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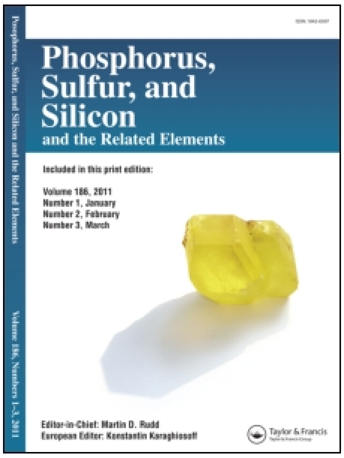

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ELECTRON SPIN RESONANCE STUDIES OF THE RADICALS OF $(Ar'O)_2P(S)Cl$ AND $(Ar''O)_3P=S$ INDUCED BY GAMMA IRRADIATION (Ar'=2,6-DIMETHYLPHENYL AND *2-TERT*-BUTYLPHENYL Ar''=*2-ISO*-PROPYL-5-METHYLPHENYL)

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ELECTRON SPIN RESONANCE STUDIES OF THE RADICALS OF $(Ar'O)_2P(S)Cl$ AND $(Ar''O)_3P=S$ INDUCED BY GAMMA IRRADIATION

(Ar′=2,6-DIMETHYLPHENYL AND 2-*TERT*-BUTYLPHENYL; Ar″=2-*ISO*-PROPYL-5-METHYLPHENYL)

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A newly synthesized and dedected stable thiophosphorylradicals, *bis*(2,6-dimethylphenoxy)thiophosphoryl and *bis*(2-*tert*-butylphenoxy)thiophosphosphoryl and alkyl radical have been observed in gamma irradiated *bis*(2,6-dimethylphenyl)chlorothiophosphate and *bis*(2-*tert*-butylphenyl)chlorothiophosphate and *tris*(2-iso-propyl-5-ethylphenyl)thiophosphate single crystals respectively. The characteristic feature is that the phosphorus hyperfine splitting are 26.76 G and 26.65 G respectively for two compounds, but the g values are very unisotropic varying between 1.9996 and 2.054. *Tris*(2-*iso*-propyl-5-methylphenyl)thiophosphate does not give phosphoryl radical on gamma irradiation. The radical observed is carbon-centered (alkyl) and forms after 1,6-hydrogen shift on isopropyl group towards sulphur atom giving methyl proton splitting with 15.86 G and a proton siplitting in the neighborhood with 5.5 G. The g value is measured to be 2.0025 for this radical.

Keywords: Thioarylphosphates; phosphate esters; esr spectroscopy; phosphoryl radicals; carbon-centered radicals

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INTRODUCTION

The large number of phosphorus centered or phosphorus containing radicals detected so far shows a large variety of behaviours. Besides the purely chemical interests, both in inorganic and organophosphorus chemistry, phosphorus centered or phosphorus containing radicals have received great attention due to that the high energy irradiation of foodstuff for preservation induces reactive phosphorus containing radicals. Electron spin resonance spectroscopy has been an important tool in the study of phosphorus-centered or phosphorus containing radicals, greatly enhancing our understanding of their structures and reactivities.These studies include phosphoranyl radicals[1], phosphinyl radicals[2,3] and phosphoryl radicals[4-12]. The phosphorus radicals which are induced and trapped in solid matrices, especially in single crystals, have long enough lifetimes for ESR investigations and show very different hyperfine and g value variations[13,14].

In the present work, we have synthesized $(Ar'O)_2P(S)Cl$ [Ar′=2,6-dimethylphenyl (I) and 2-*tert*-butylphenyl (II)], $(Ar''O)_3P{=}S$ [Ar″=2-*iso*-propyl-5-methylphenyl (III)], in order to enhance radical generating activity of the reacting compounds. We reported the synthesis and the molecular structure of the compounds in a previous works[15–18].

EXPERIMENTAL

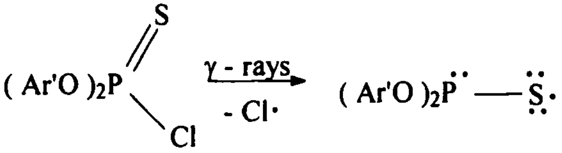
A) Synthesis

The basic route to synthesize the radical generating compounds I, II and III is similar to the procedure given in the literature[15,19]. In the preparative experiment, phosphorusthiochloride (12.71 g, 0.075 mole) was added dropwise to stirred molten 2,6-dimethylphenol (12.2 g, 0. mole) in a double necked flask kept in oil bath at 120°C and refluxed at 150°C for 48 hours. The excess of phosphorusthiochloide was removed from the product under reduced pressure. The resudial product in the flask was dissolved in boiling hexane and solution was then cooled slowly to the room temperature. Following this procedure, the well developed single crystals of the compounds were obtained.

The compounds I, II, and III used as precursors for radical generation were analyzed using IR, UV and ^{1}H-NMR spectroscopy techniques. IR and UV spectra were obtained using Perkin-Elmer 4500 IR spectrometer and a Varian DMS 100 UV/VIS spectrometer respectively. ^{1}H-NMR spectra was recorded using a Varian 360 ^{1}H-NMR spectrometer. The ESR spectra were recorded with a Varian E-109 C model X-band spectrometer equipped with a Varian variable temperature unit. Elemental analysis of samples were carried out at TUBITAK Marmara Research Centre, Gebze, Istanbul.

B) γ-Irradiation and ESR Spectra

The single crystals of $(Ar'O)_2P(S)Cl$ and $(Ar''O)_3P=S$ were irradiated with gamma rays from ^{60}Co source of 0.3 M rad/h for 24 hours at room temperature. The colourless crystals became dark brown after irradiation and $(Ar'O)_2P(S)Cl$ gave corresponding radicals via loss of Cl..



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The single crystals were glued on a lucite pillar and rotated in about three perpendicular axis. The rotation angles were read on a scale graduated in degrees. The g values were corrected by comparing with DPPH sample (g-2.0036).

RESULT AND DISCUSSION

The ESR spectra taken at room temperature show two broad lines which are assigned to $(Ar'O)_2PS.$ radical which is induced after irradiation of $(Ar'O)_2P(S)Cl$ *via* loss of Cl. as shown in Figure 1. The spectra are well resolved, and show neither any hyperfine nor site splitting at all orientations. The hyperfine splitting variation is very small throughout, a slight change between 27.7 and 25.00 G could be measured (Table I), but the g values change vigorously with orientation between 2.0504 and 1.9996

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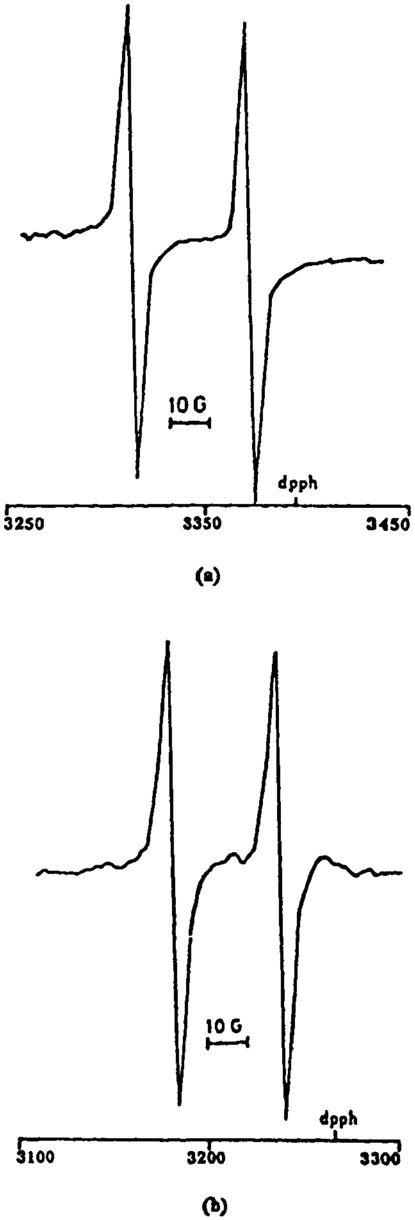
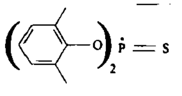
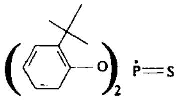


FIGURE 1 ESR Spectrum of the gamma irradiated single crystals a) *Bis* (2,6-dimethylphenyl) chlorothiophosphate at $H_{//}$ axis, b) *Bis* (2-*tert*-buthylphenyl) thiophosphate at $H_{//}$ axis

(Figure 3 and Table I). The g values and hyperfine splitting variation of the radicals were shown in Figure 2 and 3 respectively. The spectra show the interaction of unpaired electron with nucleus of spin ½, namely ^{31}P nucleus and adjacent spinless nuclei. No ^{33}S splitting could be seen because of poor signal/noise ratio. The principal values of *g* and hyperfine tensors of the radical (Ar'O)$_2$PS· were shown in Table I. When the samples were heated up to the melting points the intensities of the lines get smaller and when cooled down to the room temperature the original intensity was recovered. On cooling the crystals down to −180°C, only the intensities of the lines increase, and no any other change take place.

TABLE I The principal values of hyperfine splittings and g values of the radicals (Ar'O)$_2$PS·

Radical	*Principal hyperfine values (in G)*	*Principal g values*
	$A_1 = 27.52$	$g_1 = 2.0193$
	$A_2 = 25.61$	$g_2 = 1.9996$
	$A_3 = 27.14$	$g_3 = 2.0504$
	$a_{iso} = 26.76$	$g_{iso}=2.0346$
	$A_1 = 26.32$	$g_1 = 2.0436$
	$A_2 = 27.77$	$g_2 = 2.0004$
	$A_3 = 25.88$	$g_3 = 2.0267$
	$a_{iso}=26.65$	$g = 2.0235$

The striking feature of the radical (Ar'O)$_2$PS. is the unusually large anisotropy of the *g* values and small phosphorus hyperfine splitting compared with most of the phosphorus centred or phosphorus containing radicals observed. In known phosphinyl radicals the *g* values are close to the free electron value[2–5,9–12]. But, the radicals of the type (RO)$_2$P(X)S., where R stands for *Me, Et, Bu, Ar, etc.* and x stands for O and S, show this much of large anisotropy and small phosphorus hyperfine splitting[9], which are structurally similar to the radical, (Ar'O)$_2$PS. studied in this work. The unpaired electron is localized mainly on the sulphur atom and is responsible for the large anisotropy in *g* value. On the other hand, thio radicals having the unpaired electron localized on sulphur atom show large anisotropy in g value ranging from 2.2 to 2.0 [9]. This is consistent with the values obtained from (Ar'O)$_2$PS. radical. The nearly constant hyperfine splitting of the phosphorus atom is small with the average value of 26.76 G, Table I,

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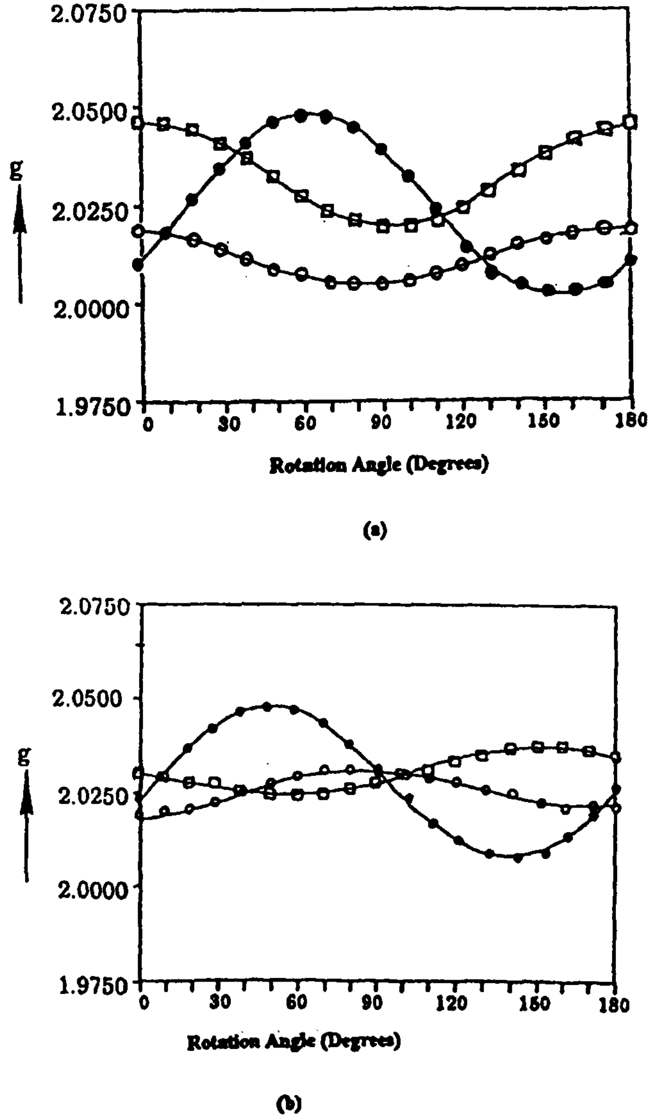

FIGURE 2 Angular variation of the *g* values in three prepenticular planes. For indication see Figure 2. a) *Bis* (2,6-dimethylphenoxy) thiophosphoryl, b) *Bis*(2-*tert*-butylphenoxy) thiophosphoryl radical

and the electron density in the S orbital of the phosphorus atom is 0.007. This is due to the spin polarisation of the S – P bond from the unpaired electron density on sulphur *p* orbital.

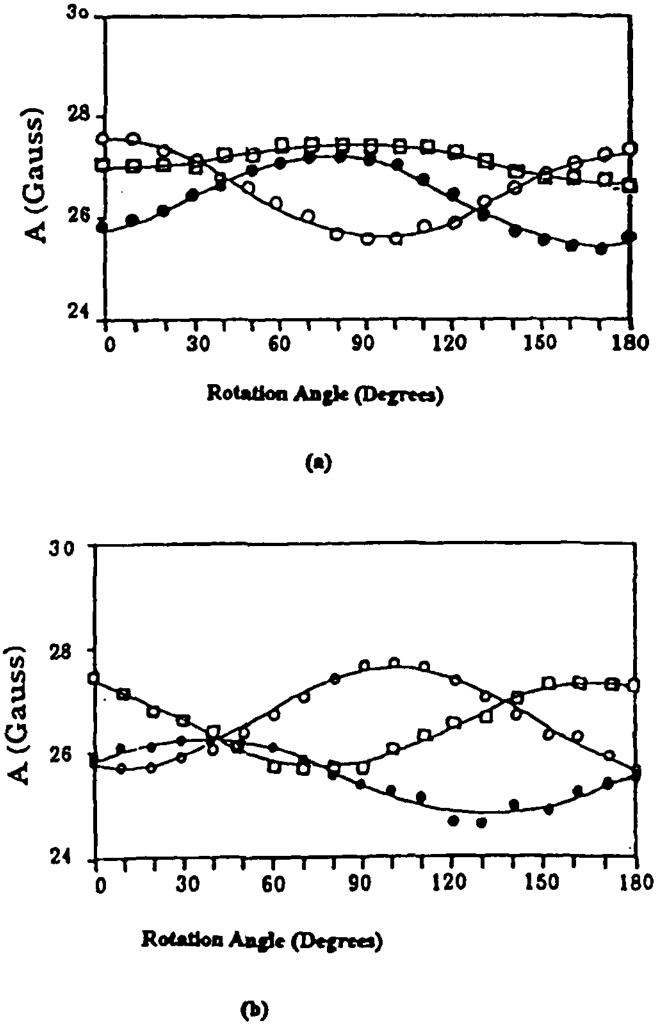

FIGURE 3 Angular variation of the ^{31}P hyperfine splitting in three prependicular planes. (O: x-y plane, •: x-z plane, □: y-z plane.) a) *Bis* (2,6-dimethylphenoxy) thiophosphoryl, b) *Bis* (2-*tert*-butylphenoxy) thiophosphoryl radical

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Similar treatments carried out on *tris* (2-isopropyl-5-methylphenyl) thiophosphate gives the spectrum shown in Figure 4 after irradiation with gamma rays. Although the same irradiation conditions are applied to the compounds I, II and III, the compound III gives totally different radical. The crystal symmetry is triclinic[17], which means that there is only one site in the ESR spectrum. The spectrum is nearly isotropic with an intensity distribution 1:2:1; 6:12:6; 15:30:15; 21:42:21; 15:30:15; 6:12:6; 1:2:1, and belongs to an alkyl radical which is discussed below.

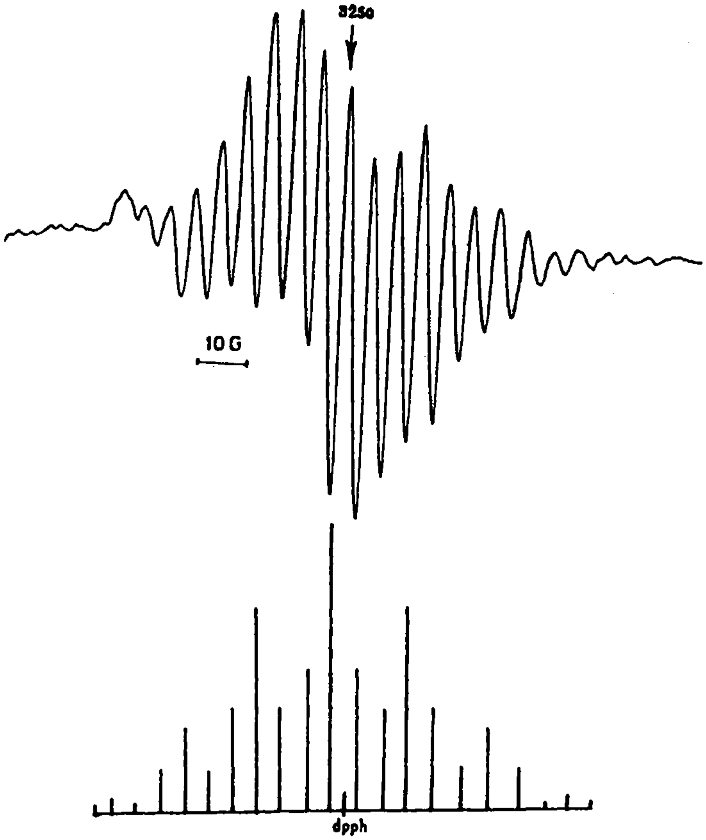

FIGURE 4 The ESR spectrum of *tris* (2-isopropyl-5-methylphenyl) thiophosphate (III) single crystal after gamma irradiation

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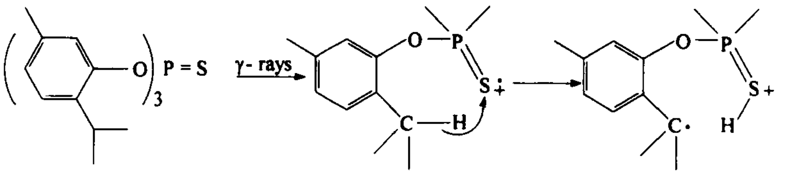
The mechanism forming the radical is the most probably 1,6-hydrogen shift towards sulphur atom. First, the irradiation forms a sulphur centred radical cation effecting the P=Sbond, but this is a highly unstable radical and immediately transfer a hydrogen from the alkyl group and forms a very stable carbon centered radicals, shown below;



The mechanism is very similar to the formation of alkyl radicals in the solution of alkylphosphates at 77 K[8] and in *bis*(2,4,6-*tri*-buthylphenyl)phosphinicchloride single crystal[10]. When the geometry of the molecule is taken into account this mechanism is strongly possible in this compound. The unpaired electron centered on *tertiary* carbon atom interacts with two methyl groups bonded to the same carbon atom and two other hydrogen atoms. One of the splitting is from the methyl groups, the next one is from the hydrogen atom bonded to sulphur atom and the other one is from the nearest hydrogen atom bonded to the aromatic ring. The splittings of these two hydrogenous are very close to each other. This sort of splittings are often observed in the radicals containing aromatic rings[20]. Since the plane of the *p* orbital of unpaired electron and the π system of the aromatic ring are completely different, interaction with the *p* orbitals are impossible. Consequently, the spectrum can be attributed to two methyl groups giving a distribution 1:6:15:21:15:6:1, and two other protons with nearly the same splittings as discussed above, which split each line of methyl spectrum into three lines, as shown in Figure 4. The hyperfine splittings of methyl protons are measured as 15.8 G and the two other protons are approximately 5.5 G. The g value is 2.0025 which is characteristic for methyl groups.

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