EPR of Gamma Irradiation Damage Centres in Single Crystals of Some Phosphonates and Derivatives

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The EPR spectra of the phosphorous centred radicals produced by γ-irradiated single crystals of three phosphorous compounds have been observed and identified as the free radicals $(OCH_3)_2\dot{P}O$ and $(OCH_3)_2\dot{P}O$.

Key words: Electon Paramagnetic Resonance; Free Radical; Phosphonate Derivatives.

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 $(OCH_3)_2\dot{P}O$ radicals. Owing to these radicals, the spectra exhibit a doublet (1:1) because of the ^{31}P nucleus. Each of the lines splits into 7 lines (1: 6: 15: 20: 15: 6: 1: 1: 6: 15: 20: 15: 6: 1) due to the $(OCH_3)_2$ protons. The proton splitting for the $(OCH_3)_2\dot{P}O$ radical in 1 is about 0.77, 0.55, and 0.48 mT and the ^{31}P splitting is approximately 5.5, 3.4, and 2.5 mT. The proton splittings for the $(OCH_3)_2\dot{P}O$ radical in 2 are about 0.66, 0.42, and 0.33 mT, and the ^{31}P splitting is approximately 5.5, 3.5, and 2.4 mT.

Such a result can arise if the unpaired electron interacts equally whith the $(OCH_3)_2$ protons. The radicals most likely formed in irradiated 1 and 2 which fit these requirements are $(OCH_3)_2\dot{P}O$ 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 $(OCH_3)_2\dot{P}O$ radicals are given in Table 1. The hyperfine constant of $(OCH_3)_2\dot{P}O$, (a_H) has been observed in the crystallographic planes *ab, bc,* and *ac*. Our average value of the phosphorus splittings attached directly to the $(OCH_3)_2$ is about 3.8 mT, the proton splittings are approximately 0.48 mT. These values agree well those derived from $(CH_3)_2\dot{P}O$ in trimethylphosphine, methylphosphine, and dimethylphosphine [1, 2]. The spin densities at the phosporus atom can be evaluated from the experimental splitting by using Mc Connel's equation $a_\rho = \rho Q$; a_ρ = 0.82 and this indicates that in the $(OCH_3)_2\dot{P}O$ radical 82% of the spin density is on the phosphorus atom. Such a result can arise if the unpaired electron interacts equally with the $(OCH_3)_2$ protons due to long-range interaction [3, 4]. Figure 3 shows the spectrum of 3 with its hyperfine splitting. In

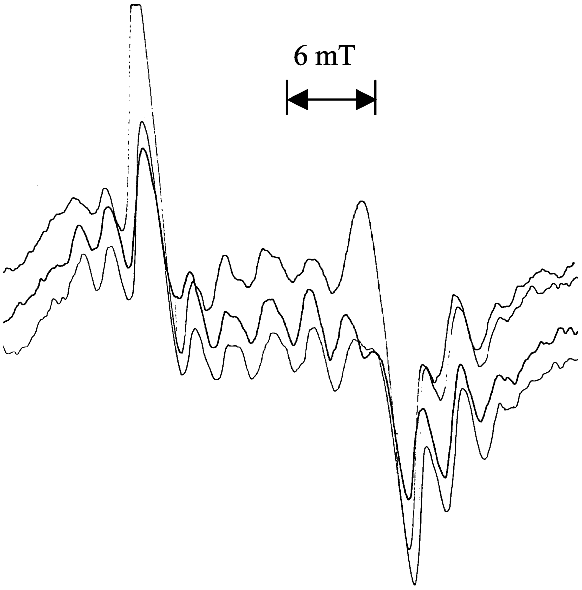

Fig. 1. EPR Spectrum of $(OCH_3)_2\dot{P}O$ radicals in $C_9H_{12}ClO_4P$ after irradiation at 300 K.

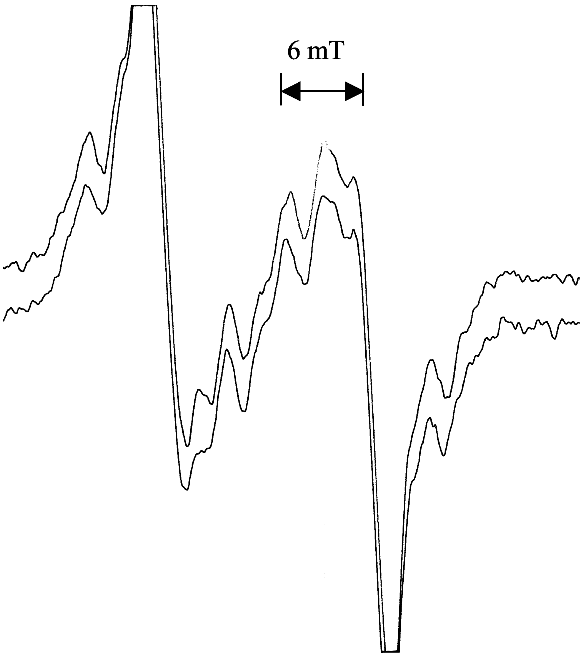

Fig. 2. EPR Spectrum of $(OCH_3)_2\dot{P}O$ radicals in $C_{10}H_{15}O_4P$ after irradiation at 300 K.

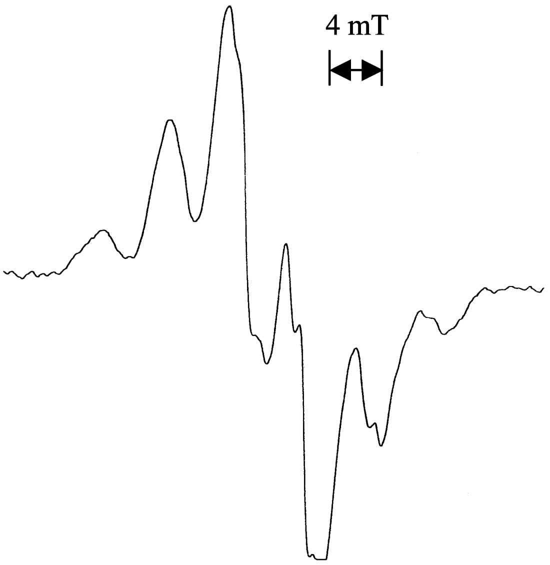

Fig. 3. EPR Spectrum of $(OCH_3)_2P\dot{O}$ radicals in $C_{11}H_{15}O_4P$ after irradiation at 300 K.

Table 1. The EPR parameters of the $(OCH_3)_2\dot{P}O$ radical observed in $C_9H_{12}ClO_4P$ and $C_{10}H_{15}O_4P$ singe crystals.

Radical	Principal values a_p(mT), a_H(mT) and g		Direction cosines		
	a_P	5.3	0.97235	0.17788	0.15129
		3.4	−0.12755	0.13813	−0.98217
		2.5	0.19561	0.97431	0.11163
	$a_{(P)av}$	3.8			
$(OCH_3)_2\dot{P}O$	a_H	0.77	0.23133	−0.85863	−0.45743
		0.55	0.57886	−0.25641	0.77406
		0.48	−0.78192	−0.44385	0.43771
	$a_{(H)av}$	0.60			
	g	2.0044	0.31639	−0.93050	−0.18456
		2.0033	0.81804	0.36612	−0.44357
		2.0028	0.48032	−0.01064	0.87703
	g_{av}	2.0035			
	a_P	5.5	0.96987	−0.20068	−0.14932
		3.5	−0.19658	−0.02586	−0.89271
		2.4	0.21456	−0.96986	0.12001
	$a_{(P)av}$	3.8			
$(OCH_3)_2\dot{P}O$	a_H	0.66	0.24869	0.58711	−0.31996
		0.42	−0.61657	−0.19209	−0.67386
		0.33	−0.14896	0.38786	0.65842
	$a_{(H)av}$	0.47			
	g	2.0038	0.29532	−0.89902	−0.18399
		2.0078	0.79804	0.40058	−0.45017
		2.0035	0.47232	−0.11068	−0.76701
	g_{av}	2.0051			

Table 2. The EPR parameters of the $(OCH_3)_2P\dot{O}$ radical observed in $C_{11}H_{15}O_4P$ singe crystals.

Radical	Principal values a_p(mT), a_H(mT) and g		Direction cosines		
	a_H	1.03	0.96116	−0.16603	−0.14023
		0.80	−0.11659	0.12689	−0.89220
		0.51	0.21462	0.96312	0.10063
	$a_{(H)av}$	0.78			
	a_P	0.77	0.22028	−0.86063	−0.44743
		0.35	0.57866	−0.24641	0.77428
$(OCH_3)_2P\dot{C}$		0.23	−0.77193	−0.43389	0.42752
	$a_{(P)av}$	0.45			
	g	2.0049	0.30539	−0.94052	−0.20735
		2.0043	0.81804	−0.35412	−0.44357
		2.0024	−0.48032	0.01047	0.87712
	g_{av}	2.0039			

these spectra, 14 lines are observed due to $(OCH_3)_2P\dot{O}$ radicals.

Owing to the $(OCH_3)_2P\dot{O}$ 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 (1:1:6: 6: 15:15: 20:20: 15: 15: 6: 6: 1:1) due to the ^{31}P atoms. The proton splittings for the $(OCH_3)_2P\dot{O}$ 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 $(OCH_3)_2P\dot{O}$

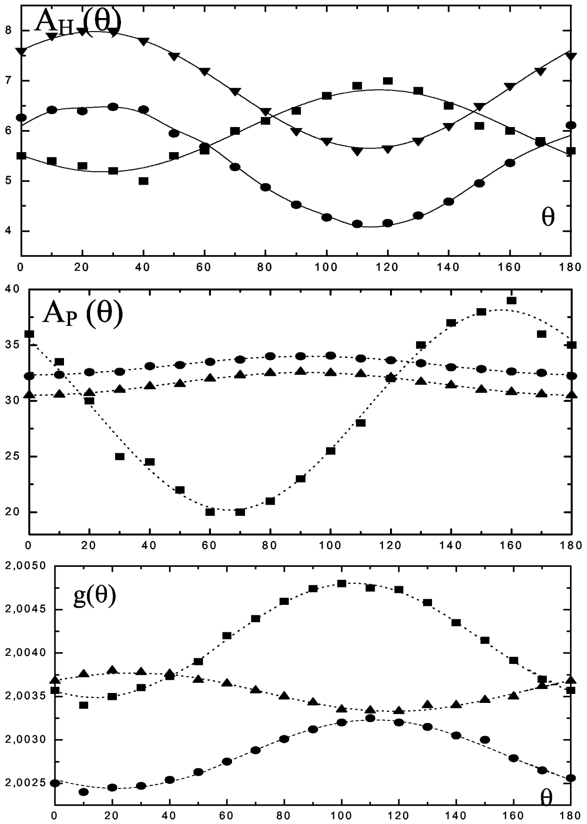

Fig. 4. The angular variations of the $A_H(\theta)$,$A_P(\theta)$ and $g(\theta)$ tensor for the $(OCH_3)_2\dot{P}O$ radical in the $C_9H_{12}ClO_4P$.

radicals are given in Table 2. The values of the hyperfine splitting, the g factor and the spin density of $(OCH_3)_2P\dot{O}$ radicals are $a_{av(H)}$ = 0.78 mT, a_p = 0.45 mT, g_{av} = 2.0032 and ρ_p = 0.7%, ρ_H = 1.5%, and ρ_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 $C_9H_{12}ClO_4P$ are orthorhombic with space group $P2_12_12_1$ 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.

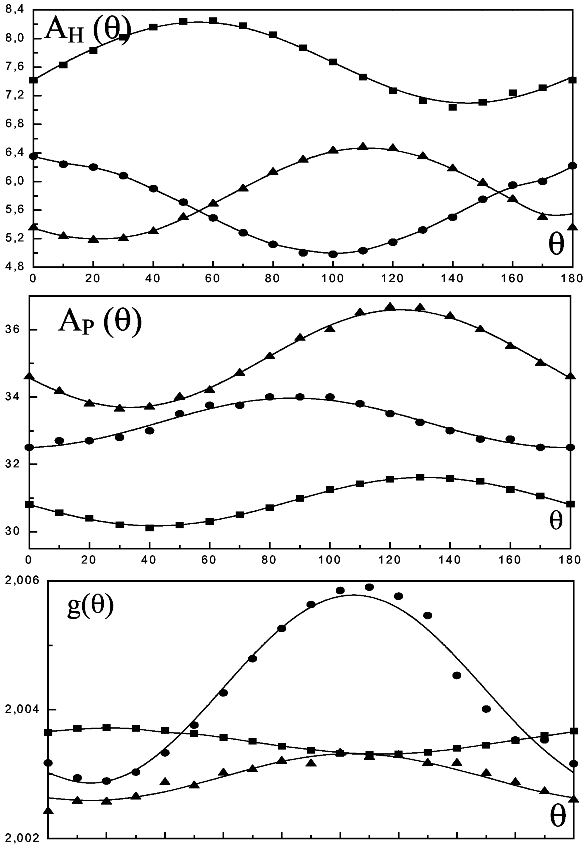

Fig. 5. The angular variations of the $A_H(\theta)$,$A_P(\theta)$ and $g(\theta)$ tensor for the $(OCH_3)_2\dot{P}O$ radical in the $C_{10}H_{15}O_4P$.

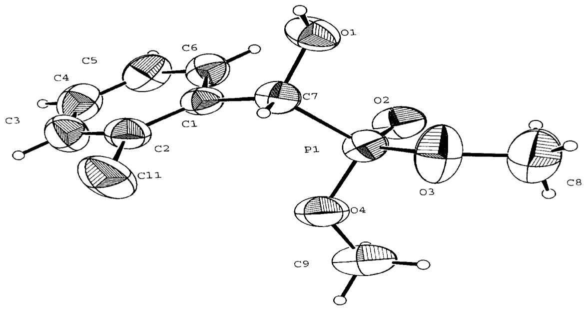

Fig. 6. The molecular crystal structure of single crystals of $C_9H_{12}ClO_4$ P.

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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