Electron Spin Resonance Spectra of an Irradiated Single Crystal of L-α-Alanine at 77°K

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In order to elucidate the radiolysis of the solid L-α-alanine, a series of investigations, including the study of the ESR spectra, have been carried out in our laboratory, the formation of a carboxylic acid anion radical, $CH_3\overset{+}{C}H(NH_3)-C(=O)-O^-$, has been proposed,[1] a radical which contains one α-proton, one β-proton, and an unpaired electron distributed on the COO group. On the basis of the existence of this radical, the initial processes of the radiolysis of solid L-α-alanine and the *G*-values of the radiation products could well be explained.

Very recently Hanna *et al.*[2] made a similar ESR study and proposed the same radical independently. However, there are some discrepancies between their results and ours with regard to the notation of the crystal axes and the principal values of hyperfine splittings.

A single crystal of L-α-alanine was irradiated at 77°K by ^{60}Co γ-rays, and its X-band ESR spectra were observed at the same temperature. The crystal axes of L-α-alanine were determined by X-ray diffraction analysis and were assigned according to the Simpson's[3] notation. The results from these experiments are listed in Table 1.

TABLE 1. THE PRINCIPAL VALUES OF THE α-PROTON AND β-PROTON HYPERFINE SPLITTING (*A*) AND THE SPECTROSCOPIC SPLITTING FACTOR (*g*) FOR IRRADIATED L-α-ALANINE AT 77°K

Principal value		Direction cosine*		
		l	*m*	*n*
A_α-proton (Av. −15.0G)	−23.0G	±0.95	∓0.23	±0.22
	−12.1G	±0.76	±0.65	∓0.04
	− 9.9G	±0.07	∓0.13	∓0.99
A_β-proton (Av. 18.3G)	21.3G	±0.21	∓0.44	±0.87
	17.5G	±0.24	±0.97	±0.43
	16.4G	±0.95	∓0.11	∓0.29
g	2.0036	±0.60	∓0.04	±0.80
	2.0034	±0.60	±0.32	±0.33
	2.0019	±0.41	±0.85	∓0.33
Normal to $-C(=O)-O^-$ plane[3]		±0.57	±0.82	±0.06

* These values give one orientation of the radical and the other three radical orientations have the following direction cosines: $-l, m, n$; $l, -m, n$; $l, m, -n$.

From these data and the results of X-ray analysis, the following information is obtained: 1) The direction of the symmetrical axis of the unpaired electron orbital which corresponds to $A_{\alpha(\mathrm{med})}$ and $g_{(\mathrm{min})}$ is nearly the same as the normal of the COO plane in the parent molecule within the range of experimental error. This indicates that the orientation of this radical is not different from that of the parent molecule. 2) As Fig. 1 shows, the calculated angles between the direction of $A_{\alpha(\mathrm{min})}$ and the directions of $C_{(1)}$-$O_{(1)}$, $C_{(1)}$-$O_{(2)}$, and the normal of the COO plane are 90°, 35°, and 90°, where $O_{(1)}$ forms one hydrogen bonding and $O_{(2)}$ forms two hydrogen bondings[3] in the unirradiated crystal of L-α-alanine. From these data, it may be concluded that the α-proton is coplanar with the COO group and that the α-proton is bonded with the $O_{(1)}$ atom by a $2p\sigma$ bond. 3) Using the equations given by McConnell *et al.*, the unpaired electron densities, ($\rho^{C_{(1)}}$ and $\rho^{O_{(1)}}$), on $C_{(1)}$ and $O_{(1)}$ were calculated and found to be 0.4 and 0.2_5 respectively (Fig. 1). In the determination of $\rho^{O_{(1)}}$, $Q_{O^-H}=-64.0$G was used.[4]

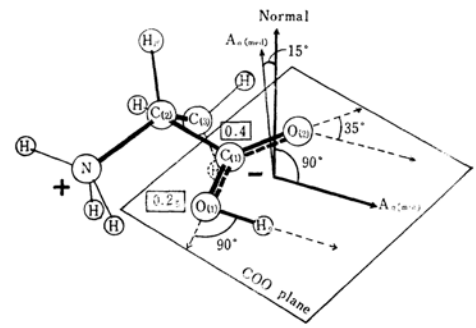

Fig. 1. Structure of carboxylic acid anion radical of irradiated L-α-alanine and unpaired electron density.

The details of this work will be published elsewhere shortly.

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2) J.W. Sinclair and M.W. Hanna, *J. Phys. Chem.*, **71**, 84 (1967).
3) H.J. Simpson, Jr., and R.E. Marsh, *Acta Cryst.*, **20**, 550 (1966).
4) T. Masuda, K. Morokuma and K. Hukui, presented at the 2nd Symposium on Electron Spin Resonance Spectroscopy, November, 1963, Kyoto, Japan.