ESR of Gamma Irradiated Single Crystals of Acetylcholine Picrate and Methoxycarbonylcholine Picrate Hemihydrate

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We have observed two radicals in the ESR spectra of γ-irradiated single crystals of acetylcholine picrate and methoxycarbonylcholine picrate hemihydrate. These radicals have been identified as the $CH_3\dot{C}OOH$ and $-\dot{C}H_2CH_2$ respectively.

The ESR technique has frequently been used for identifying irradiation damage centers in organic and inorganic substances. The present work has been undertaken on acetylcholine picrate (**1**) and methoxycarbonylcholine picrate hemihydrate (**2**). Free radicals produced by gamma irradiation in single crystals of **1** and **2** were investigated between 100 and 350 K with ESR spectra. The single crystal spectra were taken at 5-degree intervals for the magnetic field H being applied in each of the three crystallographic planes, ab, bc, and ca.

The ESR spectra of γ-irradiated single crystals of **1** are shown in Figs. 1(a) and (b). These spectra were observed when the single crystal rotates in the magnetic field. Since the spectra indicated approximately the 1 : 3 : 3 : 1 and 1 : 1 : 3 : 3 : 3 : 3 : 1 : 1 intensity pattern shown in Figs. 1(a) and (b), we have attributed them to the $CH_3\dot{C}OOH$ radical. The hyperfine splitting of the methyl protons is isotropic and the hyperfine constant a is 18 G. The g value of this radical is slightly anisotropic, its average value being g = 2.0050. The hyperfine interaction of the proton in the $-\dot{C}OOH$ radical with the unpaired electron is anisotropic, its average value being a_{OH} = 4 G. So, this value of the hyperfine interaction supports its attribution to $CH_3\dot{C}OOH$ rather then $\dot{C}H_3COOH$. The principal values and the directional cosines of the tensor g and the hyperfine constants for the proton with unpaired electron are given in Table 1.

Since no site splittings were observed, it is concluded that the 8 molecules in the unit cell of acetylcholine picrate are magnetically equivalent. This radical was also observed by other workers in X-irradiated

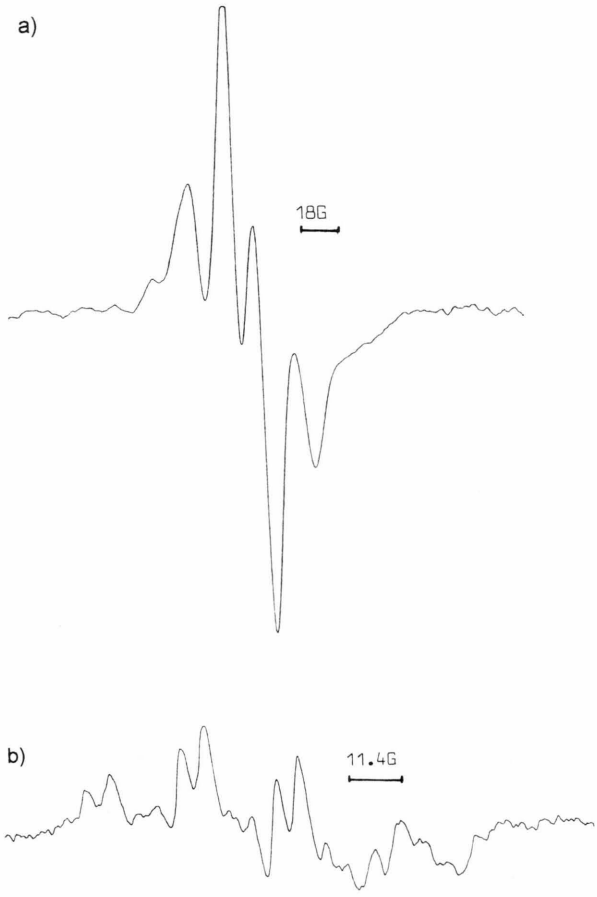

Fig. 1. a) ESR spectrum of $CH_3\dot{C}OO$ radical at 300 K and b) $CH_3\dot{C}OOH$ radical in acetylcholine picrate after irradiation at 100 K.

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Table 1. ESR results for the radical $CH_3\dot{C}OOH$ observed in Acethylcholine picrate. The error for all the calculated g values is estimated as ∓ 0.0005.

Radical	Principal values A(G) and g	Direction cosines		
$CH_3\dot{C}OOH$	$g_a = 2.0060$	0.6999	−0.4989	−0.1909
	$g_b = 2.0050$	0.1983	−0.0050	0.8992
	$g_c = 2.0040$	−0.49831	−0.7969	0.08900
	$g_{av} = 2.0050$			
	$A_{xx} = 5.7$	0.5991	0.69922	−0.2976
	$A_{yy} = 3.8$	−0.6983	0.3941	−0.4982
	$A_{zz} = 2.5$	−0.1992	0.4989	0.6992
	$a_{OH} = 4$			
	$a_{CH_3} = 18$			

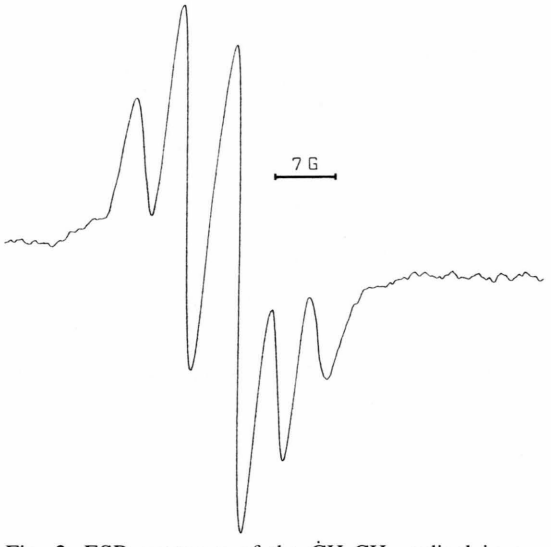

Fig. 2. ESR spectrum of the $\dot{C}H_2CH_2$ radical in a γ-irradiated single crystal of methoxycarbonylcholine picrate hemihydrate $H||a$.

acetic acid and in other compounds [1-7], acetylcholine iodide and acetylcholine bromide [8], acetylcholine β-resorcylate [9], and the hyperfine coupling of the unpaired electron to the CH_3 protons was found to be 15, 17, and 18.5 G respectively. In the present work this coupling was constant and amounted to 18 G. The hyperfine coupling of freely a tumbling methyl radical is 23 G [2], and this indicates that in $CH_3\dot{C}OOH$ radical 78% of the spin density is on the carbon and 22% is on the oxygens.

The ESR spectra recorded for **2** have approximately a 1 : 4 : 6 : 4 : 1 intensity pattern, as shown in Fig. 2, at

Table 2. ESR results for the radical $\dot{C}H_2CH_2$ observed in methoxycarbonylcholine picrate hemihydrate.The error for all the calculated g values is estimated as ∓ 0.0005.

Radical	Principal values A(G) and g	Direction cosines		
$\dot{C}H_2CH_2$	$g_a = 2.0033$	0.5554	0.0025	0.6451
	$g_b = 2.0026$	− 0.6384	0.1890	0.5499
	$g_c = 2.0024$	− 0.1399	− 0.8999	0.1299
	$a_{C_2H_4} = 7$			

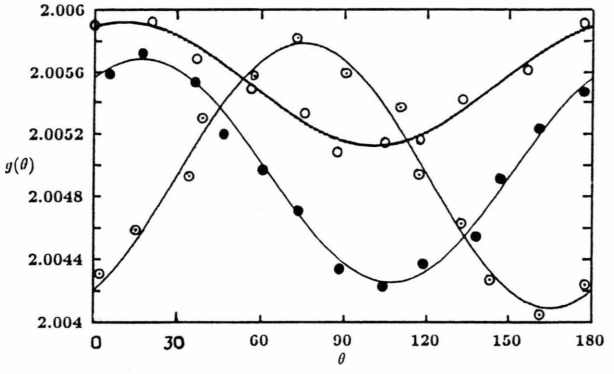

Fig. 3. Variation of the g tensor around the $a(\circ)$, $b(\bullet)$, and $c(\odot)$ axes of gamma irradiated acetylcholine picrate.

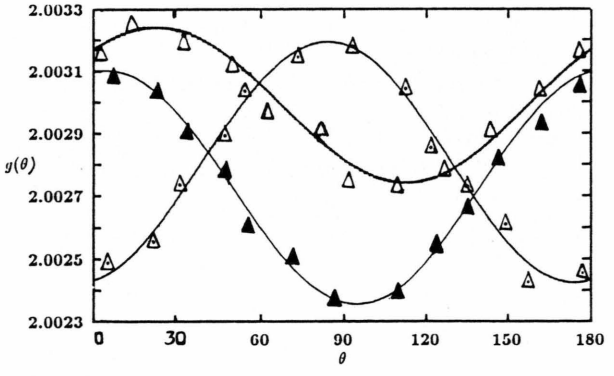

Fig. 4. Variation of the g tensor around the a(void triangles), b(full triangles), and $c(\triangle)$ axes of the gamma irradiated methoxycarbonylcholine picrate hemihydrate.

most orientations of the crystal in the magnetic field. Therefore we propose that the radical is $\dot{C}H_2CH_2$ and that the unpaired electron interacts with the protons of two methylene groups. The hyperfine interaction of the two methylene protons is approximately constant and it has $a = 7$ G at all orientations of the magnetic field in the plane perpendicular to the c axis of the

crystal. This result is similar to those on amine radicals reported by Wood et al. [10]. The g value of the radical is slightly anisotropic. The principal values of the tensor g and the directional cosines are given in Table 2. The angular variations of the g values of the $CH_3\dot{C}OOH$ and $\dot{C}H_2CH_2$ radicals at room temperature with 5-degree increments of the orientation of the magnetic field are shown in Figs. 3 and 4. The solid curves indicate the theoretical fitting of the observed data points with the coupling constants.

Experimental

The acetylcholine picrate (**1**) and methoxycarbonylcholine picrate hemihydrate (**2**) single crystals were grown from concentrated aqueous solutions. Single crystals of **1** have the orthorhombic space group Pbca with a = 18.799, b = 7.726, c = 22.878 Å. The unit cell of the crystal contains 8 molecules.Single crystals of **2** are monoclinic with space group P2/n and the unit cell dimentions are a = 11.337, b = 7.279, c = 21.424 Å, β = 103.01°. The unit cell contains 4 molecules [11].

The samples were irradiated at room temperature with a ^{60}Co γ-ray source of 0.3 Mrad/h for 24 hours. The ESR spectra were recorded using 2 mW microwave power. The low and high temperature measurements at 100 K and 350 K were carried out at a frequency of 9.13 GHz using a Variant temperature controller unit. The crystals were rotated on a Lucite pillar about their crystallographic axes, and the angles of rotation were read on a scale in degrees. The ESR spectra, using several single crystals at several times and also powder of the compound, were reproducible. The g factor was found by comparison with a DPPH sample (g = 2.0036).

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