EPR of Gamma Irradiated Single Crystal of 2,2-Dimethyl Succinic Acid

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We have observed the radical $\dot{C}HCH_2$ in the EPR spectra of α-irradiated single crystal of 2,2-dimethyl succinic acid.

Key words: Electron Paramagnetic Resonance; Free Radical; Succinic Acid Derivatives.

Introduction

The EPR technique has widely been used to identify the damage centers produced by high energy radiation [1, 2, 3]. The present work deals with 2,2-dimethyl succinic acid, 2,2-DMSA, $HOOCCH_2C(CH_3)_2COOH$. Free radicals, produced by gamma irradiation of single crystals, were investigated between 120 and 300 K with EPR spectra. The spectra were taken at 10-degree intervals for magnetic fields B applied in each of the three crystallographic planes, *ab*, *bc*, and *ca*.

The spectra were independent of temperature. The g value and hyperfine coupling change, when the crystal is rotated around the axes a, b and c, and therefore are anisotropic.

Experimental

Single crystals of 2,2-DMSA were grown from concentrated aqueous solutions. By x-ray diffraction studies [4] we found that the single crystals of 2,2-DMSA are triclinic, space group P1, unit cell dimensions $a = 5.661$, $b = 6.385$ and $c = 11.461$ Å, $V = 367.7$ Å^3, $Z = 2$.

The crystals were irradiated by a ^{60}Co γ-ray source of 0.3 M rad h^{-1} at room temperature for 24 hours. The EPR spectra were recorded with a Varian model E-109 C EPR spectrometer using 2 mW microwave power. For the low temperature measurements a Varian temperature-control unit was used. The crystals were rotated on a Lucite pillar around their crystallographic axes. The EPR spectra of several single crystals at several times, and also of powders of the compounds were reproducible. The g factor was found by comparison with a DPPH sample ($g = 2.0036$).

Results and Discussion

The EPR spectra of 2,2-DMSA shown in Figs. 1, 2, and 3 exhibit 1:3:3:1, 1:2:1:1:2:1, and nearly 1:2:2:2:1 patterns, respectively, and therefore indicate the hyperfine interaction of one α-proton and two β-protons with the electron spin; the radical must thus be $^{-}\dot{C}HCH_{2^{-}}$. Site splitting does not occur, and therefore the molecules in the unit cell of the crystal are magnetically equivalent. The hyperfine splitting of the α-proton is anisotropic, its average value a being 2.44 mT. The hyperfine splitting of two protons of the methyl protons are slightly anisotropic and the hyperfine constant a is 0.82 mT. The g value of this radical is anisotropic, its average value being $g = 1.9971$. The angular variations of the $g(\theta)$ and $A(\theta)$ tensors were computed from the experimental angular variations about the axes a, b and c. The principal values and the directional cosines of the tensor g and hyperfine interaction for an α-proton with an unpaired electron are given in Table 1.

The EPR spectrum of 2,2-DMSA in Figure 1 exhibits an intensity distribution 1:3:3:1 with 1.1 mT and 0.77 mT spacing. This EPR spectrum of gamma irradiated 2,2-DMSA single crystal was obtained along the $B_o \parallel a$ axis. The hyperfine interaction of the unpaired electron of one α-proton and two β-methyl protons, which is magnetically approximately equal, shows the intensity distribution 1:3:3:1.

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Table 1. The EPR parameters of $\dot{C}HCH_2$ radical. The error for all the calculated $\boldsymbol{g}$ values is estimated as ± 0.0005.

Radical		Principal Values of $\boldsymbol{A}$ (mT) and $\boldsymbol{g}$	Direction Cosines		
$\dot{C}HCH_2$	a_{CH}	3.19 ± 0.1	0.9619	0.2685	−0.0573
		2.19 ± 0.1	−0.0730	0.4512	0.8894
		1.95 ± 0.1	0.2646	−0.8511	0.4535
	a_{av}	2.44 ± 0.1			
	$(a_{CH_2})_{av}$	0.82			
	g_a	2.0000	0.7560	0.1426	−0.6387
	g_b	1.9963	−0.0820	0.9892	0.1164
	g_c	1.9949	0.6485	−0.0316	0.7605
	g_{av}	1.9971			

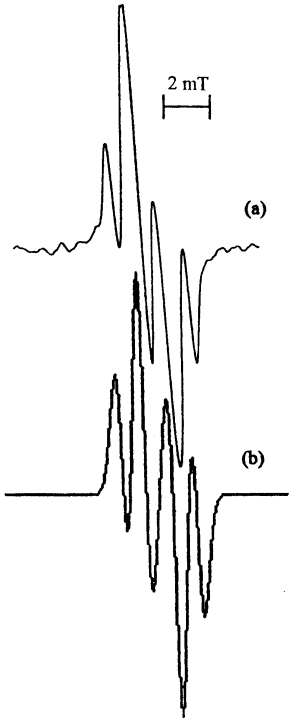

Fig. 1. EPR spectrum of γ-irradiated 2,2-dimethyl succinic acid obtained along the $B_o \| a$ axis (a), and simulated spectrum using $a_\alpha = 1.1$ mT, $a_\beta = 0.77$ mT (b).

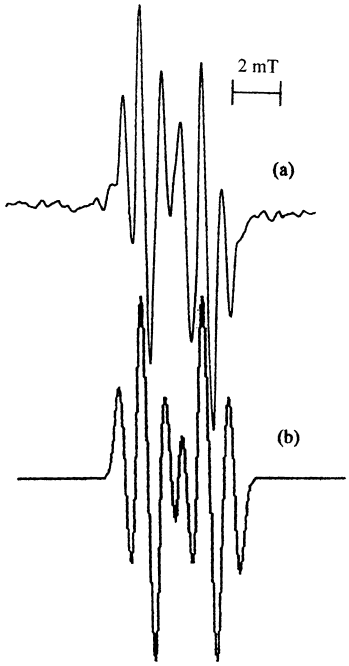

Fig. 2. EPR spectrum of γ-irradiated 2,2-dimethyl succinic acid obtained along the $B_o \| b$ axis (a), and simulated spectrum using $a_\alpha = 2.7$ mT, $a_\beta = 1$ mT (b).

When the spectrum with an intensity distribution of 1:2:1:1:2:1 is examined thoroughly, it can be seen that it consists of a doublet with a spacing of 2.7 mT. Then, each line of the doublet is further subdivided into 3 lines of spacing 1 mT, with an intensity distribution of 1:2:1, shown in Figure 2.

The EPR spectrum recorded for 2,2-DMSA has approximately the intensity pattern 1:2:2:2:1, as shown in Figure 3 at the other orientations of the crystal in the magnetic field. The binomial expansion for this spectrum is given as

$$1:2:1 + 1:2:1 = 1:2:2:2:1.$$

The spectrum for a larger number of inequivalent protons can be found by graphic construction, or by binomial expansion, which is a mathematical record of an EPR spectrum. Simple addition of the line

intensities of simple spectra, the lines being displaced relative to each other by the value of the coupling constant, yields the intensity ratio for more complicated spectra (see binomial expansion). This spectrum, corresponding to the binomial expansion, is shown in Figure 3. The reported values are $a_\alpha = 2.4$ mT, $a_\beta = 1$ mT.

The simulation of the spectrum, using the EPR simulation program of McKelvey [5] is shown in Figures 1 (b), 2 (b), and 3 (b).

This radical was observed in γ-irradiated succinic acid [6, 7] and carbamyl choline chloride [8]. The reported average values $a_{CH} = 2.15$ mT, $a_{CH_2} = 2.857$ mT, $g = 2.0030$, and $a_{CH} = 1.45$ mT, $a_{CH_2} = 2.766$ mT, $g = 2.0029$ are slightly different from our results. The hyperfine coupling constants of methyl protons reported here are smaller than the values reported in [6, 8]. These differences in the coupling constant of methyl protons can be understood from the relations of the β-protons with the hyperfine coupling constants [9].

In conclusion, we can state that γ-irradiation produces free radicals in 2,2-DMSA by abstraction of a proton.

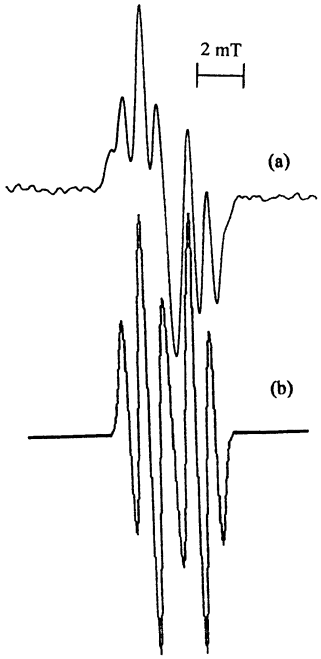

Fig. 3. EPR spectrum of γ-irradiated 2,2-dimethyl succinic acid obtained along the $B_o \| c$ axis (a), and simulated spectrum using $a_\alpha = 2.4$ mT, $a_\beta = 1$ mT (b).

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