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EPR investigation of gamma-irradiated iminodiacetic and amino acid derivatives

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Electron paramagnetic resonance spectroscopy was used to investigate the radiation damage in powder of iminodiacetic acid hydrobromide and methyl-DL-*α*-aminobutyrate hydrochloride at room temperature. It has been found that gamma-irradiation produces the $HN\dot{C}HCH_2(COOH)_2$ radical in the first and the $CH_2\dot{C}(NH_2)COOCH_3$ radical in the second. The *g* values of the radicals and the hyperfine structure constants of the unpaired electron with the protons and ^{14}N nucleus were determined. The results were found to be in good agreement with the existing literature data.

Keywords: EPR; *g*amma irradiation; free radicals; amino acid derivatives

INTRODUCTION

During irradiation of solid amino and iminodiacetic acid derivatives, free radicals are formed. Due to the fact that the unpaired electron is involved in free radicals, these species are paramagnetic and the most used method for detecting free radicals is electron paramagnetic resonance (EPR) technique [1]. When an unpaired electron in a magnetic field interacts with a nuclear spin, the spectrum splits into two or more lines, which produces a hyperfine structure in the spectrum. The splitting of the spectrum is expressed in terms of a hyperfine coupling constant (*a* value), and the relative position of the spectrum is expressed by the spectroscopic splitting factor (*g* value) [2]. EPR is one of the many spectroscopy techniques that has been used for many years to study and characterize different types of materials. The biological molecules, amino and iminodiacetic acid derivatives are examples of materials that have been studied by EPR spectroscopy through detection of paramagnetic species [3-10]. Iminodiacetic acid hydrochloride and N-(2-hyroxyethyl) iminodiacetic acid powders were gamma-irradiated and studied by EPR at room temperature [11]. The radiation damage center was attributed to $HN\dot{C}HCH_2(COOH)_2$ and $HOCH_2CH_2N\dot{C}HCH_2(COOH)_2$ radicals, respectively. Furthermore, the investigation of gamma-irradiated powders of glycyl-L-glutamine by means of EPR revealed that the radical produced by radiation was $CH_2\dot{C}(NH)COOH$ [12]. To our knowledge, iminodiacetic acid hydrobromide (IDAAHBr), $HN(CH_2COOH)_2{\cdot}HBr$, and methyl-DL-*α*-aminobutyrate hydrochloride (MDLAHCl), $CH_3CH_2CH(NH_2)COOCH_3{\cdot}HCl$, were not investigated. Moreover, these samples are biologically important organic substances. Therefore, the goal of this study was to investigate the defects, induced by gamma-irradiation in powders of IDAAHBr and MDLAHCl, and to determine their spin Hamiltonian parameters at room temperature.

EXPERIMENTAL

The samples, used in this study, were obtained from commercial sources. Powder samples of the compounds were exposed to gamma-irradiation from ^{60}Co gamma-ray source (Nordion-Canada, model JS 9600) at a dose rate of 2 kGy/h for a total of 10 h at room temperature. After irradiation, samples were kept in plastic bags at room temperature and in dark. Quartz tubes were used for the EPR measurements of the samples. The EPR spectroscopy was carried out in a Varian model X-band E-109C EPR spectrometer at room temperature. The modulation amplitude was below 5.10^{-2} mT and the microwave power was 2 mW. The *g* factors were found by comparison with a dipenhylpicrylhydrazyl (DPPH) sample at g = 2.0036. The EPR spectrum of gamma-irradiated samples was monitored during a four month period in order to follow the stability of the formed species. The EPR spectra were analyzed by a computer simulation program [13].

RESULTS AND DISCUSSION

The characteristic EPR spectrum of the

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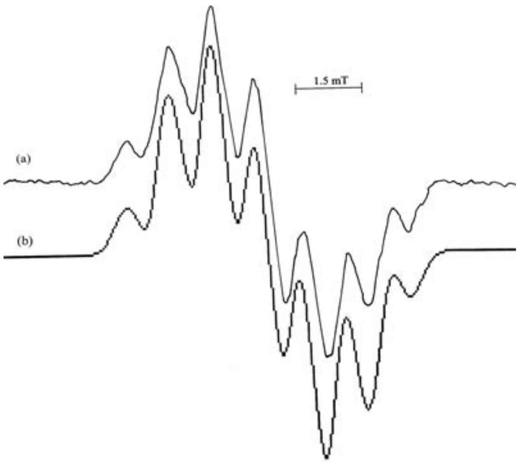

Fig. 1. (a) The EPR spectrum of gamma-irradiated IDAAHBr powder at room temperature; (b) simulation form of the spectrum using a_{CHCH2} = 1.03 mT, a_{NH} = 0.69 mT, a_N = 0.69 mT and line width 0.36 mT.

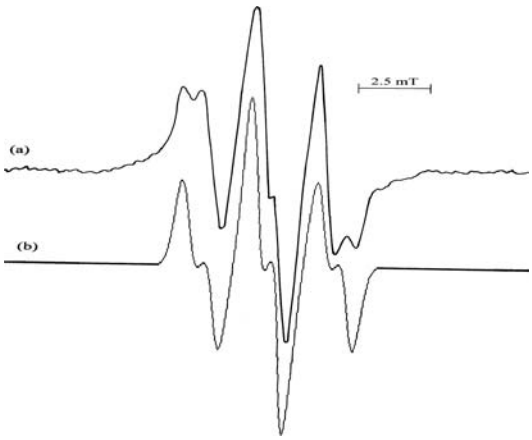

Fig.2. (a) The EPR spectrum of gamma-irradiated MDLAHCl powder at room temperature, (b) simulation form of the spectrum using a_{CH2} = 2.34 mT, a_{NH} = 0.74 mT, a_N= 0.25 mT and line width 0.30 mT.

gamma-irradiated IDAAHBr in Fig. 1a exhibits an intensity distribution of 1:5:11:14:11:5:1, and can be attributed to $H\dot{N}HCH_2(COOH)_2$ radical. Similar intensity distributions were observed in $CH_3\dot{N}H$ radical by Hadley and Volman [14]. The $HN\dot{C}HCH_2(COOH)_2$ radical exhibits an intensity distribution of 1:3:3:1 because of the α-proton and the methylene protons which are all magnetically equivalent. On the other hand, the hyperfine constants of β-protons are greater than α-proton [3, 15] in some studies. But there are some studies in which the hyperfine constants of β-protons are smaller than α-proton or equivalent [11, 12, 16]. Moreover, the spectra exhibit 4 lines with the intensity distribution of 1:2:2:1 owing to NH proton and ^{14}N nucleus (I=1) with equal coupling constants. The binomial expansion for this spectrum is given as

1:2:2:1+3:6:6:3+3:6:6:3+1:2:2:1 = 1:5:11:14:11:5:1.

The EPR spectrum for a larger number of inequivalent protons can be found by graphic construction which is a mathematical record of the EPR spectrum. The intensity ratio for more complicated spectra is obtained by direct addition of the line intensities of simple spectra, the lines being displaced relatively to each other by the coupling constant [17]. The hyperfine interaction of the unpaired electrons with one α-proton, two equivalent methylene protons, one NH proton, and ^{14}N nucleus can be taken as a_{CHCH2} = 1.03 mT, a_{NH} = 0.69 mT and a_N = 0.69 mT. The spectrum, simulated with these hyperfine parameters, is presented in Fig. 1b. The paramagnetic centre has been attributed to the $HN\dot{C}HCH_2(COOH)_2$ radical [16] in the gamma-irradiated powders of iminodiacetic acid at room temperature. This is similar to our proposed radical, and the reported values of a_{CHCH2} = 1.40 mT, a_{NH} = 0.58 mT, a_N = 0.39 mT are in good agreement with our results. Moreover, a radical similar to this has been observed in the gamma-irradiated powders of iminodiacetic acid hydrochloride [11].

The measured value of the g factor is $g = 2.0029 \pm 0.0005$. The g value of the radical, discussed here, seems to be in agreement with the literature data for their analogs and various amine radicals [18 - 20]. Consequently, it can be stated that gamma-irradiation produced free radicals in IDAAHBr by loss of the hydrogen atom bond from the carbon atom bond to the ^{14}N nucleus and COOH group.

The gamma-irradiated powder of MDLAHCl at room temperature gives the spectrum shown in Fig. 2a. This spectrum can easily be thought as consisting of 6 lines with intensity distribution of 1:1:2:2:1:1. This 6 lines in the spectra are due to the radical $CH_2\dot{C}(NH_2)COOCH_3$ in which the unpaired electron interacts significantly with two methylene protons and one NH proton. The spectrum can again be interpreted as a 1:1 doublet of a 1:2:1 triplet. In a thorough examination of the spectrum, it can be seen that it consists of a triplet with a spacing of 2.34 mT. Then each line of the triplet is further into doublet lines with spacing of 0.74 mT. A simulation of the MDLAHCl spectrum is shown in Fig. 2b, using the hyperfine coupling constants a_{CH2} = 2.34 mT, a_{NH} = 0.74 mT and a_N = 0.25 mT. There is good agreement between the experimental and simulated EPR spectra. The line width of the spectrum is somewhat larger than the hyperfine coupling constant of the nitrogen nuclei (a_N = 0.25 mT), and therefore the hyperfine splitting of the nitrogen nuclei is not observed in the spectrum. The g value of radical is g

= 2.0030 ± 0.0005. The *g* value and the hyperfine constants of the radical discussed here agree well with some other literature data [12, 16, 21, 22].

Different values of the hyperfine coupling constants of the methylene protons have been found also by the other authors [17, 23 - 26]. These differences in methylene protons caupling constants can be expressed by the relation [27]

$$a_\beta = B_0 + B_1\cos^2\theta \qquad (1)$$

Here, B_0 is the spin polarization contribution (B_0 = 0 - 0.35 mT), B_1 is hyperconjugative contribution (B_1 = 5.00 mT) and the dihedral angle, θ, is the angle between the p_π orbital of the unpaired electron and the C-H bond projections on a plane perpendicular to the C_α-C_β bond direction. Therefore, when θ varies, the hyperfine constant varies accordingly and a_β approaches zero [24]. According to the value of the hyperfine coupling constants of the methylene protons obtained in this study, the dihedral angle, θ , varies approximately between 47^0-50^0. As a conclusion, we can state that gamma-irradiation produces free radicals in MDLAHCl by loss of one hydrogen atom from CH group. The hydrogen abstraction is one of the most common mechanisms of producing free radicals in aliphatic compounds [28].

CONCLUSION

The analysis of EPR spectra indicated the presence of amine type free radical in gamma-irradiated powder samples. The EPR parameters and the structure of the radicals could be determined.

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ИЗСЛЕДВАНЕ НА ГАМА-ОБЛЪЧЕНИ ИМИНО-ДИОЦЕТНИ И АМИНОКИСЕЛИННИ ПРОИЗВОДНИ ЧРЕЗ ЕЛЕКТРОННО-ПАРАМАГНИТЕН РЕЗОНАНС

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(Резюме)

Използвана е електронно-парамагнитна спектроскопия за изследване на промените в прахове от хидробромида на имино-диоцетната киселина и хидрохлорида на метил- DL-α-маслената киселина при стайна температура. Установено е, че облъчването с гама-лъчи води до получаването на $HN\dot{C}HCH_2(COOH)_2$ – радикали при първия и $CH_2\dot{C}(NH_2)COOCH_3$– радикали при втория изследван образец. Определени са g-стойностите за радикалите и константите за свръх-фината структура на не-сдвоения електрон с протоните и ^{14}N-ядрата. Получените резултати са в добро съгласие с съществуващите литературни данни.