EPR of Gamma Irradiated Single Crystals of N-Acetyl- and N-Carbamyl-α-Aminoisobutyric Acid

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The $(CH_3)_2\dot{C}COOH$ radical has been observed in the EPR spectra of γ-irradiated single crystals and powders of N-acetyl-α-aminoisobutyric acid and N-carbamyl-α-aminoisobutyric acid.

Key words: Electron Paramagnetic Resonance; Free Radical; α-Aminoisobutyric Acid Derivatives.

1. Introduction

EPR has been applied to study irradiation damage centers in carboxylic acid and its derivatives [1 – 5]. γ-irradiated single crystals of α-aminoisobutyric acid were investigated at room temperature [6] and X-irradiated single crystals at 77 K [7]. Furthermore, γ-irradiated single crystals of α-hydroxy isobutyric acid and α-aminoisobutyric acid hydrochloride were investigated between 113 and 300 K [8]. The radiation damage centers were attributed to $(CH_3)_2\dot{C}COOH$ radicals in four studies. In the present work we have applied EPR to γ-irridiated N-acetyl-α-aminoisobutyric acid, $(CH_3)_2C(NHCOCH_3)COOH$, NA, and N-carbamyl-α-aminoisobutyric acid, $(CH_3)_2C(NHCONH_2)COOH$, NC, in single crystal and powder form at room and low temperature to determine the irradiation damage centers and their properties.

2. Experimental

NA and NC single crystals were grown from acetone solution. In its single crystal form NA is monoclinic with space group $P2_1/n$, and unit cell dimensions $a = 10.165$, $b = 8.030$, $c = 9.712$ Å, $V = 736$ Å^3, $\beta = 111.9^\circ$. The unit cell contains 4 molecules [9]. The single crystals and powders were irradiated with a Co^{60} γ-ray source of 0.3 Mrad h^{-1} at room temperature for 5 hours. The spectra were recorded with a Varian model E-109C EPR spectrometer, using 2 mW microwave power. The low temperature measurements were carried out using a Varian variable temperature control 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 **g** factors were found by comparison with a DPPH sample (g = 2.0036).

Table 1. Principal values of the methyl groups for the $(CH_3)_2\dot{C}COOH$ radical in N-acetyl-α-aminoisobutyric acid (NA), and N-carbamyl-α-aminoisobutyric acid (NC). The values are given in mT.

Principal values (±0.02 mT)	NA	NC
A_{xx}	2.34	2.26
A_{yy}	2.16	2.13
A_{zz}	2.1	2
a	2.2	2.13

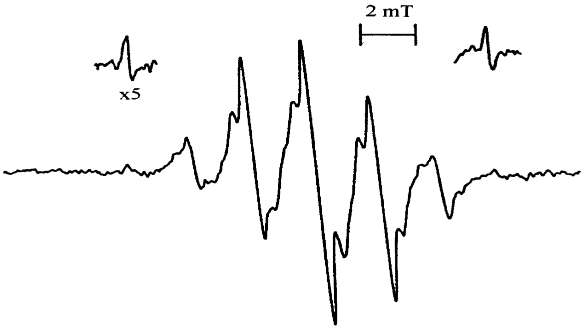

Fig. 1. EPR spectrum of γ-irradiated N-acetyl-α-amino-isobutyric acid powder at room temperature.

3. Results and Discussion

The EPR spectrum of γ-irridiated NA powder at room temperature is shown in Figure 1. The spectrum consist of 7 equally spaced (2.2 mT) lines with the relative intensity distribution 1 : 6 : 15 : 20 : 15 : 6:1. The single crystal spectrum of NA at room temperature is isotropic and equals the powder spectrum.

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Table 2. The hyperfine constants and **g** tensor values of trapped radicals of isobutyric acid derivatives.

Radical $(CH_3)_2\dot{C}COOH$	K	α_β Hyperfine coupling constant mT	**g** Tensor Average Values g_a	g_b	g_c	Method of Production	
α-Aminoisobutyric Acid	300	2.34	2.0034	2.0030	2.0022	γ-irradiated	[6]
α-Aminoisobutyric Acid	77	2.20	2.0022	2.0023	2.0024	X-irradiated	[7]
		2.17	2.0031	2.0031	2.0029		
		2.32	2.0042	2.0042	2.0033		
α-Hydroxyisobutyric Acid	113 – 300	2.22	2.0028	2.0025	2.0022	γ-irradiated	[8]
α-Aminoisobutyric Acid HCl	113 – 300	2.22	2.0029	2.0026	2.0024	γ-irradiated	[8]
N-acetyl-α-Amino-isobutyric Acid	113 – 300	2.2	2.0044	2.0042	2.0037	γ-irradiated	This work
N-carbamyl-α-amino-isobutyric Acid	113 – 300	2.13	2.0032	2.0026	2.0021	γ-irradiated	This work

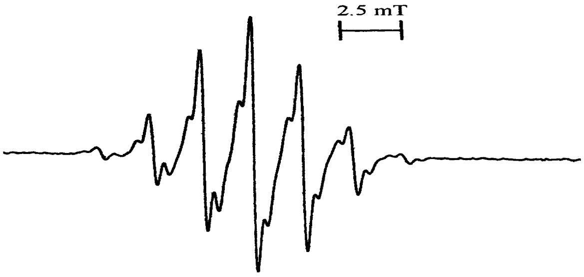

Fig. 2. EPR spectrum of γ-irradiated N-carbamyl-α-aminoisobutyric acid powder at room temperature.

This indicates that radical produced by γ-irradiation is $(CH_3)_2\dot{C}COOH$ as a result of abstraction of the $NHCOCH_3$ group from the undamaged molecules. In order to observe any anisotropy at low temperature, the experiments were performed at 113 K. The principal values of the hyperfine tensor for the methyl groups are given in Table 1. The **g** values of the radical in NA were found to be isotropic as at room temperature, i. e. 2.0041 ± 0.0005. Since no site splittings were observed, it can be concluded that the 4 molecules in the unit cell are magnetically equivalent. This radical was also observed in other γ-irradiated compounds, as shown Table 2, and their values agree with ours. The satellites flanking the main 7 lines in Fig. 1 are due to carboxylic hydrogen spin-flip transitions [8, 10 – 12]. For powders, the intensity ratio of the satellite line, I_1, to the main line, I_2, is

$$\frac{I_1}{2I_2} = \frac{3}{20}\frac{g_e^2}{B^2}\frac{\beta_e^2}{r^6},$$

where B is the magnetic field at which the main line appears and r the distance from the carbon atom containing the unpaired electron to the spin flipping carboxylic hydrogen. By using the experimental findings in Fig. 1, in the above equation we obtain $r = 1.8$ Å, and this seems to be reasonable.

Similar EPR spectra were observed for γ-irradiated NC between 113 and 300 K, and therefore the above interpretation is also valid for this compound. In this case the same radical is produced by the abstraction of the $NHCONH_2$ group from the same carbon atom.

Table 3. The EPR parameters of $(CH_3)_2\dot{C}COOH$ radical. The error for all the calculated **g** values is estimated as ± 0.0005.

Radical	Principal Values of **g**		Direction Cosines		
$(CH_3)_2\dot{C}COOH$	g_a	2.0032	0.6966	0.4408	−0.5661
	g_b	2.0026	−0.5973	−0.0806	−0.7979
	g_c	2.0021	−0.3973	0.8940	0.2071
	g_{av}	2.0026			

For NC, by using the experimental data of Fig. 2 in the above equation we obtain $r = 1.7$ Å. The single crystal data for this compound were not investigated; however, our single crystal EPR measurements indicate monoclinic symmetry of the crystal with the b axes along the long sides of the crystal. No site splitting into two compounds was observed when the magnetic field is along the b axis and whenever it is in the plane perpendicular to b. Both crystals exhibit magnetically slightly different four molecules in their unit cells. The isotropic behavior of the EPR spectra is due to the rapid rotations of the methyl groups around the C-COOH bond. The **g** values of NC were found to be slightly anisotropic as at room temperature. The principal values and the directional cosines are given in Table 3. However, the hyperfine coupling constants of the methyl groups in both compounds were very slightly anisotropic at 113 K. Their average values are 2.2 and 2.1 mT, respectively. The same $(CH_3)_2\dot{C}COOH$ radical has been observed in previous studies [6 – 8], as shown in the Table 2. In the EPR spectrum of these radicals, seven equally spaced lines of equal line width and hydrogen spin-flip transitions were observed. However, in the study by Box and Freund, at the 77 K, the absorption consists of a broad singlet and two weak satellites, and on warming [7] the satellites begin to fade at 145 K.

The negative-ion absorption fades at about 165 K, and this absorption consists of seven hyperfine lines. Also in the studies [6–8] the calculated hyperfine constant and **g** values are approximately consistent with our results. Slight differences between the average values of the hyperfine splittings of the methyl groups in the radical $(CH_3)_2\dot{C}COOH$ in these two compounds can be attributed to the slightly different matrix effects. The smallness of the anisotropy indicates the high mobility of the methyl groups in these compounds.

It can be concluded that γ-rays produce $(CH_3)_2\dot{C}COOH$ radicals by abstraction of the $NHCOCH_3$ group from NA or the $NHCONH_2$ group the from NC. The methyl groups in these radicals are very mobile and prevent a detailed establishment of any anisotropy of the hyperfine couplings of the hydrogens individually.

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