EPR of Gamma Irradiated N_α-Monochloroacetyl-α-Aminoisobutyric Acid

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Electron paramagnetic resonance of γ-irradiated single crystals of N_α-monochloroacetyl-α-amino-isobutyric acid were investigated at room temperature and 130 K. The paramagnetic center as attributed to the $(CH_3)_2\dot{C}COOH$ radical.

Key words: Gamma Irradiation; Free Radicals; α-Aminoisobutyric Acid Derivatives.

1. Introduction

EPR of γ-irradiated single crystals of N_α-monochloroacetyl-α-aminoisobutyric acid, (mClAc-Aib-OH), $(CH_3)_2C(NHCOClCH_2)COOH$ was observed and analyzed in different orientations of the crystal in the magnetic field. The crystals were investigated at room temperature and 130 K. The spectra were found to be temperature independent, and the radiation damage centers are attributed to $(CH_3)_2\dot{C}COOH$ radicals. The g values and the hyperfine coupling constants of the unpaired electron with the environmental methyl protons and OH proton were determined [1 – 8]. To our knowledge mClAc-Aib-OH has not been studied so far, and we have now undertaken a study of this compound. α-aminoisobutyric acid and their derivatives were studied with γ- and X-irradiated at between 77 K and 300 K and the samples were then gradually annealed to the room temperature in order to study the stability of the formed species [9 – 11].

The present work was undertaken to investigate the EPR spectra of γ- irradiated N_α-monochloroacetyl-α-aminoisobutyric acid, and give the EPR parameters of the paramagnetic species produced by γ-irradiation.

2. Experimental

N_α-monochloroacetyl-α-aminoisobutyric acid powder was obtained from the Institute of Organic Chemistry at the University of Padova, and its single crystals were grown from its concentrated ethyl acetate-petroleum ether solution by slow evaporation. The single crystal is orthorhombic with space group $P_{2_12_12_1}$, and its unit cell dimensions are: $a = 17.045$, $b = 8.798$, $c = 5.828$ Å. The unit cell contains four molecules [12]. The single crystals were irradiated at room temperature with a Co^{60} γ-ray source of 3 kGyh^{-1} for 5 h. The spectra were recorded with a Varian model X-band E-109 C EPR spectrometer using 2 mW microwave power. The magnetic field modulation frequency was 100 kHz. The single crystals were mounted on a goniometer, and the spectra were recorded in three mutually perpendicular planes by rotating the crystals around the a, b and c crystallographic axes with 10-degree intervals. The g values were calculated by comparison with a diphenylpicrylhydrazyl sample of $g = 2.0036$.

The γ-irradiated samples were stored at room temperature before recording the EPR spectra, and after the measurements the spectra were checked for several months to follow the stability of the formed species.

3. Results and Discussion

The EPR spectra of the $(CH_3)_2\dot{C}COOH$ radical in mClAc-Aib-OH exhibit mainly three different patterns, as shown in Figs. 1 – 3. These spectra appear when the magnetic field is parallel to the c, b and a axis, respectively. The spectra do not depend on the temperature at 300 to 130 K. A change in the g and hyperfine a values was observed when the crystal was rotated about the a, b and c axes. Their average values are $g = 2.0085 \pm 0.0005$ and $a = 1.66$ mT.

The spectra shown in Figs. 1, 2, and 3 exhibit 1:4:6:4:1, nearly 1:1:4:4:6:6:4:4:1:1 and 1:3:3:1:4: 12:12:4:6:18:18:6:4:12:12:4:1:3:3:1 patterns, respec-
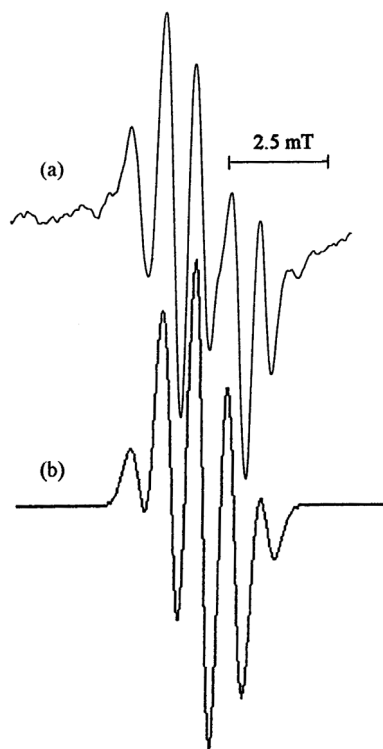
Fig. 1. The EPR Spectrum of γ-irradiated N_α-mClAc-Aib-OH obtained along the $B_o\|c$ axis (a), and its simulation (b).
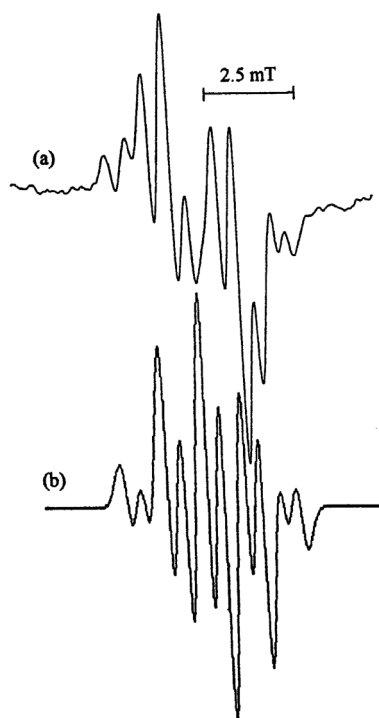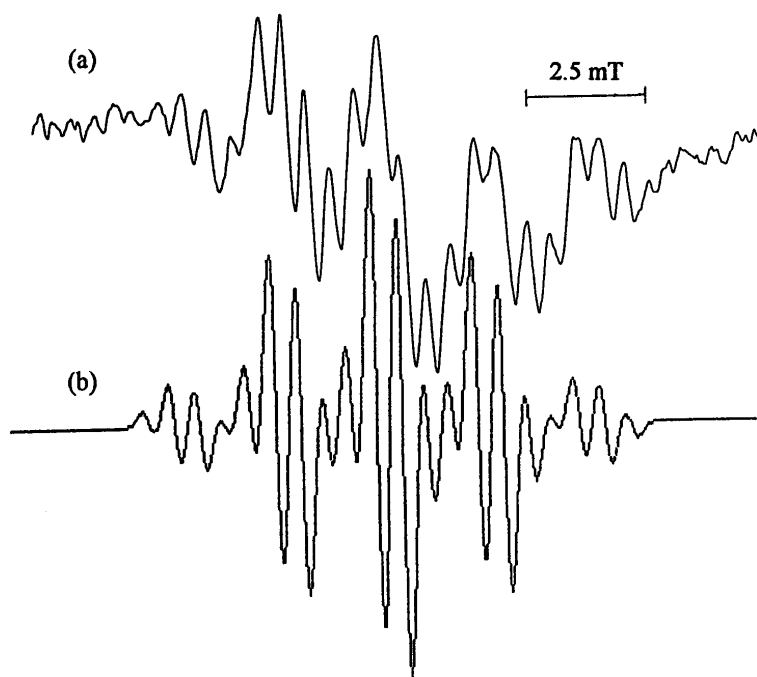

Fig. 2. Ditto for the $B_o\|b$ axis.

Fig. 3. Ditto for the $B_o\|a$ axis.

tively, and therefore indicate the hyperfine interaction of four protons with unpaired electron spin; the radical must thus be $(CH_3)_2\dot{C}COOH$, site splitting does not occur, and therefore the molecules in the unit cell of

Table 1. The EPR parameters of the $(CH_3)_2\dot{C}COOH$ radical. The error for all the calculated g values is estimated to be ± 0.0005.

Radical	Principal Values of A (mT) and g	Direction Cosines		
$(CH_3)_2\dot{C}COOH$	A_{CH3CH}			
	$A_{xx} = 2.30 \pm 0.1$	0.9052	0.3867	0.1763
	$A_{yy} = 1.68 \pm 0.1$	-0.3892	0.9209	-0.0211
	$A_{zz} = 0.99 \pm 0.1$	-0.1705	-0.0495	0.9841
	$a = 1.66 \pm 0.1$			
	A_{CH}			
	$a_{iso} = 0.65 \pm 0.1$			
	A_{CH3}			
	$a_{iso} = 0.55 \pm 0.1$			
	$g_a = 2.0106$	0.1580	-0.2144	-0.9639
	$g_b = 2.0084$	-0.1869	0.9514	-0.2427
	$g_c = 2.0064$	0.9691	0.2211	0.1097
	$g_{av} = 2.0085$			

the crystal are magnetically equivalent. The hyperfine splittings of the four protons of two methyl groups are anisotropic, its average value a being 1.66 mT. The hyperfine splitting of the one proton of the methyl protons is isotropic and the hyperfine constant a is 0.52 mT. The spectra were carefully measured when the magnetic field was parallel to the a, b, and c axes of the orthorhombic crystal. In these orientations the spectra of all crystallographically related radicals are superimposed.

The principal values and the directional cosines of the tensor g and hyperfine interaction for the β-protons with an unpaired electron are given in Table 1.

The EPR spectrum of γ-irradiated mClAc-Aib-OH, as shown in Fig. 1, exhibits an intensity distribution 1:4:6:4:1 with 0.8 mT spacing. This spectrum of γ-irradiated mClAc-Aib-OH single crystal was obtained along the $B_o \| c$ axis. The hyperfine interaction of the unpaired electrons with 4 equivalent protons of two methyl groups shows the intensity distribution 1:4:6:4:1. A spectrum simulated with the hyperfine parameters is presented in Fig. 1(b). The experimental and simulated EPR spectra were found agreewell with each other. The hyperfine constants are similar to those for carboxyl radicals [1 – 5].

The EPR spectrum of γ-irradiated mClAc-Aib-OH single crystal was obtained along $B_o \| b$ axis as shown in Fig. 2, at room temperature. The spectrum can easily be thought as consisting of ten lines with an intensity distribution of 1:1:4:4:6:6:4:4:1:1. The each line of quintets is further subdivided into doublet lines of spacing 1.5 mT with an intensity of 1:4:6:4:1. These five lines are also doublets, with a splitting constant of

0.65 mT. These inferences indicate the hyperfine couplings of the free electron with 4 equivalent protons of two methyl groups and the other one inequivalent proton of a methyl group.

Figure 3 shows the spectrum obtained with the magnetic field parallel to axis a. It also can be interpret in terms of twenty lines with relative intensities 1:3:3:1:4:12:12:4:6:18:18:6:4:12:12:4:1:3:3:1. The spectrum consists of 5 sets of 4 lines of 1:3:3:1 intensity distribution. These inferences indicate the hyperfine coupling of the free electron with 4 equivalent protons of two methyl groups, along with three different protons. Therefore the two protons of the methyl groups and the OH proton are magnetically equivalent. Each line of quintet of spacing 2.2 mT is further subdivided into four lines of spacing 0.55 mT, with an intensity distribution of 1:3:3:1, shown in Figure 3.

The spectrum consists of five lines of intensity ratio 1:4:6:4:1 with 0.75 and 2.2 mT spacing, respectively, (Figs. 1, 2, and 3) at all orientations of the magnetic field during the rotation of the crystal about its crystallographic axes. The $(CH_3)_2\dot{C}COOH$ radical produced from mClAc-Aib-OH that was also observed from irradiation of α-Aib-OH and derivatives [9 – 11, 13]. However, their spectrum exhibits different lines.

The simulation of the spectra, using the EPR simulation programme of McKelvey [14], are shown in Figs. 1(b), 2(b), and 3(b).

In the $(CH_3)_2\dot{C}COOH$ radical, only four protons of the two methyl groups show a resolvable coupling. This can be ascribed to the fact that β-coupling is angle-dependent as expressed by (1)

$$a_\beta = B_o + B_1 \cos^2 \theta, \tag{1}$$

where B_o is the spin polarization contribution ($B_o = 0 - 0.35$ mT), B_1 is the hyperconjugative contribution (≈ 5 mT) and θ is the angle between the π orbital and the C-H bond projection on a plane perpendicular to the $C_\alpha - C_\beta$ bond direction.

Presumably "invisible" protons lie close to the model plane of the singlet-occupied p orbital, so that $\theta = ca.\ 90°$, and the major second term in the equation is close to zero.

In conclusion, this finding supports the possibility that γ-irradiation produces a free radical in mClAc-Aib-OH by loss of $NHCOClCH_2$ from an undamaged molecule.

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