0.1 M$ ) of triethylphosphite in each of the solvents were frozen in liquid nitrogen as small beads. These beads were  $\gamma$ -irradiated at 77K in liquid nitrogen in a Vickrad  $^{60}\text{Co}$  source up to 2.5 h at a dose rate of  $\sim 0.2 M \text{ rad h}^{-1}$ . ESR spectra of these samples were recorded at 77K using a Varian E 109 X-band spectrometer. The samples were annealed above 77K by decanting the liquid nitrogen from the quartz insert dewar and allowing the sample to warm with continuous monitoring of the ESR spectrum. When

Fig. 1b— $\text{P}(\text{OEt})_3$  in methyltetrahydrofuran showing the loss of  $^{31}\text{P} \pm \frac{1}{2}$  parallel features on annealing to *ca.* 125K, together with outer features ( $\alpha$ )

significant changes in the ESR features were detected, the sample was recooled and the spectrum was recorded again. This procedure was repeated with samples prepared in 2-methyltetrahydrofuran,  $\text{CD}_3\text{OD}$  and methyl alcohol.

### Results and Discussion

The ESR parameters are reported in Table 1. When ESR spectrum of triethyl phosphite in methyltetrahydrofuran was recorded, it gave the usual septet due to the solvent radicals and intense parallel-type outer features separated by 264G (Fig. 1a). On annealing above 77K, a set of new features separated by 284G appeared (Fig. 1b). These inner features can be assigned to the parent radical anion,  $\cdot\text{P}(\text{OEt})_3^-$ , having a planar T-structure as shown in VIII and that of the outer features may be due to  $\cdot\text{P}(\text{OEt})_2$  with structure V. When  $\text{Et}_2\text{PCl}$  in  $\text{CD}_3\text{OD}$  is irradiated by  $\gamma$ -radiation at 77K, the chloride ion is lost due to dissociative electron capture and  $\text{Et}_2\text{P}\cdot$  radicals are produced. The similarity of its features with those obtained in outer parallel features in Fig. 1b gives a conclusive evidence for the formation of  $\cdot\text{P}(\text{OEt})_2$  radical<sup>7</sup> in the present

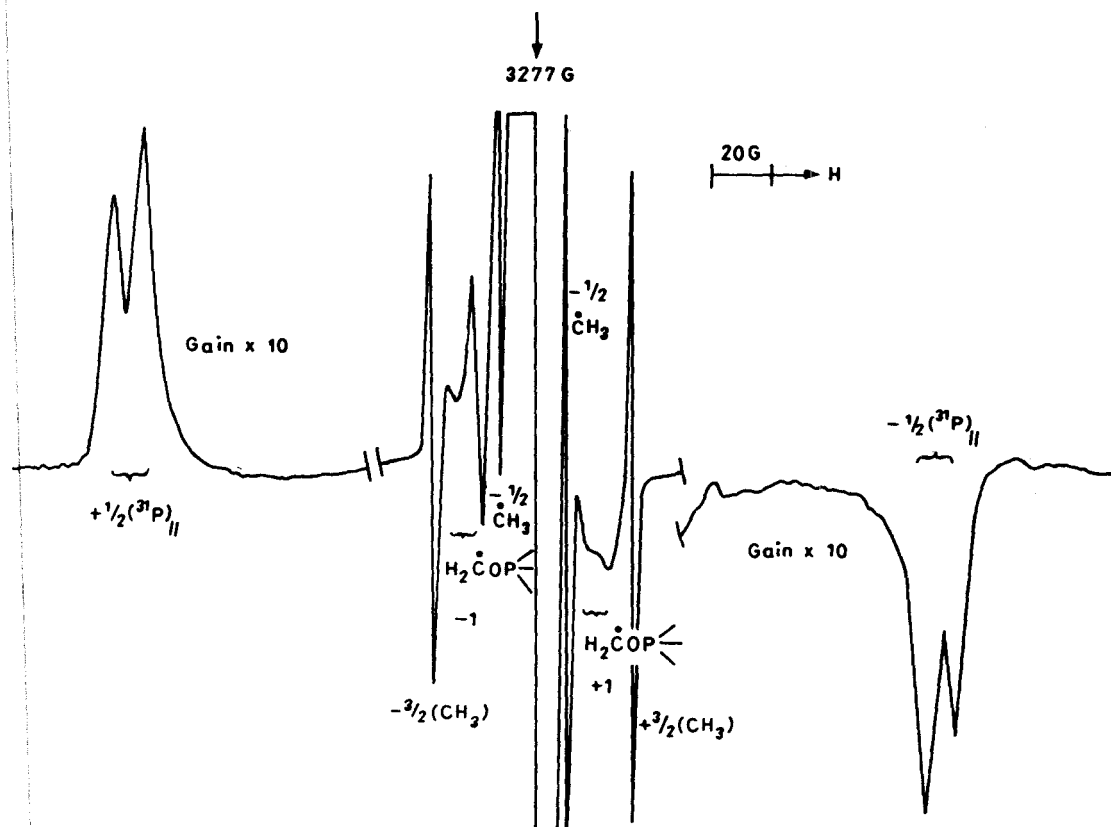


Fig. 2a— $\text{P}(\text{OEt})_3$  in methanol showing parallel feature for  $\text{P}(\text{OEt})_3$  (inner pair) and  $\text{P}(\text{OEt})_2$  (outer pair)

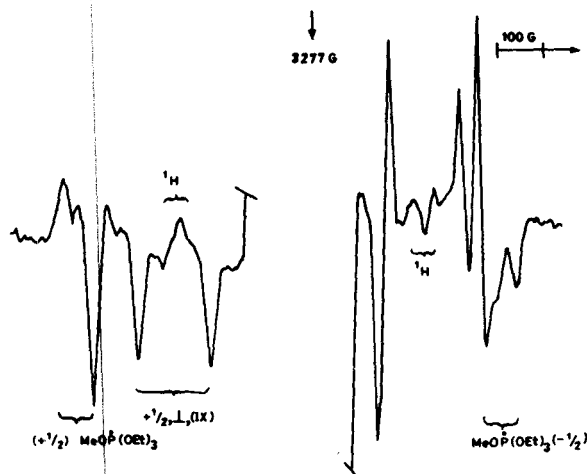


Fig. 2b— $\text{P}(\text{OEt})_3$  in methanol showing structure IX and  $\text{MeO-P}(\text{OEt})_3$

detailed below, two  $\pi$ -type species were detected and since loss of  $\text{EtO}^-$  ions is now expected, the intense feature can be assigned to the parent radical anion with planar T-structure. Since the original pyramidal species  $\text{P}(\text{OEt})_3$  has the freedom to relax in the matrix used, a planar structure is expected for the parent radical anion.

The spectra of  $\text{P}(\text{OEt})_3$  in solvents  $\text{CH}_3\text{OH}$  and  $\text{CD}_3\text{OD}$  at 77K are given in Figs. 2(a-c). These figures show the presence of two  $\pi$ -type radicals along with three other radicals. Figure 2a gives two parallel features for  $\text{P}(\text{OEt})_3^-$  (inner pair) and  $\text{P}(\text{OEt})_2$  (outer pair). The spectrum of  $\text{P}(\text{OEt})_3$  in  $\text{CH}_3\text{OH}$  (Fig. 2b) shows doublets of phosphorus doublets due to the formation of proton adduct of parent radical anions. The presence of triplets of phosphorus doublets in the case of  $\text{P}(\text{OEt})_3$  in  $\text{CD}_3\text{OD}$  (Fig. 2c) supports this argument. There are two possible structures for this species. In one structure, the SOMO is the  $\sigma^*$  orbital localized between H and P (III) having considerable anisotropy. The other structure is phosphoranyl type as in IX but with axial H having almost no anisotropy in the  $^1\text{H}$  hyperfine coupling. On careful annealing, these features were lost and a new set with larger  $^{31}\text{P}$  splitting appeared.

investigation. For the formation of the parent radical anion, the following arguments are advanced: (i) the formation of electron capture centre is evidenced by the large reduction in the blue colour which is characteristic of trapped electron, (ii) loss of  $\text{EtO}^-$  ions is unlikely at 77K in aprotic medium because these ions are so strongly basic in such media that the reverse would be expected, (iii) in methanol solvent

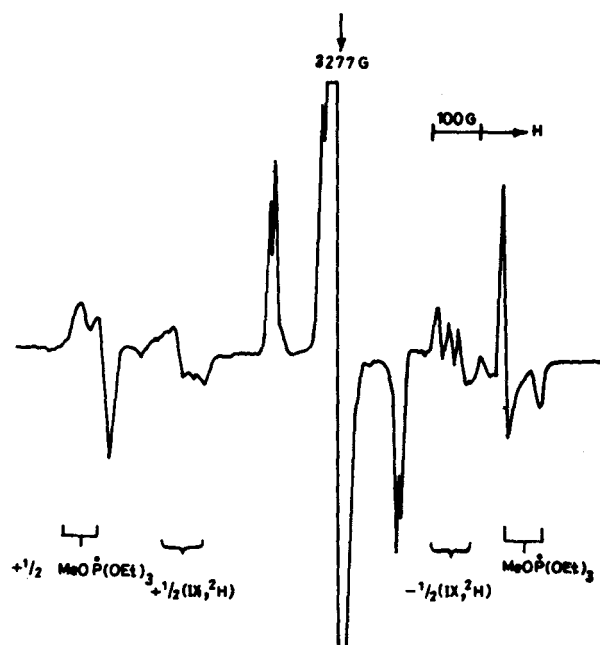


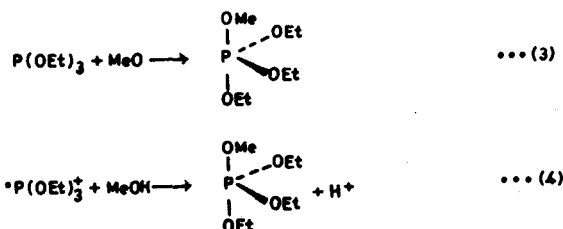
Fig. 2c— $P(OEt)_3$  in  $CD_3OD$  at 77K, showing  $DP(OEt)_3$  (IX) and  $MeO-P(OEt)_3$

This change can be assigned to a pseudo-rotation in which  $-H$  and  $-OEt$  ligands interchange their position giving structure X according to the reaction,



According to Symons and Mishra<sup>8</sup>, the structure IX should exhibit a large proton hyperfine coupling and the latter a very small coupling about 10G. About 152G hyperfine coupling constant obtained in IX and its very small value in X suggest that the protonation occurs prior to relaxation of the parent radical anion from its initially pyramidal structure to the planar structure detected in the present investigation. Thus, for the pyramidal structure VI, the basic lone-pair of electron being in the axial site, the proton will be attached on this site.

The outermost lines in Fig. 2c can be due to  $MeO-P(OEt)_3$  species as their splitting values 886G are quite close to that given by Kerr *et al.*<sup>9</sup>. Alternatively,  $MeO-P(OEt)_3$  may be with  $MeO$ -ligand in the equatorial site. However, this alternative structure is discarded on the ground that the values of methyl and ethyl derivatives reported earlier<sup>9</sup> are appreciably smaller than those observed in the present study. The formation of  $MeO-P(OEt)_3$  in  $MeOH$  is substantiated according to the equations,



When  $P(OEt)_3$  was studied in the form of pure solid material, as expected, the radical cation and radical anion centres were not observed. This is due to combination of radical cation with neighbouring radical anion giving  $\sigma^*$  dimer with structure  $(EtO)_3P \cdot P(OEt)_3^+$ . In the concentrated methanol solutions, the cation dimer,  $(EtO)_3P^+ \cdot P(OEt)_3$  was clearly observed by ESR spectroscopy.

It can be concluded from the present investigation that radical anion of  $P(OEt)_3$  has a planar  $T-\pi$  structure (VII), with the unpaired electron in a  $3p(\pi)$  orbital on phosphorus. When spin-densities are calculated in usual way<sup>10</sup>, it is found that there is very little delocalization of the electron with  $>80\%$  on phosphorus. This explains why the ESR spectra of parent radical anions are so similar to that for the phosphinyl radical,  $P(OEt)_2$  where again the SOMO is largely  $3p$  on phosphorus with very little delocalization.

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