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EPR study of gamma irradiated DL-methionine sulfone single crystals

Bünyamin Karabulut [a, *], İlkay Yıldırım [b]

[a] Department of Computer Engineering, Faculty of Engineering, Ondokuz Mayis University, Atakum 55139, Samsun, Turkey
[b] Department of Radiotherapy, Vocational School of Health Services, Biruni University, Topkapi 34010, Istanbul, Turkey

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ABSTRACT

Electron paramagnetic resonance (EPR) study of gamma irradiated dl-2-amino-4-(Methylsulfonyl) butyric acid (dl-methionine sulfone, hereafter dl-ABA) single crystals and powder was performed at room temperature. It has been found that this compound indicates the existence of $\dot{C}O_2^-$ and $\dot{N}H_2$ radicals after γ-irradiation. While g and hyperfine splitting values for the $\dot{N}H_2$ radical were observed, for the $\dot{C}O_2^-$ radical, only the g factor was measured. The EPR spectra have shown that $\dot{N}H_2$ radical has two groups each having two distinct sites and $\dot{C}O_2^-$ radical has one site. The principal g and hyperfine values for all sites were analyzed.

1. Introduction

In order to get radicals from both organic and inorganic structures, they can be exposed to gamma rays. EPR technique is used to identify the radical species formed in the structure [1]. The EPR spectroscopy is the best way to determine the properties of radicals; however, its application is limited by the lifetime of free radicals produced by gamma-irradiation [2–5]. Dl-ABA is an essential sulfur containing amino acid, which is not synthesized by the body and must be obtained from food. It supplies mineral sulfur, which improves the tone and pliability of the skin, conditions the hair, strengthens the nails, and protects the cells from the airborne pollutants. Radiation induced free radicals in amino acids and derivatives have been investigated by many researchers [6–11]. Almanov et al. studied the radicals in irradiated DL-methionine single crystals and as a result they proposed the formed radical as $CH_3SCHCH_2CH(NH_2)COOH$ [9]. Øyen et al. investigated the radiation effects on L-asparagine and proposed three different radicals as $NH_2\dot{C}OHCH_2CH(NH_3)COO$, $NH_2COCH_2CH(NH_3)\dot{C}OOH$, and $NH_2COHCH_2\dot{C}H(NH_3)^+$ [10]. Osmanoğlu et al. carried out γ-irradiated L-glutamine hydrochloride and N-carbamoyl-L-glutamic acid and proposed $\dot{C}H$, $\dot{N}H_2$, $CH_2\dot{C}(NH_2)COOH$ radicals [11]. However, no EPR report has been found specifically for dl-ABA and no proposal made for $\dot{N}H_2$ and $\dot{C}O_2^-$ radicals in the literature. In this study, as a result of the investigation of the line distributions in the EPR spectra, the $\dot{N}H_2$ (amine) and $\dot{C}O_2^-$ radicals were observed for the first time. EPR study of the $\dot{N}H_2$ (amine) and $\dot{C}O_2^-$ radicals formed in dl-ABA was performed to get information about its properties, the behavior and the environment of the radicals.

2. Experimental

The saturated solution of commercially obtained dl-ABA was prepared and single crystals were obtained by using slow evaporation technique. The selected single crystals were irradiated by a ^{60}Co γ-ray source at room temperature at a dose of about 20 kGy, then EPR spectra were recorded. The crystal structure of dl-ABA was reported by Skvortsov et al. [17]. Due to the report, it crystallizes in orthorhombic system with the unit cell parameters, $a = 5.353(1)$ Å, $b = 5.353(1)$ Å, $c = 22.961$ Å. The space group is $P3_1/c$ and the unit cell contains four molecules ($Z = 4$). The EPR spectra were recorded in the X-band frequency on a Varian E-109 C spectrometer with 100 kHz field modulation.

3. Results and discussion

The EPR spectra of gamma-irradiated dl-ABA ($CH_3SO_2CH_2CH_2CH(NH_2)COOH$) single crystal were recorded at room temperature in three mutually perpendicular planes. The crystal was mounted on a goniometer and rotated at 10° steps between 0° and 180° for

* Corresponding author.
E-mail address: bbulut@omu.edu.tr (B. Karabulut).

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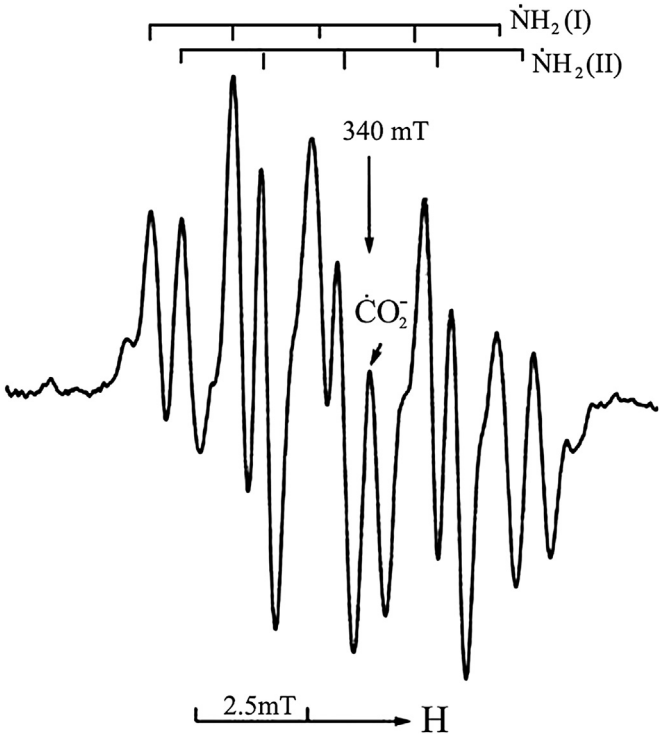
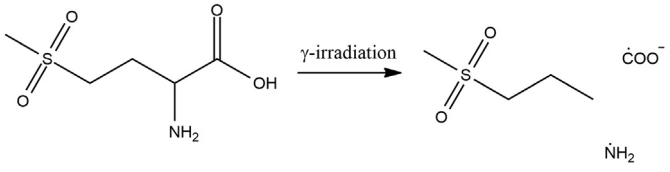


Fig. 1. EPR spectrum of the gamma irradiated dl-ABA single crystal. The magnetic field is in the *ac* plane making 110° with the *c* axis.



Scheme 1.

all planes. Fig. 1 shows one of the recorded EPR spectra of gamma-irradiated dl-ABA single crystal when the magnetic field makes 110° with the *c* axis in *ca* plane. In Fig. 1, the spectrum mainly consists of 10 lines with an intensity distribution of two groups of 1:3:4:3:1 and a single line near the central field. Two radicals are thought to be formed due to the gamma irradiation as shown in the Scheme 1. The $\dot{N}H_2$ radical has two identical protons and a single ^{14}N nucleus. Proton and nitrogen have nuclear spins 1/2 and 1, respectively. In an EPR spectrum, the identical two protons form a 1:2:1 intensity distribution and each line is splitted to a 1:1:1 intensity distribution due to an additional ^{14}N nucleus. As a result, a total of 1:3:4:3:1 intensity distribution occurs in the spectrum. Therefore, the two groups in the spectrum can be interpreted in terms of $\dot{N}H_2$ radicals and the single line as $\dot{C}O_2^-$ radical. The hyperfine lines resulting from ^{13}C nucleus are not visible in the spectrum at low and high field sides.

Table 2
The principal g and A values of $\dot{N}H_2$ and $\dot{C}O_2^-$ radicals observed in various lattices ($\Delta g = \pm 0.0003$ and $\Delta A = \pm 0.05$ mT).

Lattice	Radical	g_x	g_y	g_z	g_{iso}	A_{iso} (mT)	Reference
dl-ABA	$\dot{N}H_2$ (*I* – *I*)	2.0001	2.0090	2.0025	2.0039	1.87	*This study*
dl-ABA	$\dot{N}H_2$ (*I* – *II*)	2.0083	2.0045	1.9986	2.0038	1.84	*This study*
dl-ABA	$\dot{N}H_2$ (*II* – *I*)	2.0058	1.9986	2.0003	2.0016	1.87	*This study*
dl-ABA	$\dot{N}H_2$ (*II* – *II*)	2.0054	1.9964	2.0031	2.0016	1.87	*This study*
L-Glutamine·HCl	$\dot{N}H_2$	–	–	–	2.0037	2.04	[11]
Hydrazoic acid	$\dot{N}H_2$	–	–	–	2.0038	2.39	[12]
Ammonia	$\dot{N}H_2$	–	–	–	2.0048	2.38	[13]
dl-ABA	$\dot{C}O_2^-$	1.9976	1.9956	1.9985	1.9973	–	*This study*
Renal stone	$\dot{C}O_2^-$	1.9973	1.9973	2.0025	1.9990	–	[14]
Gypsum	$\dot{C}O_2^-$	2.0029	2.0027	1.9973	2.0009	–	[15]
Tooth enamel	$\dot{C}O_2^-$	2.0018	2.0018	1.9973	2.0003	–	[16]

The EPR spectra of gamma-irradiated dl-ABA single crystal can be expressed in terms of the spin Hamiltonian including **g** and **A** (hyperfine) tensors as:

$$\mathcal{H} = \beta \mathbf{B}\cdot\mathbf{g}\cdot\mathbf{S} + \mathbf{S}\cdot\mathbf{A}\cdot\mathbf{I} \quad (1)$$

It includes only electronic Zeeman and hyperfine interactions. The **g** and **A** (hyperfine) tensors were constructed and principal values, i.e. g_i and A_i (i = x, y, z), were calculated by using the diagonalization method as described in Ref. [18]. The calculated values were given in Table 1.

The curve fitting procedure [18] was used to plot the magnetic field values of all spectral lines against the rotation angle for all planes (Table 2). Fig. 2 shows the graph and also represents the change in hyperfine values expressed in magnetic field units. The sites of $\dot{N}H_2$ radical center I and the $\dot{C}O_2^-$ radical were indicated for the *ca* plane in Fig. 2.

From the spectral behavior, the gamma-irradiated dl-ABA single

Table 1
The EPR parameters of $\dot{N}H_2$ and $\dot{C}O_2^-$ radicals in γ-irradiated dl-ABA single crystals at room temperature ($\Delta g = \pm 0.0003$ and $\Delta A = \pm 0.05$ mT).

Radical type	Site	g values	Direction cosines			Hyperfine values (mT)	Direction cosines		
			a	b	c		a	b	c
$\dot{N}H_2$(*I*)	I	$g_x = 2.0001$	0.625	−0.380	−0.682	$A_x = 1.89$	−0.745	−0.284	0.604
		$g_y = 2.0090$	0.606	0.787	0.117	$A_y = 1.57$	0.463	−0.872	0.161
		$g_z = 2.0025$	0.492	−0.486	0.722	$A_z = 2.16$	0.480	0.400	0.781
	II	$g_x = 2.0083$	0.658	−0.655	0.372	$A_x = 1.75$	0.847	−0.505	0.165
		$g_y = 2.0045$	0.421	0.729	0.539	$A_y = 1.56$	0.511	0.860	0.012
		$g_z = 1.9986$	0.624	0.199	−0.756	$A_z = 2.22$	−0.148	0.074	0.986
$\dot{N}H_2$ (*II*)	I	$g_x = 2.0058$	−0.735	−0.678	0.029	$A_x = 1.81$	0.836	0.482	0.261
		$g_y = 1.9986$	0.511	−0.525	0.680	$A_y = 1.42$	0.451	−0.876	0.171
		$g_z = 2.0003$	−0.446	0.515	0.732	$A_z = 2.38$	0.311	−0.025	−0.950
	II	$g_x = 2.0054$	0.712	−0.559	0.425	$A_x = 1.80$	0.977	0.205	0.056
		$g_y = 1.9964$	0.692	0.454	−0.562	$A_y = 1.65$	0.186	−0.952	0.242
		$g_z = 2.0031$	0.121	0.694	0.710	$A_z = 2.17$	0.103	0.227	−0.969
$\dot{C}O_2^-$	–	$g_x = 1.9976$	0.618	0.704	0.351	–	–	–	–
		$g_y = 1.9956$	0.557	−0.706	0.437				
		$g_z = 1.9985$	0.555	−0.074	−0.828				

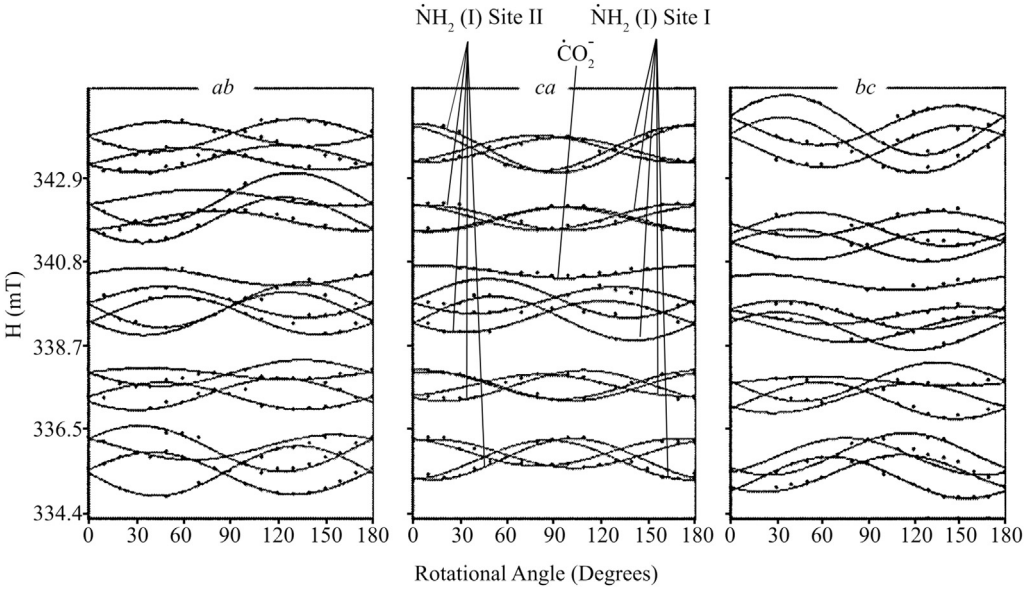


Fig. 2. Variation of the magnetic field values of all lines due to rotation angle in three mutually perpendicular planes of the gamma irradiated dl-ABA single crystal.

crystal can be collected into two groups each having two sites as shown in Fig. 2. The lines in the EPR spectrum were attributed to two different $\dot{N}H_2$ paramagnetic centers. The source of this radical is two equivalent protons, i.e. having the same bond lengths with the nitrogen atom, and one ^{14}N nucleus. The interaction between the unpaired electron of the radical and two identical protons, namely $H_{1\alpha}$ and $H_{2\alpha}$, gives 3 lines with a 1:2:1 intensity distribution. Hyperfine splitting of $H_{1\alpha}$ and $H_{2\alpha}$ are very close to each other, so in some orientations the lines overlap. Each of the hyperfine splitting of H_α protons is further separated to a 1:1:1 intensity distribution due to ^{14}N nucleus. The hyperfine interactions of the unpaired electron with the protons and the nitrogen nucleus in the EPR spectra are almost equal to each other. For the $\dot{N}H_2$ radicals, the intensity distribution in the EPR spectra was obtained as 1:3:4:3:1. The hyperfine splitting values of ^{14}N and protons appeared to be equally for these two centers. It can be inferred from the EPR spectra that the A and g values have small anisotropy. From Fig. 2, it can be said that the $\dot{C}O_2^-$ radical has a single line between 339 mT and 341 mT and so has only one site. Compared to the non-oxidized form of dl-ABA or dl-methionine [9], different radicals were obtained as a result of irradiation.

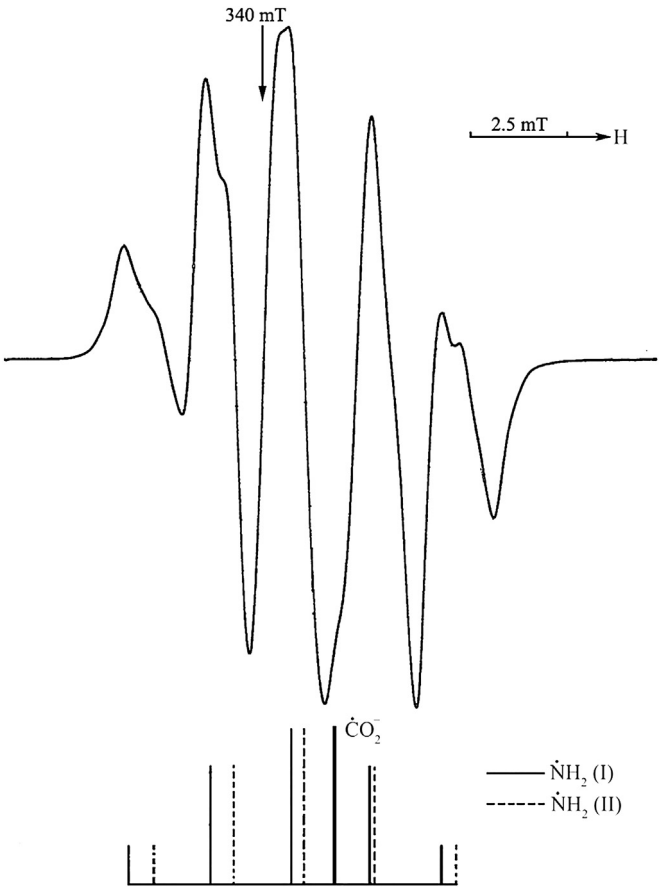


Fig. 3. Powder EPR spectrum of the gamma irradiated dl-ABA. Solid lines and dashed lines represent the $\dot{N}H_2$ radical centers I and II, respectively, while the bold line represents $\dot{C}O_2^-$ radical.

The EPR spectra taken at the liquid nitrogen temperature have not changed significantly compared to those at the room temperature. Therefore, detailed comparison for the temperature range has not been carried out. The results are shown in Table 1. Due to the behavior of the spectrum, the complex is said to have two groups and each group consists of two sites, as shown in Fig. 2.

Fig. 3 shows the recorded EPR spectrum of radiation induced dl-ABA powder. The g values are 1.9958, 1.9941 and 1.9879 for the two $\dot{N}H_2$ and one $\dot{C}O_2^-$ paramagnetic centers, respectively. The hyperfine values for the group I and II of $\dot{N}H_2$ radicals are 2.13 and 1.80 mT, respectively. The protons and nitrogen have nearly the same hyperfine values. The results are said to be compatible with the single crystal values. The stick diagram under the figure represents the intensity distributions of the radicals. Solid lines and dashed lines represent the $\dot{N}H_2$ radical centers I and II, respectively, while the bold line represents $\dot{C}O_2^-$ radical.

4. Conclusion

From the EPR spectra of gamma irradiated dl-ABA single crystals; we conclude:

i. The site symmetry conforms the orthorhombic crystal system.

ii Two groups of $\dot{N}H_2$ radicals have been identified and each of the groups has two distinct sites.

iii The EPR analysis shows that the $\dot{N}H_2$ radicals have rhombic symmetry while the $\dot{C}O_2^-$ radical has nearly axial symmetry.

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