On the ESR Studies of the Photoisomerization of Triethylphosphite

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Although a number of inorganic phosphorus compounds have been studied by means of the ESR technique, a few reports have been published on the organic phosphorus compounds especially, UV-irradiated trialkylphosphite has never been subjected to ESR measurements. In this study, we wish to report the results obtained by the ESR measurements using the elevated-temperature method. We undertook those measurements in order to investigate the mechanism of the following photoisomerization reaction[1]:

$$P(OEt)_3 \xrightarrow{h\nu} EtP(O)(OEt)_2$$

This reaction has recently been reported on by LaCount *et al.*,[2] also but they have not suggested any mechanism for the photochemical formation of the phosphonate.

When a degassed sample of neat triethylphosphite (TEP) was irradiated at 77°K with a 400 Watt high-pressure mercury arc, two kinds of ESR signals were observed, as is shown in Fig. 1a. The (P_1) spectrum has an anisotropic doublet of 370—600 gauss separation and a high g value (2.02), while the other (spectrum C) contains an sixfold line of 25.6 gauss separation and a g value close to the free spin value. The P_1 spectrum showed a characteristic change upon the elevation of the temperature; when the temperature was raised to 100°K, the P_1 spectrum disappeared completely and a new ESR signal (P_2 spectrum) with an anisotropic doublet of 713—870 gauss separation and a g value of 2.03 appeared (Fig. 1b). The observed g and A values of P_1 and P_2 are summarized in Table 1. At 110°K, the P_2 signal vanished.

TABLE 1. LIST OF PHOSPHORUS-RELATED RADICALS FORMED IN IRRADIATED TEP

	$A_\perp$(G)	$A_\parallel$(G)	$\bar{g}$
P_1 Spectrum	596	369	2.021
P_2 Spectrum	860	713	2.032

On the other hand, the C spectrum did not show any significant change except for a great decrease in the intensity during the ESR measurements. The C spectrum as is shown in Fig. 1c, was identified as an ethyl radical. It is well known that the phosphorus atoms in trivalent phosphorus compounds take p^3-hybrid and partially sp^3 hybrid, while in tetravalent phosphate compounds the phosphorus atoms take stable sp^3 hybridization. There fore, the spectra with regard to phosphorus radicals obtained from the trivalent phosphorus compounds may be expected to have a large anisotropic character of a hyperfine structure. When we calculated the orbital spin density of an unpaired electron of these radicals from the isotropic and anisotropic parts of the hyperfine coupling tensor, it is estimated that P_1 has 12.3% 3s- and 73.9% 3p-character, while P_2 has 21.3% 3s- and 50.8% 3p-character. Thus, we may assign the P_1 radical to the $\rangle PO\cdot$-type radical with a p^3 hybrid and the P_2 radical to the $\rangle\dot{P}(O)$-type radical with a sp^3 hybrid. Therefore, the photochemical primary processes of TEP may be depicted as follows:

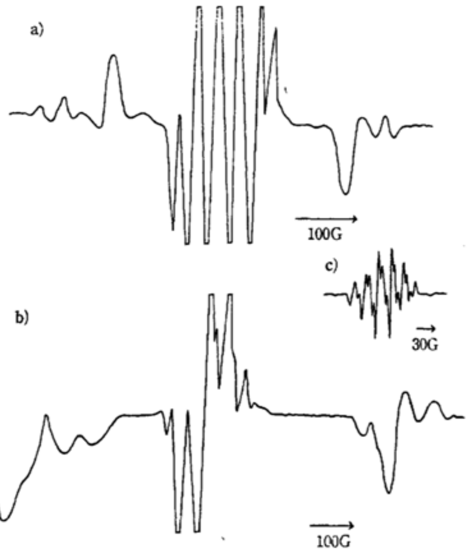
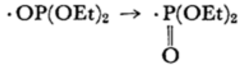


Fig. 1. ESR spectra of UV-irradiated TEP.

a) measured at 77°K.
b) measured at 100°K.
c) measured in the region of g=2.00, at 77°K

$$P(OEt)_3 \xrightarrow{h\nu} (EtO)_2PO\cdot + \cdot Et \qquad (1)$$



$$\cdot OP(OEt)_2 \rightarrow \cdot \underset{\underset{O}{\|}}{P}(OEt)_2 \qquad (2)$$

Further details will be published in the near furture.

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[1] K. Terauchi, Y. Okamoto and H. Sakurai, Presented at the 19th Annual Meeting of the Chemical Society of Japan, Tokyo, March, 1966.

[2] R. B. LaCount and C. E. Griffin, *Tetrahedron Letters*, **1965**, 3071.