

ESR of γ -Irradiated L-Ascorbic Acid

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Single crystals of L-ascorbic acid (Vitamin C) were examined by ESR techniques after γ -irradiation. All experiments were conducted at room temperature. Strong stable β -proton spectra were observed. Fairly unstable other β -proton radicals were also detected at the temperature.

Any phase transitions were not found in the temperature range from -150°C to 200°C by DSC and dielectric measurements.

Introduction

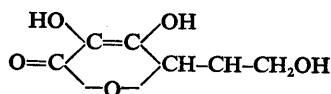
Extensive ESR studies have been carried out on intermediate radicals in the oxidation of ascorbic acid in solutions^{1,2}. However, no experiment was reported for irradiated single crystals. In view of the radical formation of the crystal like *amino acid* crystals, we tried to investigate the ESR measurements for vitamins. Ascorbic acid was examined for the simplicity of the crystal growth and its space group which belongs to polar crystals.³ Possibilities of ferroelectrics might be expected to this groups.

At first we checked the existence of any phase transitions of this crystal between 77K to 473K by dielectric and DSC measurements. The melting point of this crystal is about 470K. As the phase of this crystal belongs to non-centrosymmetric point groups at room temperature, we tried to observe the dielectric D-E hysteresis loops at the temperature. However, we could not obtain any evidences of ferroelectric phase at room temperature by these preliminary experiments.

ESR measurements were examined for γ -irradiated single crystal to investigate the radical formations. As ESR measurements for oxidation mechanism of this crystal were reported by many investigators, we are interested in radicals produced by higher energy sources. Comparison of ESR data with irradiated Rochelle salt were performed, because of the resemblance to the spectra observed in irradiated Rochelle salts,^{4),5)}

Crystal structure

A substance with the formula $\text{C}_6\text{H}_8\text{O}_6$ is hexuronic acid, but this was changed to L-ascorbic acid or Vitamin C because of its healing effect on scurvy. The structural formula is



The crystal structure was determined by Cox and Goodwin,⁶ and further progress was made by Hvoslef³ in 1968. Hvoslef established more precise hydrogen parameters by means of neutron diffractions. The unit cell contains two molecules A and B in the asymmetric unit. The four molecules in the unit cell are related in

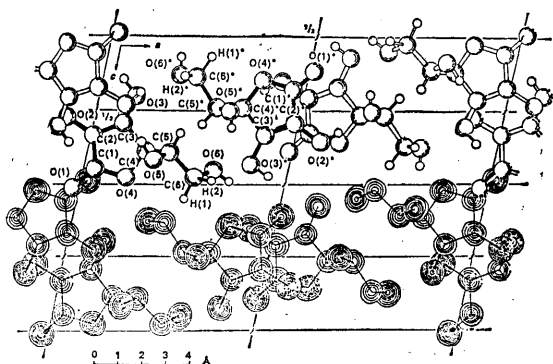


Fig. 1. View of the structure of L-ascorbic acid along [010]. (after Hvoslef (3))

pairs by pseudo screw axes along $[010]$ in the positions ($x = 1/4, z = 5/8$) and in ($x = 3/4, z = 5/8$). L-ascorbic acid crystallizes in the monoclinic space group $P2_1$ with four formula units in cell dimensions $a = 17.299(8)$, $b = 6.353(3)$, $c = 6.411(3)\text{\AA}$, $\beta = 102^\circ 11'$. The crystal structure is shown in Figure 1.

Experimental

ESR experiments were performed using a conventional ESR spectrometer operating at 9.4 GHz microwave frequency and 100 KHz modulation.

Crystal of L-ascorbic acid were grown from aqueous solutions by slow evaporation at room temperature. In order to avoid oxidation of the substance, the crystal growth was performed in dry nitrogen gas atmosphere. Relatively large, tabular transparent crystals were obtained with the dimensions $0.5 \times 0.5 \times 1.0\text{ cm}^3$. X-ray measurements were performed to determine the crystal orientations. Figure 2 shows the X-ray diffraction patterns observed at room temperature. Figure 3 shows its crystalline form and its crystal planes. Although the

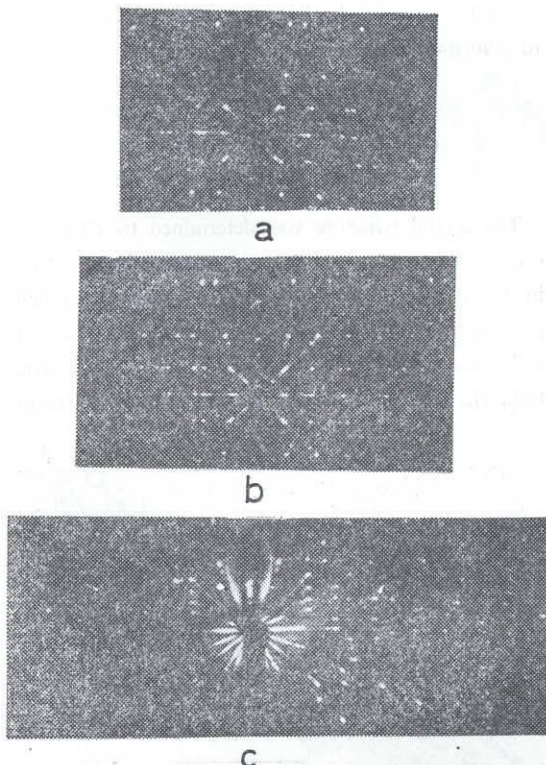


Fig. 2. Oscillation X-ray patterns of L-ascorbic acid. (a) rotation along c^* , (b) along b , and (c) along a axis.

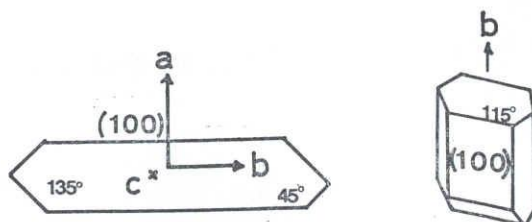


Fig. 3. The crystal form of L-ascorbic acid and the coordinate axes employed.

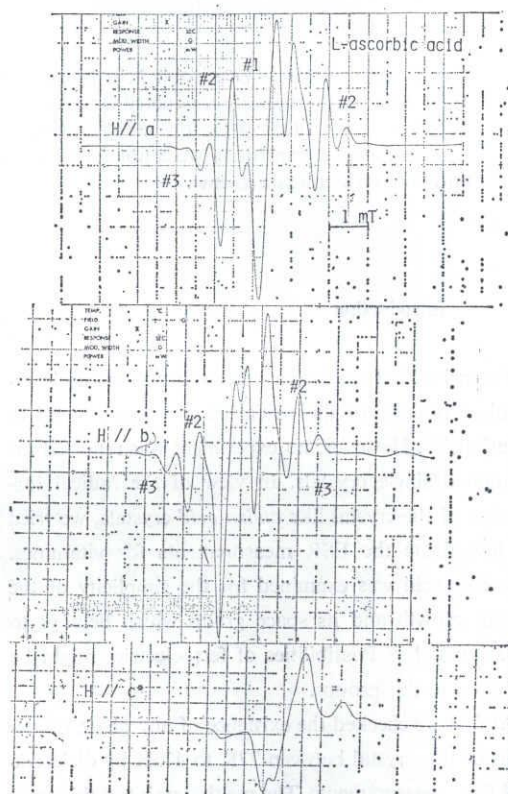


Fig. 4. ESR spectra of γ -irradiated L-ascorbic acid.

crystal was yellow in color, the oxidations were only on surface, which was checked by cutting the crystal. Deuterated crystals were prepared by recrystallizing the ordinary acid from D_2O .

Suitably sized crystals were irradiated at room temperature with ^{60}Co γ -rays, dosages of up to 2 Mrads. The axis of rotation was perpendicular to the main magnetic field of the spectrometer, and the spectra were recorded at intervals of 10° . One of the paramagnetic centers is very stable even at room temperature. Figure 4 shows the ESR spectrum at room temperature, which seems to be almost same spectra as observed in γ -irradiated Rochelle salt crystal. In order to determine the number

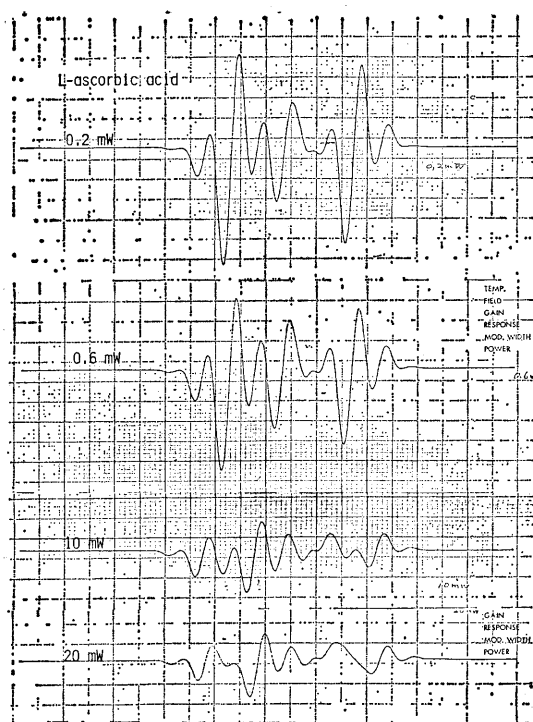


Fig. 5. Saturation effects of ESR spectra observed in γ -irradiated L-ascorbic acid.

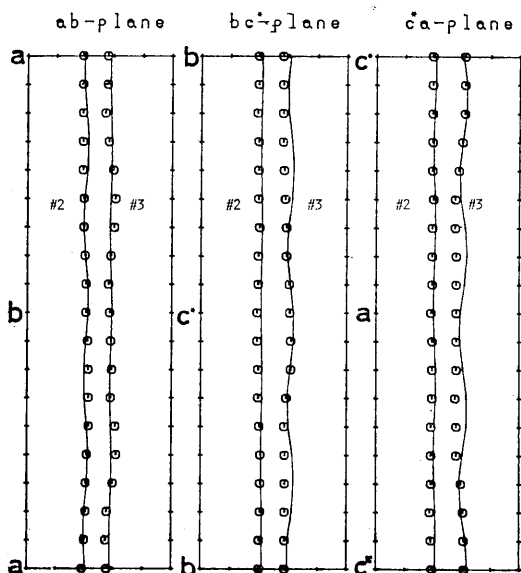


Fig. 6. Calculated (solid lines) and observed (dots) points of ESR signals of irradiated ascorbic acid.

of the paramagnetic centers, the saturation effects of radicals by microwave power measured at room temperature (Fig. 5). The angular dependences of the spectra

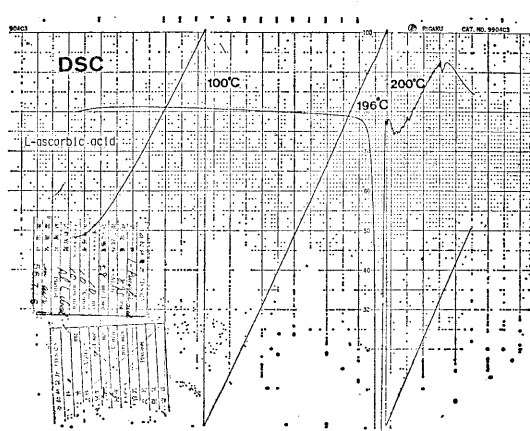


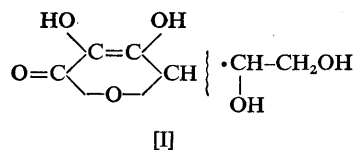
Fig. 7. DSC signals of L-ascorbic acid measured from -150°C to 200°C . Melting point of this crystal is about 190°C .

were also measured in order to determine the radical orientations, precisely. (Fig. 6). The spectra were divided three groups, one of them (center #2) depends a little on the orientations of the magnetic fields, and the others are almost isotropic. The central part of the spectra (center #1), shows very strong intensity just after irradiations, and seems to change to outer doublet spectra for a few weeks as observed in irradiated Rochelle salts. In this paper, center #1 is still remain as unknown radical. These centers are almost identical in deuterated crystals.

Structures of the paramagnetic centers

[1] Center #2

The center which easily saturates by microwave power shows a α -proton h/f s coupling, that is, about 2 mT. From the observed patterns and from considerations of the structure of the L-ascorbic acid molecule, at first we assume that the free radical observed in irradiated L-ascorbic acid is one of the form



The radical [I] is very resemblance to one observed in irradiated Rochelle salt.⁵⁾ The C-H hydrogen has both an isotropic Fermi term caused by a slight spin density on the H atom and a dipole-dipole term caused by appreciable spin density on the carbon atom. The spin

Hamiltonian which describes the C-H interaction is expressed adequately by

$$\mathcal{H} = g\beta HS_z + (A_{xx}I_x + A_{xy}I_x + A_{yy}I_y)S_z \quad (1)$$

in which the first term represents the direct interactions of the C-H hydrogen molecules with the fields. From this spin Hamiltonian, two doublet of spacing in magnetic field units

$$d_+ = (A_+ + A_-)/2g\beta \quad (2a)$$

$$d_- = (A_+ - A_-)/2g\beta \quad (2b)$$

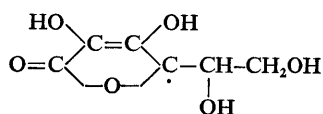
are expected, where

$$A_{\pm} = [(A_{xx} \pm 2g_I\beta_I B)^2 + c^2]^{1/2} \\ c^2 = (A_{xx}^2 + A_{yy}^2) \quad (3)$$

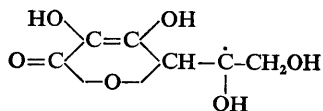
The precise calculation had been already established by Miyagawa.⁷⁾ From the experimental data, we get the principal values of A tensors which are listed in Table I. From these principal values of *hfs* coupling tensors calculated from ESR data did not show the typical α -proton anisotropy. By comparing these observed *hfs* A tensors, we suppose that the center #2 should be typical β -proton radical rather than α -proton, although the A tensor have almost same as α -proton. Therefore the form of the radical seems to be

Table I. Values and direction cosines of the *hfs* tensors.

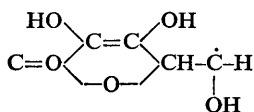
center	Value	Direction cosines in <i>a, b, c</i> ,* axes		
#2	1.94 mT	(.764	.529	-.369)
	2.14	(-.576	.817	-.024)
	2.07	(.288	.230	.929)
#3	2.88	(.928	.372	-.014)
	2.96	(-.366	.918	.147)
	3.18	(.067	-.132	.989)



[II]



[III]



[IV]

In these center, we may expect the *hfs* coupling of OH group at same time, however, in Rochelle salt we could

not observe such *hfs* coupling for center #3 radicals. Observed A tensors are very much same values of rotated center as $\cdot\text{CH}_2\text{COOH}$ center in TGS, but we could not expect such a dynamical motions of these bonds.

[II] center #3

Almost isotropic spectra were observed. The center #3 has just same *g*-values in any orientations as center #2. However, the saturation effects by microwave power are different from each other, then these radicals are not same species.

The relation has been proposed for β -hydrogen *hfs* coupling

$$A = A_1 + A_2 \cos^2\theta \quad (4)$$

Here θ , the dihedral angle, is the angle between π -spin orbital and C-H bond. The values of A_2 is approximately 4.3 mT and A_1 is usually very small. For observed spectrum we get $A = 3.02$ mT, then the magnitudes of the *hfs* coupling indicate an orientation such that $\theta = 40^\circ$. For this center we may assume one of the radicals [II] and [III]. Two β -protons (H_1 and H_2) should be observed at same time. For the identification of centers, we must study much more. For the center #2, we obtain $\theta = 53^\circ$ as $A_{iso} = 2.05$ mT from the relation (4).

DSC and Dielectric measurements

In order to check the phase transition, DSC measurements were performed between -150°C to 250°C . The melting point of this crystal is about 190°C (Fig. 7). Much more symmetric phase should be expected at high temperature, however, any DSC signals were observed except decomposition till melting point. We may expect ferroelectricity at room temperature along *b*-axis. No peak was recorded on dielectric constants at 1 KHz between -150°C to room temperature.

Conclusions

We observed three centers in γ -irradiated ascorbic acid at room temperature. These centers were proposed to be β -proton radicals as [II] and [III].

Although the space group of this crystal belongs to a polar crystal at room temperature, no D-E hysteresis loops were observed at the temperature.

No phase transition to much highsymmetric space group were detected in DSC measurements.

Acknowledgment

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