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EPR studies of the free radicals generated in gamma irradiated amino acid derivatives

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ABSTRACT

Gamma irradiated powder forms of *N*-acetyl-DL-aspartic acid, *N*-carbamoyl-DL-aspartic acid and *N*-methyl-L-serine were investigated by electron paramagnetic resonance spectroscopy (EPR) at room temperature. In these compounds, the paramagnetic centers formed after irradiation were attributed to the $HOOCCH_2\dot{C}HCOOH$, $COOH\dot{C}HCHNH$ and $HOCH_2\dot{C}HCOOH$ radicals, respectively. The g values and the hyperfine coupling constants for the radical species are with values of $g = 2.0038 \pm 0.0005$, $a_\alpha = 2.15$ mT, $a_\beta^{(1)} = 3.84$ mT and $a_\beta^{(2)} = 2.15$ for the first radical, $g = 2.0039 \pm 0.0005$, $a_\alpha = 1.7$ mT, $a_\beta^{(1)} = 0.62$ mT, $a_\beta^{(2)} = 0.54$ mT, $a_\gamma = 0.53$ mT for the second radical and $g = 2.0039 \pm 0.0005$, $a_\beta^{(1)} = 2.40$ mT, $a_\beta^{(2)} = 1.83$ mT and $a_\alpha = 1.83$ mT for the third radical. The free radicals formed in three compounds were found to be stable for three months at room temperature. It was concluded that, spin density was concentrated predominantly in the $2p_\pi$ orbital of the carbon atom.

1. Introduction

There are many studies examining the effects of free radicals on amino acids, food and drugs [1–3]. Free radicals have very negative effects on living tissues and cause many diseases as well as ageing [4,5]. It is known that EPR spectroscopy is one of the most powerful methods used to determine the identity and structure of free radicals [6–8]. For this reason, EPR spectroscopy is widely used in the investigation of radiation damage centers in amino acids and their derivatives [9–15]. Mariko Ogawa et al. studied the EPR of gamma-irradiated powders of L-glutamic acid and L-glutamic acid hydrochloride and the radiation damage centers formed after irradiation were attributed to the $HOOCCH_2CH_2\dot{C}H(NH_3^+)$, $HOOCCH_2CH_2CH(NH_3^+)\dot{C}OOH$, $HOOCCH_2CH_2CHC\dot{O}OH$, $HOOCCH_2CH_2C(NH_3^+)COO^{\cdot}$ and $HOOCCHCH_2CH(NH_3^+)COO^{\cdot}$, radicals [16]. Moreover Zengin et al. [17] were studied powders of γ-irradiated some glutamic acid derivatives between 100 and 350 K and the radiation damage center of these samples were attributed to the $CH_3CO\dot{N}H$, $-\dot{C}_3H_5$,$-\dot{C}H$ and $-\dot{N}H_2$ radicals respectively. Aspartic acid, being a non-essential amino acid, is a major excitatory neurotransmitter in the central nervous system [18]. Serine is a key component for the synthesis of neurotransmitters glycine and D-serine in brain [19]. Therefore we aim to investigate the defects formed by gamma-irradiation of *N*-acetyl-DL-aspartic acid (NADLAA), *N*-carbamoyl-DL-aspartic acid (NCDLAA) and *N*-methyl-L-serine (NMLS), and to determine their spin hamiltonian parameters at room temperature.

2. Experimental

The samples used in this work were purchased from Aldrich. Powder samples of the compounds were gamma-irradiated with ^{60}Co γ-ray source at a dose rate of 0.85 kGy/h for about 30 h at room temperature. Irradiated samples were kept in plastic bags at room temperature in the dark. The samples were placed in quartz tubes and EPR spectra were recorded at room temperature. The EPR measurements was carried out in Varian model X-band E-109C EPR spectrometer using 2 mW microwave power, microwave frequency of 9.8 GHz, modulation amplitude 0.1 mT, magnetic field modulation frequency 86 kHz. The EPR spectra of the powder samples are shown in Figs. 1a, 2a and 3a, respectively. The *g* values at the center of the spectra were found by comparison with a dipenhylpicrylhydrazyl (DPPH) sample ($g = 2.0036$). The simulations obtained using the McKelvey [20] simulation program are shown in Figs. 1b, 2b and 3b, respectively.

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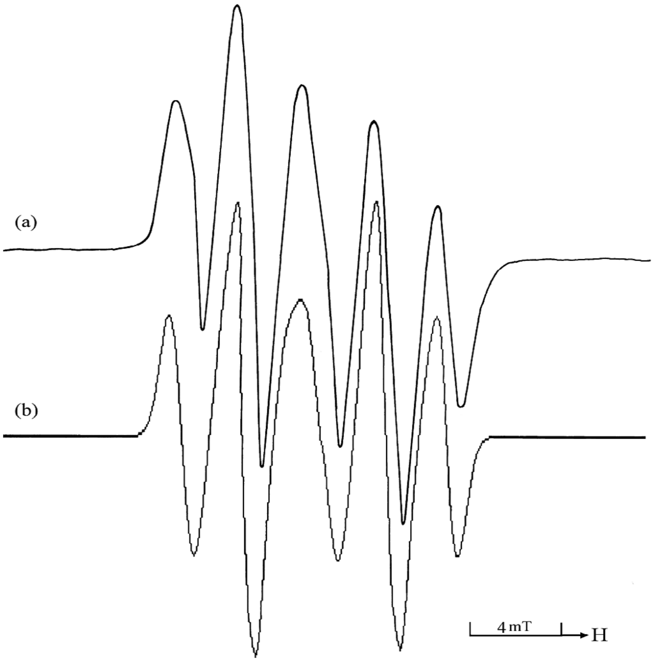

Fig. 1. (a) The EPR spectrum of gamma irradiated NADLAA powder at room temperature. (b) Simulation form of the spectrum using a_α = 2.15 mT, $a_\beta^{(1)}$ = 3.84 mT, $a_\beta^{(2)}$ = 2.15 mT and linewidth 0.58 mT.

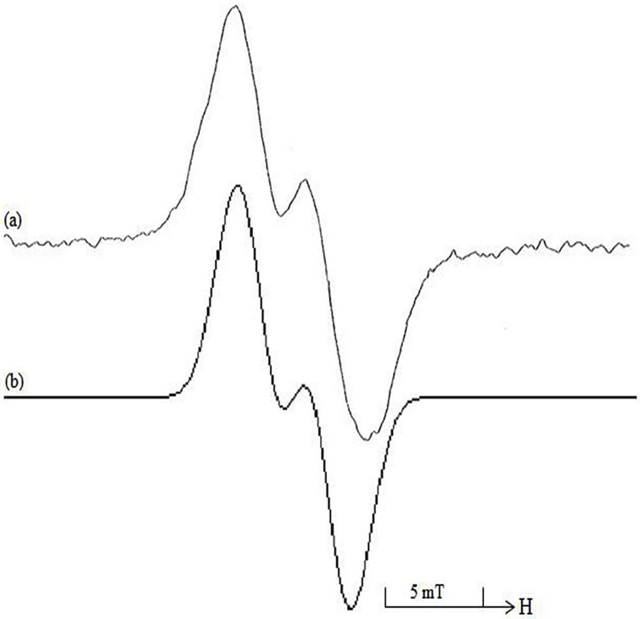

Fig. 2. (a) The EPR spectrum of gamma irradiated NCDLAA powder at room temperature. (b) Simulation form of the spectrum using a_α = 1.7 mT, $a_\beta^{(1)}$ = 0.62 mT, $a_\beta^{(2)}$ = 0.54 mT, a_γ = 0.53 mT.

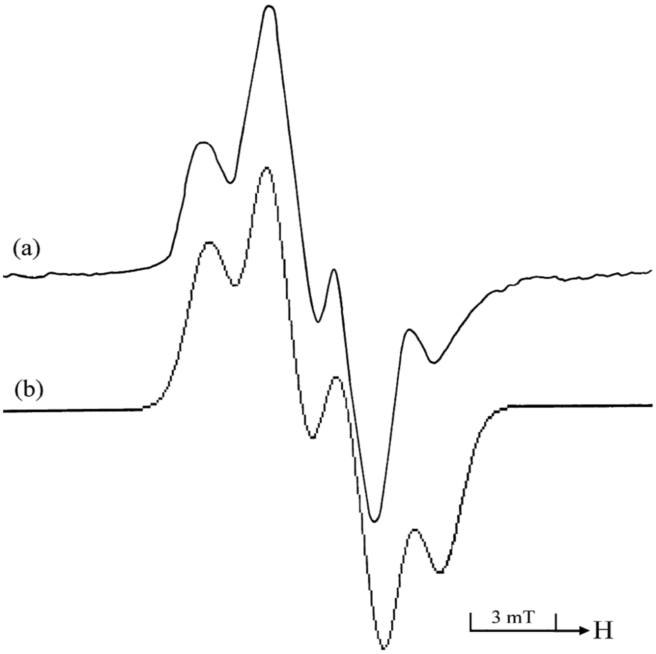

Fig. 3. (a) The EPR spectrum of gamma irradiated NMLS powder at room temperature. (b) Simulation form of the spectrum using a_α = 1.83 mT, $a_\beta^{(1)}$ = 2.40 mT, $a_\beta^{(2)}$ = 1.83 mT and linewidth 1.12 mT.

3. Results and discussion

EPR spectrum of gamma irradiated NADLAA powder is shown Fig. 1a. The radical species formed in this spectrum can be identified from the number of hyperfine lines. The spectrum with an intensity distribution of 1:2:2:2:1 consists of a doublet with a spacing of 3.84 mT. Then each line of the doublet is further subdivided into three lines of spacing 2.15 mT, with an intensity distribution of 1:2:1. It is concluded that the binomial expansion for the spectrum is:

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

Graphic construction, which is a mathematical record of an EPR spectrum, can be used to interpret the EPR spectrum for a larger number of inequivalent protons [21]. 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) [22]. These inferences lead us to the result that the unpaired electron interacts with one α-proton and two β-protons which are magnetically inequivalent. The hyperfine interaction with the protons are $a_\alpha = 2.15$ mT, $a_\beta^{(1)} = 3.84$ mT and $a_\beta^{(2)} = 2.15$ mT α-proton and $\beta^{(2)}$–protons are magnetically equivalent. The hyperfine splitting of other H atoms are somewhat smaller than the line width of the spectrum; therefore, there is some asymmetry visible on the low field line of the experimental spectrum. g value of the spectrum attributed to the $HOOCCH_2\dot{C}HCOOH$ radical is calculated as $g = 2.0038 \pm 0.0005$. The simulation of spectrum obtained with the hyperfine values given above is shown in Fig. 1b. The spectrum and intensity distribution obtained in this study are similar to the gamma irradiated L-glutamic acid hydrochloride powders [23]. However, the hyperfine coupling constants of the beta protons are smaller than those of our study. In another study, $HOOCCH_2CH_2\dot{C}HCOOH$ radical were formed in gamma irradiated glutamic acid and glutamic acid hydrochloride single crystals at temperature range of 77–300 K [16]. The hyperfine constants were calculated as $a_\beta^{(1)} = 4.58$ mT, $a_\beta^{(2)} = 2.39$ mT and $a_\alpha = 2.33$ mT. This radical and hyperfine coupling constants values are similar to radical obtained from L-glutamic acid hydrochloride. The g value of this radical is in accordance with their analogs and various other alkyl type radicals [24–26]. The discussed radical here are planar structures. The unpaired electron is often delocalized over α-carbon