661. *The Electron Spin Resonance Spectra of γ-Irradiated Fumaric Acid.*

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The electron spin resonance spectra of an irradiated crystal of fumaric acid are studied. A radical of the form $R{\cdot}CH(C\dot{O}_2H){\cdot}CH(CO_2H)$ is the major product and there is a lesser species which appears to be $CH_2(CO_2H){\cdot}\dot{C}H(CO_2H)$. Crystal-structure information derived from the spectra suggest that the fumaric acid lies in planes perpendicular to the *b*-axis of the monoclinic cell with its C–H bonds at an angle of 68° to a twinning plane which is very easily developed.

Electron spin resonance studies of the radicals formed by both *X*- and γ-irradiation of saturated dicarboxylic acids,[1–7] have shown that the radical observed at room temperature is usually one in which a hydrogen atom is lost from the parent acid, most often adjacent to the carboxyl group. This is accompanied by a rehybridisation of the free-radical carbon, from an sp^3 tetrahedral distribution of bonds to a planar sp^2 arrangement, with the unpaired electron effectively localised in the remaining carbon $2p$-orbital, perpendicular to the radical plane.

It is of interest to study the effects of irradiation on unsaturated dicarboxylic acids, where the carbon atoms already use planar sp^2 hybridisation. A π-type radical, *i.e.*, one in which the unpaired electron is located in an orbital perpendicular to the radical plane, would be formed by loss of an electron from a π-molecular orbital of the parent acid, leaving a positive ion. Loss of hydrogen, breaking a C–H bond, would give a substituted vinyl radical for which the remaining hydrogen might have a coupling near 380 Mc./sec., the value in the formyl radical.[8]

An irradiated single crystal of fumaric acid did not give electron spin resonance spectra of either of these species, but rather a dominant spectrum assigned to a radical of the form $R{\cdot}CH(CO_2H){\cdot}\dot{C}H(CO_2H)$ (I). Some minor lines were also present, some of which are attributed to the $CH_2(CO_2H){\cdot}\dot{C}H(CO_2H)$ radical (II). Since the detailed results give helpful information for a crystal-structure determination and give evidence of incipient polymerisation they are of some interest, even though these types of aliphatic radical are reasonably well known.[1–7]

Experimental

Maleic acid, could not be persuaded to grow suitable crystals, but crystals of the corresponding *trans*-acid, fumaric acid, could be grown by the slow cooling of a saturated aqueous solution. The crystals were all badly formed, showing re-entrant angles, and Fig. 1 indicates the crystal used for most of the measurements. Multiple-twinning is indicated and indeed twinning was confirmed by *X*-ray measurements; these measurements also showed that *Y* was the *b*-axis of the monoclinic unit cell of all sections of the crystal. *XY* is the twinning plane and *Z* is perpendicular to this plane.

The crystals were irradiated with γ-rays of mean energy 1 Mev at the Spent Fuel Irradiation Unit, Atomic Energy Research Establishment, with doses up to 50 Mrads at room temperature. The radical yield was lower than that for most aliphatic acids, but detailed studies were not made. The spectra were measured at 9000 Mc./sec. on a superheterodyne spectrometer.

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[1] McConnell, Heller, Cole, and Fessenden, *J. Amer. Chem. Soc.*, 1960, **82**, 766.
[2] Heller and McConnell, *J. Chem. Phys.*, 1960, **32**, 1535.
[3] Pooley and Whiffen, *Mol. Phys.*, 1961, **4**, 81.
[4] Horsfield, Morton, and Whiffen, *Mol. Phys.*, 1961, **4**, 169.
[5] Morton and Horsfield, *Mol. Phys.*, 1961, **4**, 219.
[6] Heller, *J. Chem. Phys.*, 1961, **36**, 175.
[7] Rowlands and Whiffen, *Mol. Phys.*, 1961, **4**, 349.
[8] Adrian, Cochran, and Bowers, *J. Chem. Phys.*, 1962, **36**, 1661.

Three sets of spectra were obtained with the magnetic field perpendicular to X, Y, and Z axes in turn at 10° intervals. g-factors were measured by determining the centre of the pattern relative to an $N'N'$-diphenyl-N-picrylhydrazyl marker assumed to have $g = 2{\cdot}0036$. The OO'-dideuterio-acid was grown from deuterium oxide, and the nature of the exchange confirmed by infrared spectrosocopy.

Analysis of the Spectra.—Irradiation gave rise to at least two radicals, one being in much higher concentration than the others. The most abundant radical showed hyperfine interaction with two hydrogen atoms (Fig. 2). One coupling showed the characteristic anisotropy of an α-hydrogen and the other the more isotropic behaviour of a β-hydrogen atom. The electron spin resonance spectra for the crystal rotations about the X- and the Z-axis showed only one magnetically distinct site. Rotation about Y indicated two sites, presumably one in each of the twins. This indicates that the Y-axis is a principal direction for all tensors. Since the damaged site is derived from a fumaric acid molecule, which can have a centre, a plane, and a twofold axis of symmetry, the only plausible arrangement is that the fumaric acid molecules lie perpendicular to the b-axis of the monoclinic cell and that the two ends of the molecule are related by this two-fold axis.

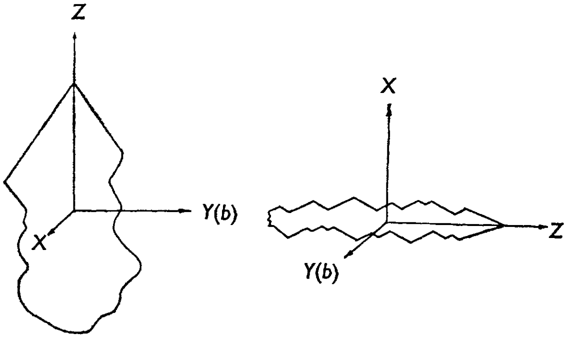

FIG. 1. Sketch of typical crystal and axes chosen.

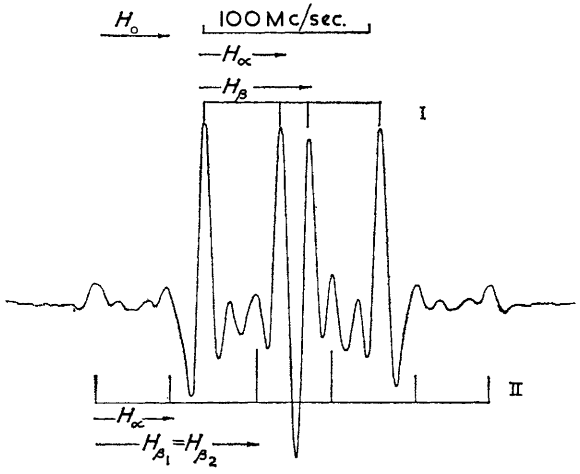

FIG. 2. Second derivative of the electron spin resonance absorption with magnetic field parallel to the Z-axis.

The disposition of the four strong lines attributed to radical (I) were consistent with the hyperfine-coupling tensors shown in the Table. The values for the first hydrogen are typical [9,10] of hydrogen attached to carbon in π-electron radicals. The intermediate principal coupling is expected to be perpendicular to the radical plane and it is indeed found parallel to Y, that is the b-axis. This supports the finding that the XZ plane is indeed the plane of the fumaric acid. The C–H bond lies along [9] the direction of smallest numerical coupling and is therefore at 68° to the twin plane; it is to be expected that the C–H bond of the undamaged fumaric acid is in almost exactly the same direction. The second hydrogen has the small anisotropy

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[9] McConnell and Strathdee, *Mol. Phys.*, 1959, **2**, 129.

Hyperfine-coupling tensor information for dominant radical (I). The upper and lower signs refer to the separate twins consistently.

Nucleus	Hyperfine coupling	Direction cosine in *XYZ* axes	Nucleus	Hyperfine coupling	Direction cosine in *XYZ* axes
H_α	−57 Mc./sec.	(0,1,0)	*g*-tensors	2·0033	(0,0,1)
	−90 ,,	(cos 22°, 0, ± sin 22°)		2·0043	(1,0,0)
	−33 ,,	(sin 22°, 0, ∓ cos 22°)		2·0029	(0,1,0)
	−60 ,,	Isotropic component			
H_β	+64 Mc./sec.	(cos 77, 0, ± sin 77)			
	+52 ,,	(sin 77, 0, ∓ cos 77)			
	+51 ,,	(0,1,0)			
	+56 ,,	Isotropic component			

expected [2,3,10] for a hydrogen on the carbon atom adjacent to the free-radical carbon and has a fairly low value suggesting [2,3,11] that it must lie not too far from the free-radical plane. All these facts are consistent with a radical $R{\cdot}CH(CO_2H){\cdot}\dot{C}H(CO_2H)$ (I).

The other radicals were present in too small an amount for precise analysis, but there was one species which consistently gave two lines outside those of radical (I). With the magnetic field in the *XZ* plane the toal spread varied from 280 to 218 Mc./sec. and was 242 Mc./sec. for the field along *Y*. The details are exactly those to be expected for a radical containing one hydrogen atom attached to the free-radical centre with a C–H bond parallel to the corresponding C–H of radical (I). The remaining total coupling of about 190 Mc./sec. was almost isotropic and is best attributed to two further hydrogens with couplings of 95 Mc./sec. each.

For some orientations of the crystal further lines could be seen in the positions to be expected for such a coupling scheme, though there were indications that the couplings near 95 Mc./sec. were not exactly equal at all orientations but varied separately in the range 85—105 Mc./sec. These facts are consistent with the radical, $CH_2(CO_2H){\cdot}\dot{C}H(CO_2H)$ (II). The same lines were present in the *OO′* dideuteriofumaric acid after irradiation; only very minor spectral changes occurred because of the deuteration. The radical (II) has been studied previously in irradiated succinic acid [2,3] in which lattice very similar couplings were obtained.

DISCUSSION

Since the spectra were examined a few hours after irradiation at room temperature they are not necessarily those of the primary products of radiation damage. It must be presumed that initially an unstable radical, R·, is formed and that this reacts with the acid

$$R\cdot + CH(CO_2H){:}CH(CO_2H) \longrightarrow RCH(CO_2H){\cdot}CH(CO_2H)\ \text{(I)}$$

The nature of R is unknown and it might be the radical (II). Further, radical (I) itself might act as R·, leading to polymerisation. If the fumaric acid is packed in hydrogen-bonded layers, models suggest that R· must be formed in the layer above or below that of the acid with which it reacts; if R is out of the plane of the radical the β-hydrogen attached to the same carbon must lie somewhere near the plane, in agreement with the fairly low coupling of 56 Mc./sec.

It is known that hydrogen atoms add readily to double bonds and the formation of the second radical by a process

$$H\cdot + CH(CO_2H){:}CH(CO_2H \longrightarrow CH_2(CO_2H){\cdot}\dot{C}H(CO_2H)\ \text{(II)}$$

is not unexpected. The α-hydrogen attached to the free-radical centre would still be nearly parallel to its original direction, and hence to the $\dot{C}$–H bond in radical (I), as observed. Since both carboxyl groups are roughly in the plane, the C–H of the CH_2 group should make, in projection on the plane perpendicular to the central C–C bond, an angle of about 60° with the molecular plane. The exact form of the coupling to be expected is

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[10] Whiffen, *Pure Appl. Chem.*, 1962, **4**, 185.

[11] Horsfield, Morton, and Whiffen, *Mol. Phys.*, 1961, **4**, 425.

somewhat uncertain,[7] but it is clear that a form $\beta \cos^2 \theta$ with β about 130 Mc./sec. is generally acceptable.[2,3,11] θ is here the angle to the perpendicular to the plane, which is likely to be 30°, by the argument above, and a coupling of 97 Mc./sec. is calculated; this is to be compared to the observed value of about 95 Mc./sec. for each hydrogen. The same formula gives $\theta = 49°$ for the β-hydrogen in radical (I).

Although this work has not produced any new form of radical and has not indicated the mechanism for formation of the radicals in irradiated fumaric acid, it has suggested that incipient polymerisation is possible in this lattice and has provided evidence about molecular arrangement which might assist an *X*-ray structure determination.

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