ESR of Gamma Irradiation Damage Centers in Single Crystals of Some Glutamic Acid Derivatives

D. Mehmet Zengin, Mehmet Birey, Huseyin Aktas, Ahmet Hancer,
and Atilla M. Murathan[a]

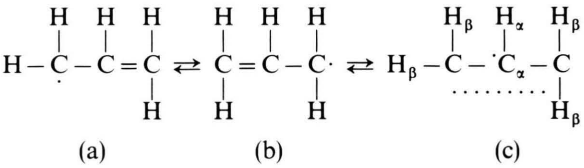
Faculty of Science, Ankara University, 06100 Tandogan, Ankara, Turkey
[a] Faculty of Engineering and Architecture, Gazi University, 06570 Maltepe, Ankara, Turkey

Z. Naturforsch. **51a,** 895–897 (1996); received January 24, 1996

We have observed four radicals in the ESR spectra of γ-irradiated single crystals of some glutamic acid derivatives. These radicals, produced by gamma-irradiation, in single crystals of N-Acetyl-L-Glutamic acid, L-Glutamic acid and DL-Glutamic acid hydrochloride were identified as $CH_3CO\dot{N}H$, $-\dot{C}_3H_5$, $-\dot{C}H$, and $-\dot{N}H_2$ radicals respectively.

Free radicals produced by gamma irradiation in single crystals of N-Acetyl-L-Glutamic acid (**1**), L-Glutamic acid (**2**) and DL-Glutamic acid hydrochloride (**3**) have been investigated between 100 and 350 K with ESR. The single crystal spectra have been taken at 5-degree intervals with the magnetic field **B** lying in each of the three crystallographic planes *ab*, *bc*, and *ca*.

Figure 1 shows the spectrum of **1** with its hyperfine splitting. In these spectra, 16-lines are observed due to $CH_3CO\dot{N}H$ and $\dot{C}_3H_5$ radicals. Owing to the $CH_3CO\dot{N}H$ radical, the spectra exhibit an outer doublet (1:1) because of the proton directly attached to the nitrogen, and each of the outer lines splits into triplet lines (1:1:1) due to the nitrogen. Owing to the other allyl radical ($\dot{C}_3H_5$) produced by gamma irradiation, inner 10-lines are also observed between these triplet lines. Inner doublet splittings are due to α-protons of the radical, then each line splits into five lines (1:4:6:4:1) owing to the β-protons of this radical. The proton splitting for the $CH_3CO\dot{N}H$ radical is about 8.9 mT, and the nitrogen splitting is approximately 0.8, 0.6, and 0.4 mT. The α and β-proton splittings are approximately 3.4 and 0.6 mT, respectively. Such a result can arise if the unpaired electron interacts equally with the α-proton and to a somewhat lesser extent with four other equivalent β-protons. The radical most likely formed in irradiated **1** which fits these requirements is the allyl radical ($\dot{C}_3H_5$). The greater density of the electron at the nuclei of either α and β protons farthest from the site of the unpaired electron can be accounted for in terms of conjugation. The resonance form of the allyl radical in **1** is as follows:



In this resonance formula, the allyl radical formed is believed to have the structure (c) as well as to a lesser extent the two conjugated structures (a) and (b) [1].

The angular variations of the $\boldsymbol{g}(\theta)$ and $\mathbf{A}(\theta)$ tensors are computed from the experimental angular variations about the axes *a*, *b* and *c*. All the values obtained from the four radicals are given in Table 1. The hyperfine constant of $CH_3CO\dot{N}H$, (a_H), has been observed in the three crystallographic planes *ab*, *bc* and *ca*, but the splittings of the CH_3 protons could not be seen in all the planes. The g values and the hyperfine constant (a_H) have been observed to be almost isotropic for the $CH_3CO\dot{N}H$ radical, but the hyperfine constants of nitrogen are anisotropic. Our splitting value are very similar to those derived from the $R-\dot{N}H$ radical produced by different species [2–8]. The splittings and g-values given in Table 1 for the $CH_3CO\dot{N}H$ radical are very similar to those reported in [2–4 and 8]. However, we stress that our $g_{av} = 2.0043$ is smaller than the one reported in [5, 7].

The spectra of **2** and **3** consist of 11 lines. In the spectra, the outer doublet is due to the $-\dot{C}H$ radical in **2** and **3**. Our average value of the proton splitting directly attached to the carbon is about 8.3 mT. These splittings quite agree with those derived from the $-\dot{C}H$ radical in succinic acid [9]. The inner 9-lines of

---

Reprint requests to D. M. Zengin.

0932-0784 / 96 / 0800-0895 $ 06.00 © – Verlag der Zeitschrift für Naturforschung, D-72072 Tübingen

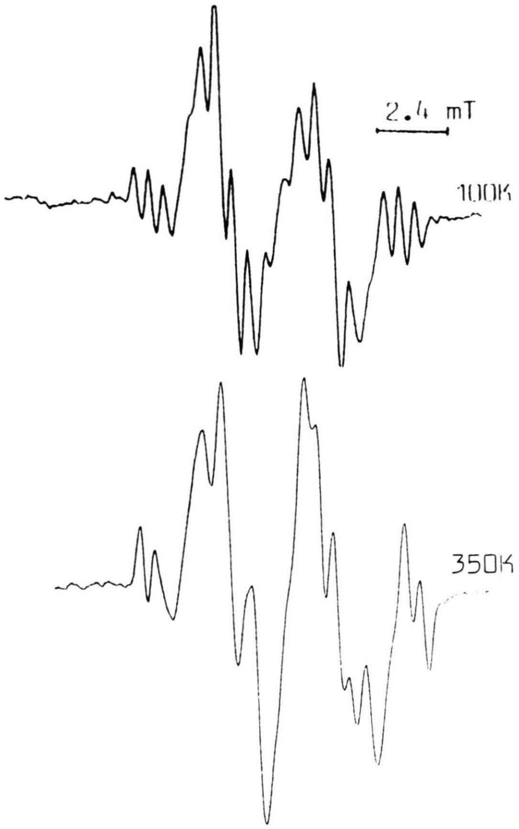


Fig. 1. ESR spectrum of N-Acetyl-L-Glutamic acid single crystal with a frequency of 9.13 GHz at 100 K (top) and 350 K (bottom).

the spectra are due to the $-\dot{N}H_2$ radical in **2** and **3**. This radical exhibits a three-line spectrum because of the nitrogen, then each of these three lines also splits into three lines owing to the two protons. Our average value of the nitrogen splittings attached directly to the proton is about 1.95 mT, and the proton splittings are approximately 1.0 mT. These values agree well with those derived from the $-\dot{N}H_2$ radical in NH_3OHCl, $(NH_3OH)_2SO_4$ and $N_2H_6SO_4$ [10]. The crystal structure of **2** and **3** has been determined by Dawson [11], and it has been reported that the crystal must have been either L or D. A similar argument has also been given by Lin et al. [12]. Lin et al's spectra were obviously quite similar to our spectra. They compared their observed values with the results produced by the radical of succinic acid, $HOOCCH_2\dot{C}HCOOH$, which has been studied by Heller and McConnell [9]. The present values of ***g*** and the hyperfine constants for the $-\dot{C}H$ and $-\dot{N}H_2$ radicals in **2** and **3** are also given in Table 1. The obtained values for these radicals are quite consistent with their data [9–12]. The ESR spectra of these radicals were unchanged and undiminished at room temperature for more than two months after irradiations.

Table 1. The ESR parameters of $CH_3CO\dot{N}H$, $\dot{C}_3H_5$ and $\dot{N}H_2$ radicals. The error for all the calculated **g** values is estimated as ±0.0005.

Radical		Principal values of **A** (mT) and **g**	Direction cosines		
$CH_3CO\dot{N}H$	a_H	9.0∓0.1	0.8388	0.1500	0.5234
		8.9∓0.1	−0.5375	0.0753	0.8399
		8.8∓0.1	0.0866	−0.9858	0.1438
	a_{av}	8.9∓0.1			
	a_N	0.8	0.1637	0.9855	0.04499
		0.6	−0.8443	0.1635	0.5103
		0.4	−0.5103	0.0456	0.8588
	a_{av}	0.6			
	g_a	2.0052	0.2132	−0.6811	0.7005
	g_b	2.0044	0.9559	−0.0025	−0.02934
	g_c	2.0033	0.2016	0.7322	0.6506
	g_{av}	2.0043			
$\dot{C}_3H_5$	a_α	3.7	0.4724	−0.7848	0.4012
		3.5	0.2443	0.554	−0.7959
		3.0	0.8468	0.2780	0.4534
	a_{av}	3.4			
	a_β	0.7	−0.0878	0.9761	0.1989
		0.6	0.8586	0.0271	0.5117
		0.5	−0.5048	0.21578	0.8358
	a_{av}	0.6			
	g_a	2.0043	0.8139	0.5697	−0.1138
	g_b	2.0042	0.0728	0.9434	0.9923
	g_c	2.0038	0.5763	−0.8165	0.0353
	g_{av}	2.0041			
$\dot{C}H$	a_H	8.3	−0.231	−0.905	0.139
		8.2	−0.904	0.235	0.059
		8.4	0.112	0.119	0.909
	g_{av}	2.0042	−0.06	−0.32	0.80
			0.22	0.75	∓0.33
			0.82	−0.23	0.05
$\dot{N}H_2$	a_N	1.95			
	a_H	1.0			
	g_{av}	2.0042			

Experimental

Single crystals of **1**, **2** and **3** were grown from concentrated aqueous solutions. From the X-ray diffrac-

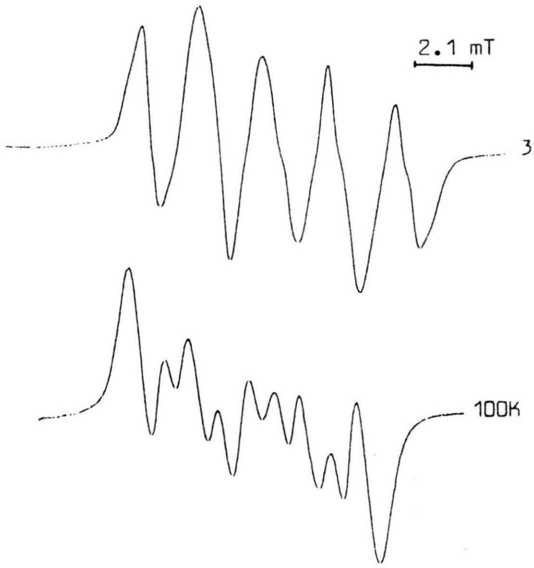


Fig. 2. ESR spectrum of L-Glutamic acid and DL-Glutamic acid hydrochloride single crystals with a frequency of 9.13 GHz at 350 K (top) and 100 K (bottom).

tion studies we found that the single crystals of **1** are orthorhombic with space group $P2_12_12_1$ and unit cell dimensions $a = 0.489$, $b = 1.292$ and $c = 1.386$ nm. The unit cell contains four molecules. The crystals **2** and **3** also belong to the orthorhombic space group $P2_12_12_1$ with $a = 0.516$, $b = 1.180$ and $c = 1.330$ nm. Their unit cells contain four molecules too [11]. The samples were irradiated at room temperature with a ^{60}Co γ-ray source of 0.3 Mrad/h for 24 hours. The ESR spectra were recorded with a Varian model E-109 C ESR spectrometer using 2 mW microwave power. The low and high temperature measurements from 100 K to 350 K were carried out using a variant temperature controller unit. The crystals were rotated on a Lucite pillar around their crystallographic axes. The ESR spectra of several single crystals at several times and also powders of the compounds were reproducible. The g factor was found by comparison with a DPPH sample ($g = 2.0036$).

Acknowledgements

The authors wish to express their sincere gratitude to Professor F. Köksal for providing the facilities for the experimental studies in the Department of Physics, University of Ondokuz Mayis. Thanks also are due to the Turkish Scientific and Technical Research Council (TUBITAK) for support.

[1] P. B. Ayscough and H. E. Evans, Trans. Faraday Soc. **60,** 801 (1964).
[2] N. Cyr and W. C. Lin, J. Chem. Phys. **50,** 3701 (1969).
[3] P. W. Lau and W. C. Lin, J. Chem. Phys. **51,** 5139 (1969).
[4] N. Cyr and W. C. Lin, J. Chem. Comm. 1967, 192.
[5] W. M. Fox and P. Smith, J. Chem. Phys. **48,** 1868 (1968).
[6] M. C. R. Symons, J. Chem. Phys. **55,** 1493 (1971).
[7] H. W. Shield, P. Hamrick, and W. Redwine, J. Chem. Phys. **46,** 2510 (1967).
[8] M. Birey, H. Aktas, and D. M. Zengin, Z. Naturforsch. **49 a,** 946 (1994).
[9] C. Heller and M. McConnell, J. Chem. Phys. **32,** 1535 (1960).
[10] F. Köksal, O. Cakir, I. Gumrukcu, and M. Birey, Z. Naturforsch. **40 a,** 903 (1985).
[11] B. Dawson, Acta Cryst. **6,** 81 (1953).
[12] W. C. Lin, C. A. McDowell, and J. R. Rowlands, J. Chem. Phys. **35,** 757 (1991).