www.dergipark.gov.tr
ISSN:2148-3736
El-Cezerî Fen ve Mühendislik Dergisi
Cilt: 7, No: 3, 2020 (1371-1376)

El-Cezerî Journal of Science and Engineering
Vol: 7, No: 3, 2020 (1371-1376)
DOI :10.31202/ecjse.771932

ECJSE

Research Paper / Makale

Gamma Irradiated of Amino Acid Derivatives Examined by EPR and Simulation Methods

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Received/Geliş: 20.07.2020 **Accepted/Kabul:** 16.09.2020

Abstract:. Amino acids of solid state DL-beta-amino-n-butyric acid (BABA), Triethylene tetramine hexa acetic acid (TTHAA) and DL-Asparagine monohydrate (DLAMH) have been investigated by Electron Paramagnetic Resonance Spectroscopy. Free radicals formed in irradiated powder crystals have been examined at temperatures of 300 Kelvin. The structure of the free radical and the hyperfine structure constants were reported. The free radicals formed in the compounds were found to be stable for three months, fifteen days and two months respectively. The obtained results are in agreement with the literature values.

Keywords : Electron Paramagnetic Resonance, Gamma-Irradiation, Free Radicals, Amino Acid.

Gama Işınları ile Işınlanmış Amino Asit Türevlerinin EPR ve Simulasyon Metodu ile İncelenmesi

Öz: Katı durumdaki DL-beta-amino-n-butirik asit, Trietilen terami hekza asedik asit ve DL-asparagin monohidrat aminoasitleri Elektron paramanyetik rezonans spektroskopisi ile incelendi. Işınlanmış toz kristallerde oluşan serbest radikaller 300 Kelvin sıcaklıklarında incelendi. Serbest radikalin yapısı ve aşırı ince yapı sabitleri tespit edildi. Bileşiklerde oluşan serbest radikallerin sırasıyla 3 ay, 15 gün ve 2 ay boyunca stabil olduğu görüldü. Elde edilen sonuçlar literatür değerleri ile uyumludur.

Anahtar Kelimeler: Elektron Paramanyetik Rezonans, Gama Işınlaması, Serbest Radikaller, Amino Asit.

1. Introduction

Electron Paramagnetic Resonance (EPR) has generally used for the investigation of free radicals formed in the ɣ-irradiated biological systems and identification [1-5]. EPR spectroscopy has been identificated the radicals and electronic structures in irradiated amino acids and derivatives. [6-13]. EPR of free radicals in α-aminoisobutyric acid and their derivatives were investigated x and γ-irradiated at between 77K and 300K [11-14]. EPR parameters investigated components were compared with those of ethylenediaminetetraacetic acid and diethylene diaminepentaacetic acids [15]. The gamma-irradiated powders of N-acetyl-DL- aspartic acid and N-carbamoyl-DL-aspartic acid were investigated and the EPR spectroscopic properties were determined [16]. Free radicals formed in L-asparagine and L-aspartic acid were studied at the temperature range of 77-293K [17]. The EPR spectra of L-asparagine H_2O of x-irradiated single crystals were investigated [18]. The

How to cite this article
İpek Işıkcı N., Osmanoğlu Y.E. "*Synthesis, Characterization, Thermal and Electrical properties*", El-Cezerî Journal of Science and Engineering, 2020, 7 (3); 1371-1376.

Bu makaleye atıf yapmak için
İpek Işıkcı N., Osmanoğlu Y.E. *"Sentezi, Karakterizasyonu, Termal ve Elektriksel Özellikleri"*, El-Cezerî Fen ve Mühendislik Dergisi 2020, 7 (3); 1371-1376.
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radical observed in L-asparagine H_2O after x-irradiated is $CO(NH_2)\dot{C}HCH(N^+H_3)CO^-_2$ radical. Asparagine has been known to play a key role in the biosynthesis of glycoprotein and is also important for the synthesis of many other proteins. The nervous system needs this amino acid to be able to keep balance [17]. This paper studies the radicals formed in biologically important samples such as DL-ß-amino-n-butyric acid (BABA), Triethylene tetramine hexa acetic acid (TTHA) and L-asparagine monohydrate (DLAMH). The results of this study were compared with those obtained previously in the literature.

BABA significantly reduced disease severity levels in plants [19]. Hwang and et al. [20] reported that the plants were protected against Phytophthora capsici infections at a level of 75% by spraying BABA on pepper plants at the first branching stage at a dose of 1000 µg ml^{-1}.

2. Experimental Methods

The samples were taken from commercial places. The samples were irradiated by ^{60}Co γ-ray source of 0.3 Mrad/h for 12 h at room temperature. The EPR spectra were recorded with a Varian E-109 Line Series EPR spectrometer using 2mW microwave power. Modulation amplitude was 2 G and modulation frequency was 100kHz. The g-factor was determined by comparison with a diphenylpicrylhydrazyl (DPPH) sample with of g=2.00036 [21]. The spectra after the measurements were examined for three months to observe the stability of the species produced in the samples. The spectra simulated using a computer program [22] are presented in Figures 1b,2b and 3b,3c,3d, respectively.

2. Results and Discussion

The EPR spectrum obtained after ɣ-irradiated of DL-ß-amino-n-butyric acid (BABA) in solid state is presented in Figure 1a. The spectrum consists of nine lines cannot be resolved with g= 2.0030 ± 0.0005. The radical formed in BABA molecule after irradiation, however, recommend that the ($COOH\dot{C}HCHCH_3NH_2$) radical is owing to the division of one hydrogen atom from the α-carbon atom of methylene group. The observed hyperfine splittings are in good agreement with the value of a_{CH} = 0.8 mT, $a^1_{CH_3}$ = 1.05 mT, $a^2_{CH_3}$ = 1.5 mT, a_N= 0.38 mT. These results are to those on amine radicals reported by Wood et al. [22]. These lines could not be appeared as clearly in the spectrum. It is not seemed that a small nitrogen splittings of about 0.38 mT. The linewidth of the spectrum is somewhat larger than the hyperfine coupling constant of the nitrogen nuclei, and therefore the hyperfine splitting of the nitrogen nuclei is not observed in the spectrum. A similar situation has been observed in some studies in the literature [23-26]. The intense nine-line spectrum arises from the hyperfine interaction with four protons of nearly equal magnitude. Examination of the spectrum shows a relation between intensity and character of the EPR lines and the chemical structure of sample. The linewidths are on the order of 0.4 mT. The lifetime of the radical has been three months.

The characteristic EPR spectrum of γ-irradiated Triethylene tetramine hexa acetic acid (TTHA) powder at room temperature is shown in Figure 2a. This spectrum shows only one singlet broad of g= 2.0015 ± 0.0005, in which free electron interacts significantly with one α-proton and two β protons and one nitrogen nucleus. When the microwave power increased from 0.05 to 5mW in the sample, which was irradiated at 20 kGy, we observed lines labelled with the numbers of 1, 2, 3, 4, 5, 6 and 7, respectively. The paramagnetic center thought to be formed in the molecule is attributed to the $CH_2N\dot{C}HCH_2$ radical, which may be a consequence of removal of H from carbon atom. The hyperfine splitting of a_N= 0.25 mT is very small from the linewidth of the spectrum so it is not seen in the spectrum.. The simulation spectrum was obtained using hyperfine coupling constants a_α= 1.6

mT, a_β^1= 1.1 mT, a_β^2 = 0.65mT, a_N= 0.25 mT and linewidth 0.4 mT. The hyperfine coupling constants and g value we calculated for this radical are similar to the same values for amine radicals found in ref. [15-18, 27].

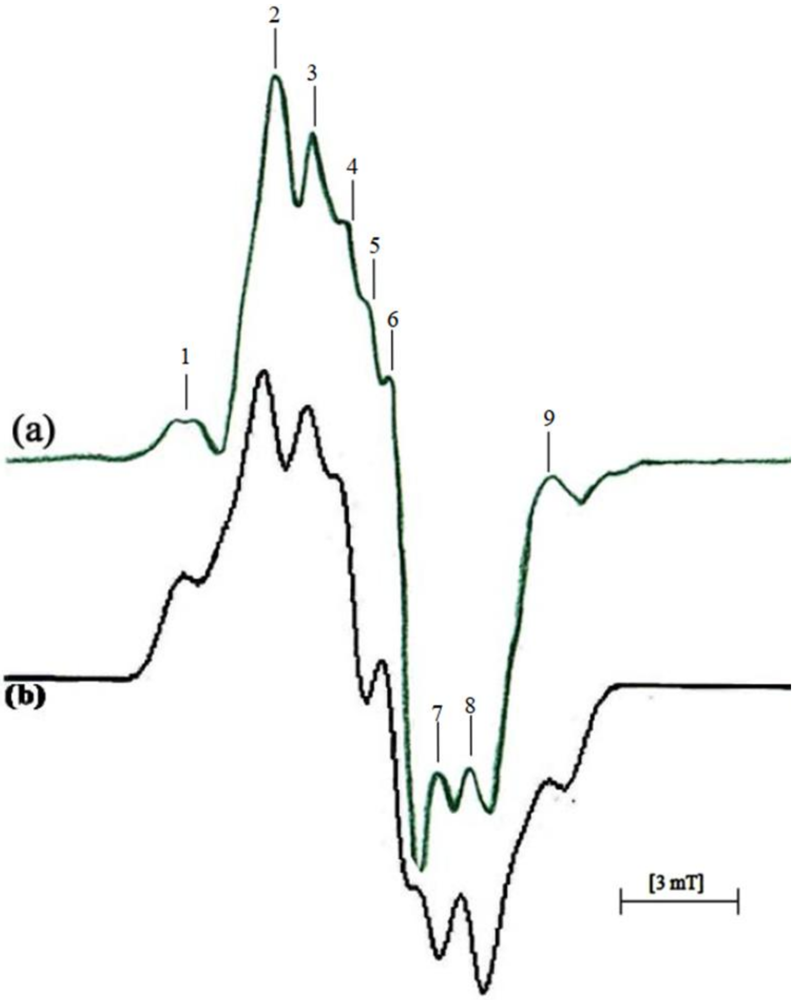

Figure 1. The EPR spectrum of γ-irradiated BABA powder (a) and simulation of the spectrum (b).

The spectrum simulated with calculated hyperfine parameters is shown in Figure 2b. Simulation of EPR spektrum anda the experimental spectrum are seen to agree well with each other (Figure 2a, 2b). This radical's half-life is consistent for fifteen days.

The EPR spectrum of DL-Asparagine monohydrate (DLAMH) was measured several times over the period of 3 month and irradiated to 20 kGy. The two different radicals species produced in DL-asparagine monohydrate (DLAMH) molecule after irradiation is shown in Fig.3a,3c,3d. The spectrum in Fig.3a. represents the sum spectra of corresponding to two different radical species formed in the irradiated DLAMH molecule. Two radical species are stabilized at room temperature. Hyperfine splittings are less resolved due to overlapping spectra and the line broadening. Therefore, The superposition of some lines obstructed the recognition of the spectrum, as seen Fig.3a. The presence of this type radical in amino acids is very interesting. The existence of two different radical species was obtained due to a good similar between simulated and experimental spectrum. The first radical, emphasized to be the radical of type $NH_2CH\dot{C}H$, the nine signals produced by abstraction of a hydrogen atom from the CH_2 group in DL-asparagine monohydrate molecule. Coupling constants of determined for the first radical are a_{CH_2}= 4.7mT, a_{NH_2}= 1.78mT, a_N= 1.3mT. The protons of two methylene groups are inequivalent.

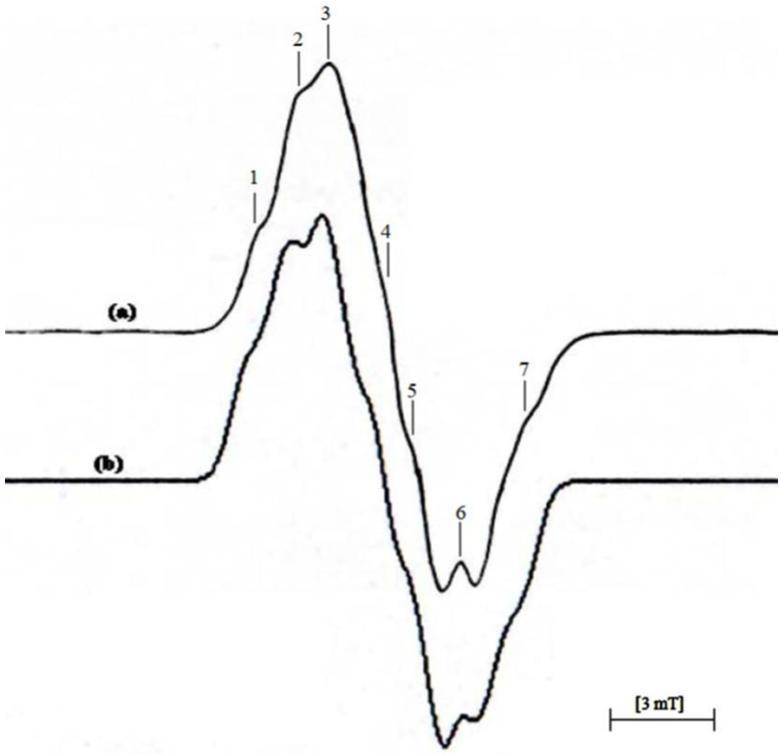

Figure 2. The EPR spectrum of γ-irradiated TTHA powder (a) and simulation of the spectrum (b).

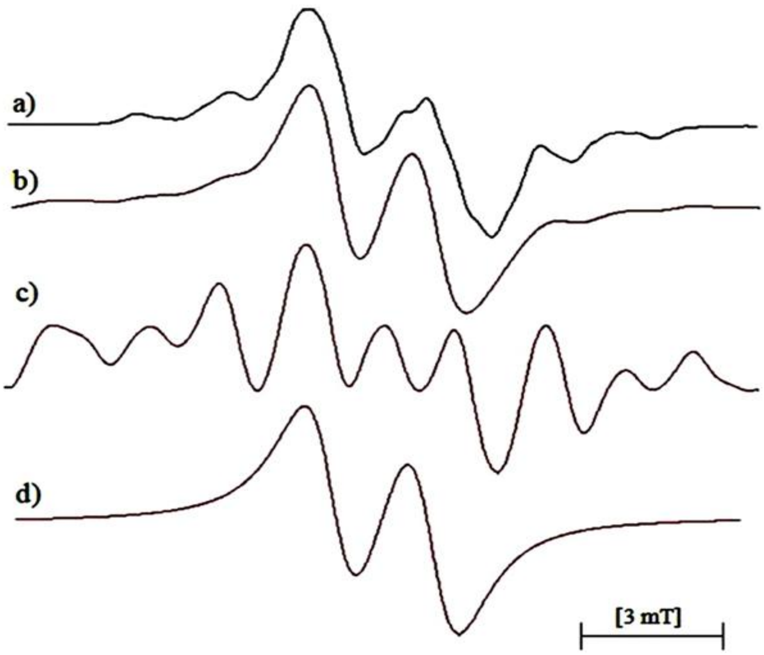

Figure 3. The experimental spectrum of γ-irradiated DLAMH at room temperature(a), the total spectrum simulated, (b) Simulation of the radical I (c) and simulation of the radical IIFT-IR spectrum of poly (d).

The line width of these signals are contributed to spin-spin and dipole-dipole interaction. The second radical can be induced due to H_2O in the molecule structure [18]. The characteristic spectrum of hydroxyl radicals trapped in water molecule consists of a broad doublet. The spectrum of the second radical gives a doublet with 1.06 mT peak to peak line width. The unpaired electron in this radical is localized on $OH^{\cdot}$ of hyperfine splitting with a_{OH} = 2.04 mT. The EPR spectrum of the second radical consists two broad lines of intensity distribution of 1:1. The unpaired electron interacts with OH proton. The g value measured from the spectrum of DL-asparagine monohydrate is g= 2.0024. It can be expressed that the g value of the radical discussed here in agreement with the literature data [28-31]. The simulated spectra in Figure 3c and 3d were obtained using computer simulation of EPR spectra, coupling constants and the structure of free radicals. EPR and ENDOR spectra of L-asparagine.H_2O of x-irradiated single crystals were studied at room temperature by Close D.M. et al.[18]. It was suggested that the radical observed in L-asparagine.H_2O is CO(NH2) $\dot{C}HCH(N^+H_3)CO^{-2}$

3. Conclusions

The spectroscopic parameters and radical structures determined in this research 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 EPR spectrum obtained for DLAMH has been attributed to the superposition of spectra of two different radicals. The superposition of spectra was obtained by simulation method. The free radicals produced in BABA, TTHAA, DLAMH were found to be stable after measurements of three months, fifteen days and two months respectively.

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