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Simulation Study of Paramagnetic Centers Induced in Glycine Tertbutyl Ester Hydrochloride and L-α-alanine Ethyl Ester in Solid State

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Abstract: The paramagnetic centers formed in glycine tert-butyl ester hydrochloride and L-α-alanine ethyl ester after irradiated was determined using EPR spectroscopy. The EPR spectra of the samples were attributed to the $H_2N\dot{C}HCO_2C(CH_3)_3$.HCl and $CH_3\dot{C}HCOCH_2CH_3$ radicals, respectively. The magnetic parameters obtained from the spectra were evaluated. The spectra were seen to be stable for more than 2 months at 300 K. Magnetic parameters and the electronic structure of the paramagnetic centers (radicals) were determined with a simulation method.

Keywords: Electron paramagnetic resonance; paramagnetic center; amino acid; irradiation; simulation method.

Katı Durumdaki Glisin Tert-Butil Ester Hidroklorür Ve L-A-Alanin Etil Ester'de Oluşan Serbest Radikallerin Simülasyon Metodu İle İncelenmesi

Öz: Gama ışınlaması sonucu glisin tert-butil ester hidroklorür ve L-α-alanin etil ester'de oluşan paramanyetik merkezler belirlenmiştir. EPR spektroskopisinde elde edilen deneysel spektrumlar, $H_2N\dot{C}HCO_2C(CH_3)_3$.HCl and $CH_3\dot{C}HCOCH_2CH_3$ paramanyetik merkezlere (radikallerine) atfedilmiştir. Bu spektrumlardan elde edilen manyetik değerler hesaplanmıştır. Spektrumların oda sıcaklığında 2 aydan daha fazla kararlı (sönmediği) kaldığı görülmüştür. Radikallerin (paramanyetik merkez) manyetik parametreleri ve elektronik yapıları similasyon metoduyla doğrulanmıştır.

Anahtar kelimeler: Elektron paramanyetik rezonans; paramanyetik merkez; amino asit; ışınlama; simülasyon metod.

1. Introduction

There are many studies with EPR of free radicals formed in the γ- irradiated biological systems [1-5]. Electron paramagnetic resonance (EPR) spectroscopy of irradiated amino acids and their derivatives have been widely used to identification of the radicals and electronic structures [6-13]. The γ- and x-irradiated single crystals and solid state glycine and derivatives were investigated at between 77 K and 300 K with EPR. Spectroscopic properties and hyperfine constants were determined [14-17]. Alanine and alanine derivatives have been studied by many workers using EPR spectroscopy [18-20]. Alanine is an important role for living organisms [18]. This paper studies the radicals formed in biologically important samples such as glycine tert-butyl ester hydrochloride

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(GTBEHCl) and L-α-alanine ethyl ester (LAEE). The results of this study were compared with those obtained previously in the literature.

2. Material and Methods

GTBEHCl and LAEE were obtained from commercial sources. The samples were gamma-irradiated with ^{60}Co γ-ray source for approximately 12 hours at 300K. The EPR spectra were recorded using 2 mW power and 100 kHz magnetic field modulation at 300 K by Varian model X-band E-109C EPR spectroscopy. The paramagnetic centers induced in the samples were measured in terms of stability soon after the irradiation. The spectra are presented in Fig. 1a and Fig. 2a respectively. The g values were determined by using DPPH. EPR spectrum has also confirmed using simulation method. The spectra simulated are given in Figs.1b,2b.

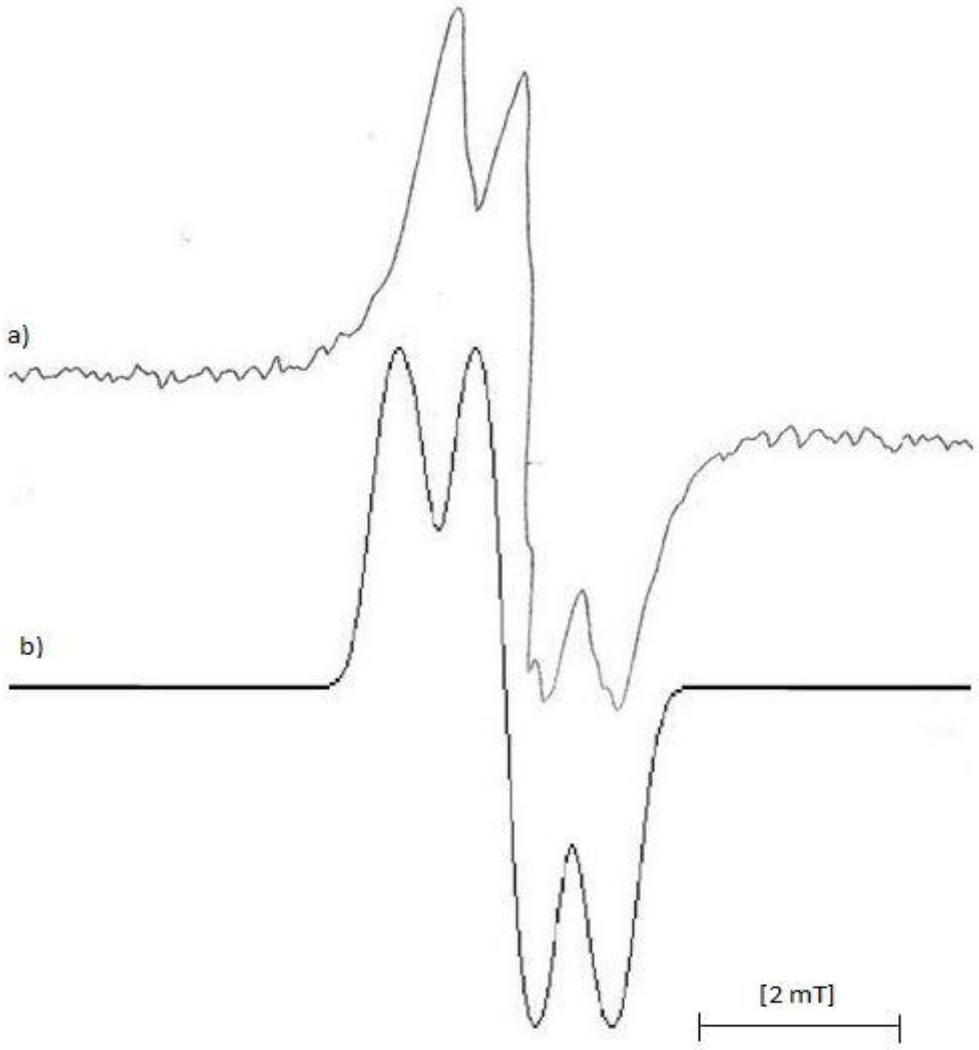

Fig. 1. a) The experimental spectrum of γ-irradiated **glycine tertbutyl ester hydrochloride** at 300 K.

b) Simulated form of the spectrum using a_{CH} = 1.32 mT, a_{NH} = 1.3 mT, a_N = 0.36 mT and linewidth 0.50 mT.

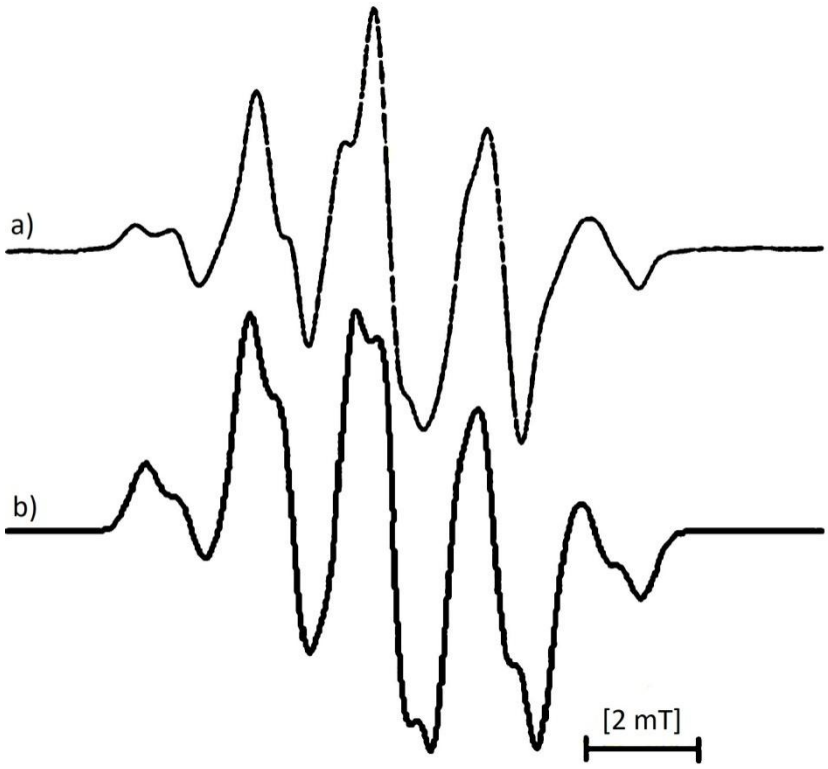

Fig. 2. a) The experimental spectrum of γ-irradiated **L-α-alanine ethyl ester** at 300 K.
b) Simulated form of the spectrum using $a^1_{CH} = a^1_{CH3} = a^2_{CH3} = a^3_{CH3}$=2.40 mT, a^1_{CH2} = 1.0 mT and a^2_{CH2} = 0.63 mT and linewidth 0.45 mT.

3. Result and discussion

EPR spectrum of glycine tert-butyl ester hydrochloride (GTBEHCl) at 300 K can be seen in Figure 1a. The spectrum simulated with hyperfine parameters (a_{CH} = 1.32 mT, a_{NH} = 1.3 mT, a_N= 0.36 mT) is presented in Fig.1b. The spectrum may consist of three lines of 1:2:1. The free electron interacts with one CH protons and one NH_2 and N nitrogen atom , which show lines of 1:2:1. The linewidth (ΔH= 0.50 mT) is larger than the coupling constant of N nitrogen atom (a_N= 0.36 mT), and therefore splitting of N nitrogen atom was not seen in the spectrum. The observed spectrum is due to the structure,

$$NH_2CH_2CO_2(CH_3)_3.HCl + \gamma\text{-ray} \rightarrow NH_2\dot{C}HCO_2C(CH_3)_3.HCl \quad (1)$$

Therefore, the paramagnetic center can be attributed to $NH_2\dot{C}HCO_2C(CH_3)_3$.HCl radical in eq.1. The results indicate that paramagnetic species is carbon centered π-radical. The experimental spectrum is identical with that obtained from simulated spectrum. The g = 2.0030± 0.0005 value verify the literature data for amino alkyl type radicals [11,14]. In amino acids, in general, H-abstraction radicals are formed as a result of hydrogen atom from methylene group at room temperature. This radical is stable for 2 months. The coupling values of irradiated glycine were reported by Sanderud [21] and by Morton [22] are similar to our results. The structures of radiation formed radicals in glycine derivatives have been studied by Osmanoğlu and et all. In this work the obtained hyperfine splitting values are very close to our values [16].

The spectrum of the intensity distribution of approximately 1:1:4:4:6:6:4:4:1:1 is seen in the central part of the spectrum of LAEE in Fig. 2a. When γ- irradiated spectrum of LAEE is examined, it is suggested that a quintet line of 12 mT. The each line of the quintet was subdivided into 2 lines of

1:1. The spectrum of 1:1:4:4:6:6:4:4:1:1 in Fig. 2a. can be attributed to the $CH_3\dot{C}HCOCH_2CH_3$ radical. It can be suggested that this radical is a result of the abstraction of the NH_2 from the LAEE molecule. The spectrum is less resolved due to the hyperfine constants of a^1_{CH2}, a^2_{CH2} being close in value. The free electron interacts with α-proton and three β-protons which are equal. The magnetic parameters were reported as $a^1_{CH} = a^1_{CH3} = a^2_{CH3} = a^3_{CH3}$=2.40 mT, a^1_{CH2} = 1.0 mT and a^2_{CH2} = 0.63 mT, and the linewidth was determined as 0.45 mT. The g factor was evaluated to be g = 2.0039 ± 0.0005. The simulated spectrum is given in Fig. 2b. The spectrum in Fig.2a agrees with in Fig.2b spectrum. Another spectrum was observed in γ-irradiated L-alanine ethyl ester hydrochloride (LAEEHCl) (23). The magnetic parameters of paramagnetic center induced in γ-irradiated LAEEHCl are smaller than our experimental results. The reported values are a_{CH}= 1.85 mT, a_{CH2}= 2.10 mT, g= 2.0033. The radical formed DL- alanine ethyl ester hydrochloride (DLAEEHCl) at 300 K is similar to the radical which was seen in the γ-irradiated LAEE. Moreover, similar radicals and spectra were obtained in L-α-alanine and derivatives (14,23-24).

3. Conclusion

The spectroscopic parameters and radical structures determined in this study are in compliance with the previously obtained results in the literature. The investigation of the magnetic properties of the radicals obtained in the amino acids can be helpful for similar radicals formed in biological systems. The radicals produced in the above samples after γ-irradiated are carbon-centered π-radicals. The free radicals produced in the samples were found to be stable after measurements of several months.

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