Free radicals produced by γ-irradiation in single crystals of dimethyl methylphosphonate (1), dimethyl ethylphosphonate (2) and dimethyl phosphonate (3) have been investigated between 70 and 350 K with EPR. The single crystal spectra have been taken at 5-degree intervals with the magnetic field B lying in each of the three crystallographic planes ab, bc, and ca.

Figures 1 and 2 show the spectrum of 1 and 2 with its hyperfine splittings. In these spectra, 14 lines are observed due to \((\text{OCH}_3)_2\,\cdot\,\text{PO}\) radicals. Owing to these radicals, the spectra exhibit a doublet (1:1) because of the \(^{31}\text{P}\) nucleus. Each of the lines splits into 7 lines (1: 6: 15: 20: 15: 6: 1: 6: 15: 20: 15: 6: 1) due to the \((\text{OCH}_3)_2\) protons. The proton splitting for the \((\text{OCH}_3)_2\,\text{PO}\) radical in 1 is about 0.77, 0.55, and 0.48 mT and the \(^{31}\text{P}\) splitting is approximately 5.5, 3.4, and 2.5 mT. The proton splittings for the \((\text{OCH}_3)_2\,\text{PO}\) radical in 2 are about 0.66, 0.42, and 0.33 mT, and the \(^{31}\text{P}\) splitting is approximately 5.5, 3.5, and 2.4 mT.

Such a result can arise if the unpaired electron interacts equally with the \((\text{OCH}_3)_2\) protons. The radicals most likely formed in irradiated 1 and 2 which fit these requirements are \((\text{OCH}_3)_2\,\cdot\,\text{PO}\) radicals. The angular variations of the \(g(\theta)\) and \(A(\theta)\) tensors are computed from the experimental angular variations about the axes \(a, b, c\). All the values obtained from the \((\text{OCH}_3)_2\,\text{PO}\) radicals are given in Table 1. The hyperfine constant of \((\text{OCH}_3)_2\,\text{PO}\), \((\alpha_H)\) has been observed in the crystallographic planes \(ab, bc,\) and \(ac\). Our average value of the phosphorus splittings attached directly to the \((\text{OCH}_3)_2\) is about 3.8 mT, the proton splittings are approximately 0.48 mT. These values agree well with those derived from \((\text{CH}_3)_2\,\text{PO}\) in trimethylphosphine, methylphosphine, and dimethylphosphine [1, 2]. The spin densities at the phosphorus atom can be evaluated from the experimental splitting by using McConnell’s equation \(\alpha_P = \rho^*Q\); \(\alpha_P = 0.82\) and this indicates that in the \((\text{OCH}_3)_2\,\text{PO}\) radical 82% of the spin density is on the phosphorus atom. Such a result can arise if the unpaired electron interacts equally with the \((\text{OCH}_3)_2\) protons due to long-range interaction [3, 4]. Figure 3 shows the spectrum of 3 with its hyperfine splitting. In
these spectra, 14 lines are observed due to (OCH$_3$)$_2$PO radicals.

Owing to the (OCH$_3$)$_2$PO radicals, the spectra exhibit intensity ratios 1: 6: 15: 20: 15: 6: 1 due to (OCH$_3$)$_2$ protons, and each of the lines splits into doublet lines (1:2:6: 6: 15:15: 20:20: 15: 15: 6: 6: 1:1) due to the $^{31}$P atoms. The proton splittings for the (OCH$_3$)$_2$PO radicals are about 1.03, 0.8, and 0.51 mT, and the $^{31}$P splitting is approximately 0.77, 0.35, and 0.23 mT. All the values obtained from the (OCH$_3$)$_2$PO
radiicals are given in Table 2. The values of the hyperfine splitting, the $g$ factor and the spin density of (OCH$_3$)$_2$PO radicals are $a_{av}(H) = 0.78$ mT, $a_p = 0.45$ mT, $g_{av} = 2.0032$ and $\rho_p = 0.7\%$, $\rho_H = 1.5\%$, and $\rho_O = 98\%$, respectively. These agree well with the trimethyl phosphite given in [5]. The $g$ and hyperfine constant values of this radical are given in Table 2.

**Experimental**

The single crystals in this work were grown in the laboratory by slow evaporation of concentrated ethyl alcohol and petrol ether solutions of the compound. From the X-ray diffraction studies we have found that the single crystals of C$_9$H$_{12}$ClO$_4$P are orthorhombic with space group P2$_1$2$_1$2$_1$ and their unit cell dimensions are $a = 7.5666$, $b = 7.9229$, and $c = 12.0421$ Å. There are 4 molecules in a unit cell. The single crystal structure is shown in Figure 6.

The crystals were irradiated at room temperature by a $^{60}$Co $\gamma$ ray source of 0.3 M rad/h$^{-1}$ for 72 hours. The spectra were recorded with a varian E109 C model ESR spectrometer using 2 mW power. The low and high temperature measurements were carried out using a variant temperature control unit between 70 and 350 K. The crystals were rotated on a lucite pillar about
their crystallographic axes, and the angles of rotation were read on a scale marked with lines from known single crystals several times. The g factors were found by comparison with a DPPH sample ($g = 2.0036$).

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