156. *Electron Spin Resonance Studies of Radiation Damage in Some Aliphatic Acids and Salts.*

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Radicals trapped in solid aliphatic dibasic acids and a few monobasic acid salts subjected to high-energy *X*- or γ-rays have been identified by electron spin resonance. The hyperfine coupling constants have been measured and are discussed. Some comments are made on radical stability, with respect to both the present work and other dibasic acids previously studied.

Electron spin resonance (e.s.r.) is a technique by which it is possible to identify free radicals in organic materials damaged by high-energy radiation. Much of the previous work has been undertaken on single crystals which has the advantage of greater precision and certainty, but can be tedious if a complete set of crystal orientations is studied. Now that the pattern of such results is established, it seemed opportune to investigate a large number of compounds less exhaustively. The purpose of this investigation is two-fold: to identify the chemical site or sites of radiation damage and to investigate the variation of hyperfine coupling constants as a function of radical structure. The majority of the compounds studied were substituted aliphatic dibasic acids in order to supplement the work on the parent acids; the exact choice was dictated by availability, and the requirement that the material forms stable crystals at room temperature. Some monobasic acid salts were also included.

Experimental

Electron Spin Resonance Measurements.—Measurements were made at room temperature with a spectrometer [1] working at 9000 Mc./sec. with superheterodyne detection. First- and second-derivative presentations were available. Hyperfine coupling constants were measured against field markers provided [2] by proton resonance signals. Polycrystalline samples were held in open glass tubes and single crystals were mounted on Perspex posts. Single-crystal spectra were recorded at 10° or 15° intervals as the crystal was rotated with respect to the magnetic field; spectra for three mutually orthogonal axes were recorded. All spectra had *g*-factors close to 2·003. Hyperfine coupling constants were measured to an accuracy of about ± 2 Mc./sec., the exact value depending on line-widths. γ-Irradiations were carried out by the Spent Fuel Irradiation Unit, A.E.R.E., Harwell, with γ-rays of mean energy 1 Mev, the sample being at room temperature. Doses up to 10 Mrad were used. *X*-Irradiations were made with a 150 kv tube for several hours, again at room temperature. In the cases where the effects of the two types of radiation were compared no difference in the nature of the radicals formed was observed. The total dose affected only the radical yield and not the nature of the radicals formed. The effect of dose, dose rate, and nature of radiation were therefore not studied systematically. Materials were commercial samples; in each case the melting point was in agreement with literature values.

Propane-2,2-*dicarboxylic Acid* (I).—γ-Irradiated polycrystalline samples gave clean spectra of 7 lines with intensity ratios of 1 : 6 : 15 : 20 : 15 : 15 : 6 : 1 and a separation of 62 Mc/sec. The radical * must be $\cdot C(CH_3)_2CO_2H$, which confirms the unpublished results quoted by Heller.[3] No change was observed on heating the sample at 100°c for 5 min.

Butane-1,1-*dicarboxylic Acid* (II).—Single crystals of acid (II) grew readily from aqueous solution, and were studied after irradiation with γ-rays. The spectra [Fig. 1(*a*)] mostly showed three lines, the central feature being broader and twice the integrated intensity of each of the outer pair. At a few orientations distinct splittings could be seen on the central line. The best analysis that could be made suggests two protons of isotropic couplings 60 and 64 Mc./sec.

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* The radical trapped in compound (I) will sometimes be referred to as " radical (I) " for brevity. If more than one radical had been present they would have been designated (Ia), (Ib), etc. as in Table 1 below.

[1] Horsfield, Morton, and Whiffen, *Trans. Faraday Soc.*, 1961, **57**, 1657.

[2] Horsfield, Morton, and Moss, *J. Sci. Instr.*, 1961, **38**, 322.

[3] Heller, *J. Chem. Phys.*, 1961, **36**, 175.

with a small anisotropic range of ±5 Mc./sec. each; these are surely both β-hydrogens and the radical must be $\cdot C(CO_2H)_2CH_2CH_2CH_3$.

Heptane-4,4-*dicarboxylic Acid* (III).—An *X*-irradiated polycrystalline sample gave a spectrum with a dominant pattern of eight lines. This same pattern was apparent for a single, triclinic crystal for which an analysis was made. The couplings were nearly isotropic, and the approximate principal values were β_1: 93, 85; and 80 Mc./sec.; β_2: 65, 61, and 57 Mc./sec.; and β_3: 26, 17, and 17 Mc./sec., giving isotropic couplings of 86, 61, and 20 Mc./sec., respectively.

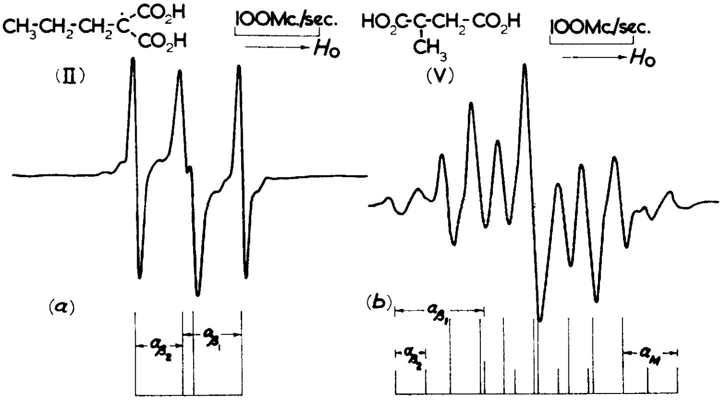

FIG. 1. (a) First derivative spectrum of a γ-irradiated crystal of butane-1,1-dicarboxylic acid (II). (b) First derivative spectrum of γ-irradiated polycrystalline propane-1,2-dicarboxylic acid (V), heated at 100° (10 min.); reconstruction below.

Accurate analysis was difficult owing to the presence of one or more other radicals whose spectra overlapped with the main spectrum; insufficient information could be gleaned from the neglected lines to suggest the nature of the species responsible. The nature of the main radical is not clear; the most likely suggestion is that one carboxyl group has been lost to give the radical $\cdot C(CH_2CH_2CH_3)_2CO_2H$, the coupling to one of the four β-hydrogens being too small to observe. If this is correct, then it is surprising that the lines were always sharp, $\Delta\nu_{MS} \sim 9$ Mc./sec. Heating of the polycrystalline sample at 100° for 30 min. caused the intensity of the spectrum to be halved, but only brought about small changes of shape.

2-*Methylpropane*-1,1-*dicarboxylic Acid* (IV).—The polycrystalline acid (IV) gave a many-line spectrum with narrow components, after irradiation with γ- or *X*-rays. As was expected a single crystal gave virtually the same spectrum for any orientation.

The most prominent features were a set of eight lines with intensity ratios of 1 : 7 : 21 : 35 : 35 : 21 : 7 : 1 and a separation of 66 Mc./sec. The hydrogens concerned must surely be six, from two methyl groups, and one other. The radical could be $\cdot C(CH_3)_2CH(CO_2H)_2$ (IV*a*) or rotating $\cdot CH(CH_3)_2$ (IV*b*) in which the anisotropy is averaged to zero. In no case was there evidence, even in the single crystal, of further resolution so that the coupling of the seventh hydrogen must be very similar to that of the methyl-group hydrogens.

When the powder or a crystal was heated at 70°C for an hour, new, weak lines appeared; at room temperature they slowly decayed with a half-life of about 5 days, and could be redeveloped on heating. The unirradiated material gave no radicals on heating. Only the wing-lines could be clearly identified; they appeared to have an intensity pattern of 1 : 6 : 15. . . . . , with a separation of 66 Mc./sec., indicating that two methyl groups are attached to the free-radical centre. The total spread between the outermost lines was 529 Mc./sec., leaving 133 Mc./sec. unaccounted for; there was no appreciable anisotropy or evidence for two further hydrogens, so this is best attributed to splitting from one β-hydrogen. If this is the case it is difficult to see how the radical can be other than $\cdot C(CH_3)_2CH(CO_2H)_2$ (IV*c*) although if two β-hydrogens are present the radical $\cdot C(CH_3)_2CH_2CO_2H$ (IV*c*), formed by loss of carbon dioxide from (IV*a*) or (IV*c*) is a possibility. Assuming that the second radical is (IV*c*) then (IV*a*) and (IV*c*) would be conformational isomers with different β-couplings. The preparation of $(CH_3)_2CHCD(COOD)_2$ has been postponed, after one unsuccessful attempt, until more starting material is available.

Propane-1,2-*dicarboxylic Acid* (V).—Polycrystalline acid (V), irradiated with γ-rays, gave a detailed spectrum upon which a strong, rather broad central feature was superimposed. After heating the irradiated sample to 100°C for 10 min. this feature virtually disappeared and the spectrum shown in Fig. 1(*b*) was obtained. This has sharp lines, which suggests that no α-hydrogens are present; the analysis shown in Fig. 1(*b*) provides a reasonable fit. The fit for the intensities is not expected to be very exact for polycrystalline samples, as slight anisotropies can cause different features to have different widths. The analysis relates to five hydrogens with isotropic hyperfine couplings of 96, 67, 67, 67, and 38 Mc./sec. This would be expected for the radical $\cdot C(CH_3)(CO_2H)CH_2CO_2H$ if the 67 Mc./sec. coupling corresponds to the hydrogens of a rotating methyl group, and the 38 and 96 Mc./sec. couplings correspond to the two hydrogens of the methylene group; the latter hydrogens may be non-equivalent in the crystal. The spectrum was unchanged at 77°K, at which temperature the methyl group must still be rotationally mobile.[4]

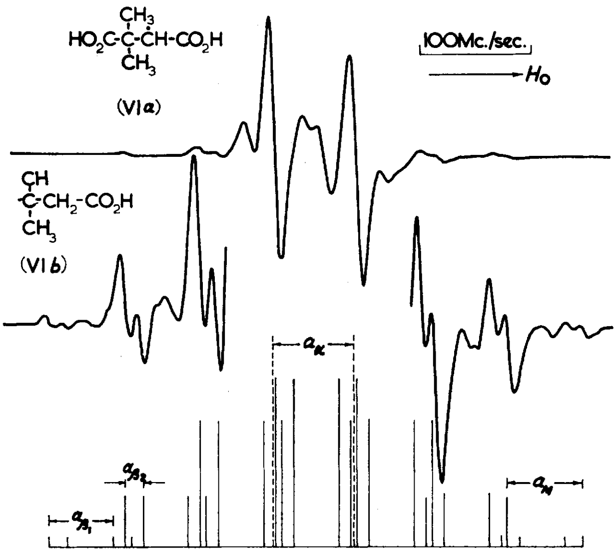

FIG. 2. First derivative spectrum of a freshly *X*-irradiated crystal of 2-methylpropane-1,2-dicarboxylic acid (VI). Above, low gain; centre, wings at increased gain. Suggested reconstruction below: full lines, $\cdot C(CH_3)_2CH_2CO_2H$ (VI*b*); dotted lines, $\cdot CH(CO_2H)C(CH_3)_2CO_2H$ (VI*a*).

2-*Methylpropane*-1,2-*dicarboxylic Acid* (VI).—An *X*-irradiated polycrystalline sample gave a very wide, complex, many-line spectrum. Since crystals grew easily from aqueous solution, an irradiated single crystal was studied; this gave spectra consistent with triclinic symmetry, that is without multiple sites for each radical species.

Fig. 2 shows a typical spectrum; this is dominated by a two-line feature, but at high gain a well-developed many-line spectrum can be seen in the wings. The central two lines were examined in a complete set of crystal orientations; their separation changed in the manner to be expected [5,6] for an α-hydrogen with principal values of its coupling tensor of −91, −61, and −24 Mc./sec.; isotropic coupling −59 Mc./sec. The spectra were somewhat overlapped by a line at the centre, possibly the strongest line of the other radical, so that the lowest value, −24 Mc./sec., may be somewhat in error. The radical responsible for these spectra must surely be $\cdot CH(CO_2H)C(CH_3)_2CO_2H$ (VI*a*) this being the most heat-stable of the radicals formed.

The total spread of the spectrum of the freshly-irradiated crystal was about 470 Mc./sec. The most prominent feature was a doublet in each wing, with separation about 19 Mc./sec.

[4] Horsfield, Morton, and Whiffen, *Mol. Phys.*, 1962, **5**, 115.
[5] McConnell and Strathdee, *Mol. Phys.*, 1959, **2**, 129.
[6] Whiffen, *Pure Appl. Chem.*, 1962, **4**, 185.

About 65 Mc./sec. inside each of these doublets was another doublet, with the same separation of 19 Mc./sec. and six times the intensity. A further pair of doublets, somewhat distorted by weaker lines and of roughly fifteen times the intensity, could also be seen; an intensity pattern 1 : 6 : 15 : 20 : 15 : 6 : 1 typical of six equivalent hydrogens is suggested. It thus appears that two methyl groups are attached to the free-radical centre; there is also a coupling of 19 Mc./sec. to one β-hydrogen and, to complete the spectrum, a further coupling of about 61 Mc./sec. is required. The analysis is indicated in Fig. 2. The radical must be $\cdot C(CH_3)_2CH_2CO_2H$ (VI*b*), formed by loss of the carboxyl group. Although exact analysis is not very accurate, owing to overlapping components, tensors have been obtained for each nucleus; the six methyl hydrogens had an isotropic coupling of 65 Mc./sec. with a total anisotropic spread from 64 to 68 Mc./sec. The smallest β-hydrogen tensor had principal values +27, +17, +14 Mc./sec. (isotropic coupling, +19 Mc./sec.). The other β-hydrogen tensor was found mainly from difference measurements and is less accurate; the values obtained were +70, +66, and +47 Mc./sec. (isotropic coupling, +61 Mc./sec.) but the lowest value, in particular, is uncertain.

A spectrum obtained immediately after *X*-irradiation for 2 hr. at room temperature indicated a concentration ratio for the radicals (VI*a*) to (VI*b*) of about 10 : 1, which changed to 100 : 1 after heating the crystal at 100°C (15 min.).

There is evidence for the presence of a third species with a spectrum having a total spread of 410 Mc./sec. This suggests that the radical may contain two methyl groups attached to the free-radical centre; $\cdot C(CH_3)_2CO_2H$ (VI*c*) is a possibility, but an insufficient number of the lines were free from overlapping to confirm this suggestion.

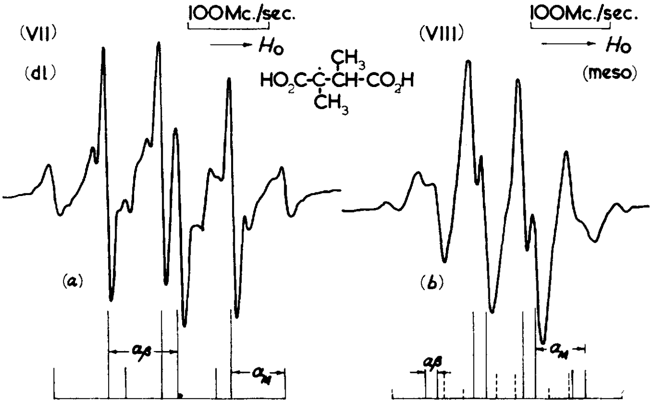

FIG. 3. First derivative spectra of *X*-irradiated polycrystalline butane-2,3-dicarboxylic acid, after heating at 100° (30 min.), and their interpretation for the radicals $\cdot C(CO_2H)(CH_3)CH(CH_3)CO_2H$: (a) Racemic isomer (VII); (b) Meso isomer (VIII). Dashed lines at positions for radical (VII) repeated in (b) indicate possible impurity.

Butane-2,3-dicarboxylic Acid (*racemic*) (VII) (*m.p.* 200—205°).—This material was synthesised by G. O'Neill of this division and the separation of isomers carried out according to the method of Bone and Sprankling.[7] Polycrystalline (VII) irradiated with *X*-rays gave a spectrum overlapped by a broad central feature. Heating of this sample at 100° (30 min.) gave a clear narrow-line spectrum [Fig. 3(*a*)]. The main analysis is clear in terms of four hydrogens with isotropic couplings of 88, 66, 66, and 66 Mc./sec., as indicated. Each line is flanked by weak satellites separated by 14 Mc./sec. from the main line, and these are attributed to " spin-flip " transitions [8] of other hydrogens; as is to be expected for weak transitions, they proved to be less easily saturated at high power levels. The radical $\cdot CH(CO_2H)CH(CH_3)CO_2H$ with rotating methyl-group couplings of 66 Mc./sec. and a coupling of 88 Mc./sec. to the CH hydrogen, would be expected to give such a spectrum. The spectrum was unchanged at 77°K.

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[7] Bone and Sprankling, *J.*, 1899, **75**, 839.

[8] Trammell, Zeldes, and Livingston, *Phys. Rev.*, 1958, **110**, 630.

Butane-2,3-*dicarboxylic Acid* (*meso*) (VIII) (*m. p.* 114—125°).—The spectrum of an *X*-irradiated polycrystalline sample of this isomer also had a broad central feature when examined immediately. Heating of this sample to 100° for 30 min. gave rise to the spectrum shown in Fig. 3(*b*). The analysis, given in terms of four hydrogens of coupling constant 64, 64, 64, and 17 Mc./sec., covers the main features of the spectrum. In addition, there are two weak lines in the wings which are probably due to another species which quite possibly arises from a trace of the racemic isomer (VII) (the existence of a trace of impurity is suggested by the wide melting range). The suggested radical is again $\cdot C(CH_3)(CO_2H)CH(CH_3)CO_2H$; this is the same radical as that suggested for the racemic isomer, but the very different coupling to the CH hydrogen, 17 Mc./sec. as compared to 88 Mc./sec., indicates a different geometrical configuration. This is only to be expected since the host lattices are different. Again, the spectrum was unchanged at 77°K.

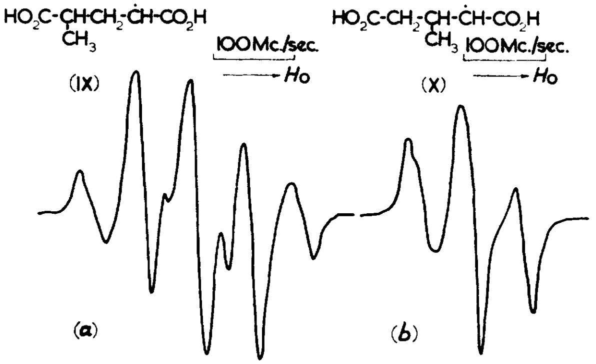

FIG. 4. First derivative spectra of *X*-irradiated polycrystalline (a) butane-1,3-dicarboxylic acid (IX) and (b) 2-methylpropane-1,3-dicarboxylic acid (X).

Butane-1,3-*dicarboxylic Acid* (IX).—*X*-Irradiated polycrystalline acid (IX) gave the spectrum shown in Fig. 4(*a*) there being five broad lines with a total spread of 260 Mc./sec. The shape of this spectrum is similar to those of irradiated polycrystalline glutaric and adipic acid,[9,10] and the experimental results must be interpreted in terms of two β-hydrogens, with different coupling constants, and one α-hydrogen giving an anisotropic interaction. Therefore the radical $\cdot CH(CO_2H)CH_2CH(CH_3)CO_2H$ (IX) is suggested, with an isotropic coupling constant of -60 Mc./sec. for the α-hydrogen, and of 130 and 65 Mc./sec. for the β-hydrogens. These numerical values are only very approximate, owing to considerable line-widths ($\Delta\nu \sim 30$ Mc./sec.) in the spectrum. There was no change in the shape of the spectrum after heating the sample at 80° (1 hour).

2-*Methylpropane*-1,3-*dicarboxylic Acid* (X).—An *X*-irradiated polycrystalline sample gave the spectrum shown in Fig. 4(*b*). The three lines have different widths ($\Delta\nu_{ms}$: low-field line, 42 Mc./sec.; central line, 28 Mc./sec.; high-field line, 27 Mc./sec.) and typical asymmetric shapes; intensity ratios were approximately 1 : 2 : 1, and the total spread of the spectrum was about 126 Mc./sec. This type of spectrum is to be expected from a radical with one α- and one β-hydrogen, in this case $\cdot CH(CO_2H)CH(CH_3)CH_2CO_2H$ (X); 63 Mc./sec. is typical for an α-hydrogen splitting, though the isotropic coupling will be somewhat less, and is in the range for a β-hydrogen as well. The spectrum was unchanged in shape, though diminished in intensity, after heating at 80° (30 min.).

3-*Methylbutane*-1,3-*dicarboxylic Acid* (XI).—*X*-Irradiated polycrystalline acid (XI) gave a spectrum very like that of *X*-irradiated (IX), shown in Fig. 4(*a*). The radical with one α- and two β-hydrogens must be $\cdot CH(CO_2H)CH_2C(CH_3)_2CO_2H$, but the total spread is narrower than that of Fig. 4(*a*) and, though the coupling constants have not been accurately obtained they must be near -60 Mc./sec. for the α-hydrogen, and 123 and 61 Mc./sec. for the

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[9] Abraham, Ovenall, and Whiffen, *Trans. Faraday Soc.*, 1958, **54**, 1128.
[10] Molin, Chkheidze, Buben, and Voevodskii, *Zhur. strukt. Khim.*, 1961, **2**, 293.

two β-hydrogens. No change in the shape of the spectrum occurred on heating the sample at 60° (30 min.), but the radicals disappeared entirely at 75° (30 min.).

2,2-*Dimethylpropane*-1,3-*dicarboxylic Acid* (XII).—Freshly *X*-irradiated polycrystalline acid (XII) gave a clear spectrum of two broad lines ($\Delta\nu_{ms}$; low-field line, 31 Mc./sec.; high-field line 24 Mc./sec.) with a separation of 63 Mc./sec. This is typical of an α-hydrogen suggesting the radical $\cdot CH(CO_2H)C(CH_3)_2CH_2CO_2H$. This was confirmed by single-crystal measurements. The crystal is monoclinic with two distinguishable sites related by the *b*-axis, and there was considerable overlapping of lines from radicals in different sites, and accurate hyperfine information could not be readily obtained. The best fit was for a tensor with principal values −88, −55, and −30 Mc./sec. (isotropic coupling, −58 Mc./sec.); these are sufficiently close to the typical values to confirm that it is an α-hydrogen which is involved, as suggested above. There were also a few weak unexplained lines, which might be due to a small amount of another species. It can be seen that the isotropic coupling of −58 Mc./sec. is not in exact accord with the polycrystalline splitting of 63 Mc./sec. This is to be expected [11,12] because the average splitting is the root mean square of the principal coupling constants, *i.e.*, $3^{-\frac{1}{2}}(88^2 + 55^2 + 30^2)^{\frac{1}{2}} =$ 62·5 Mc./sec., which is in good agreement with the polycrystalline observation. Similar downward adjustments have been made to the α-hydrogen splittings of radicals (IX), (X), (XI), (XIV), and (XV) to give the approximate isotropic couplings listed in Table 1.

Pentane-2,4-*dicarboxylic Acid* (*mixed isomers*) (XIII).—*X*-Irradiated polycrystalline acid (XIII) gave a five-line symmetrical spectrum with intensity ratios of 1 : 4 : 6 : 4 : 1 and equal separation between lines of 68 Mc./sec. This type of spectrum must be interpreted in terms of four hydrogens with equal coupling constants. The lines were fairly narrow ($\Delta\nu_{ms}$ ~17 Mc./sec.) and it would appear that there is no α-hydrogen. The suggested radical is $\cdot C(CH_3)(CO_2H)CH_2CH(CH_3)CO_2H$, in which the two β-hydrogens on the central carbon atom have couplings of 68 Mc./sec. and <17 Mc./sec. The remaining three hydrogens which interact are those of the methyl group. Heating at 100° (30 min.) caused no change in the spectrum.

Cyclohexane-1,1-*diacetic Acid* (XIV).—*X*-Irradiated polycrystalline acid (XIV) gave a spectrum of two equally intense lines with a separation of 58 Mc./sec. and line-widths of 33 Mc./sec. This pattern shows that the unpaired electron interacts only with one α-hydrogen. The radical $\cdot CH(CO_2H)C < [CH_2]_5CH_2CO_2H$ (XIV) is suggested.

There was no change in the shape of the spectrum after the sample had been heated at 100° for 30 min.

2-*Methylbutane*-1,4-*dicarboxylic Acid* (XV).—*X*-Irradiated polycrystalline acid (XV) gave a broad-line spectrum very similar to that obtained from (XI). One α-hydrogen and two β-hydrogens, with couplings of 124 and 62 Mc./sec., appear to be present, and the suggested radical is $\cdot CH(CO_2H)CH_2CH(CH_3)CH_2CO_2H$. The spectrum was unchanged after the sample had been heated at 80° for 30 min.

Sodium Cyclobutanecarboxylate (XVI).—Cyclobutanecarboxylic acid itself is a liquid at room temperature; therefore its sodium salt (XVI) was used for measurements. After *X*-irradiation, this salt gave a well-resolved five-line spectrum [Fig. 5(*a*)] with a total spread of 362 Mc./sec. The lines were equally spaced and had intensity ratios of 1 : 4 : 6 : 4 : 1 and line-widths of 13 Mc./sec. Thus the unpaired electron interacts only with four equivalent β-protons, and the radical $[CH_2]_3 > \dot{C}CO_2^-$, with coupling constants of +90 Mc./sec. for each β-proton, is suggested.

The radicals were stable at room temperature, but loss of e.s.r. signal occured after the sample had been heated to 100° for only 2 min.

Cyclobutane-1,1-*dicarboxylic Acid* (XVII).—Polycrystalline samples of (XVII), subjected to *X*-rays, gave fairly sharp spectra, which appeared to be due to two different radicals. When the sample was heated at 100° for 10 min. the spectrum changed markedly to leave predominantly that of one of the radicals; this spectrum had five lines with intensity ratios of 1 : 4 : 6 : 4 : 1 and equal separation between adjacent lines of 90 Mc./sec. This spectrum closely resembled that of Fig. 5(*a*); this is to be expected for the radical $[CH_2]_3 > \dot{C}CO_2H$ (XVII*a*), formed by loss of a carboxyl group. A monoclinic crystal, grown from alcohol, was also examined; although there was some change of line-width with crystal orientation,

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[11] Zeldes, Trammell, Livingston, and Holmberg, *J. Chem. Phys.*, 1960, **32**, 618.

[12] Whiffen, " Free Radicals in Biological Systems," Ed. Blois, Academic Press, New York, 1961, p. 227.

indicating incipient resolution, for all directions examined, the couplings were in the narrow range 88—93 Mc./sec. Fig. 5(*b*) shows the spectrum of an unheated crystal, and the solid lines in the reconstruction indicate the spectrum of the cyclic radical.

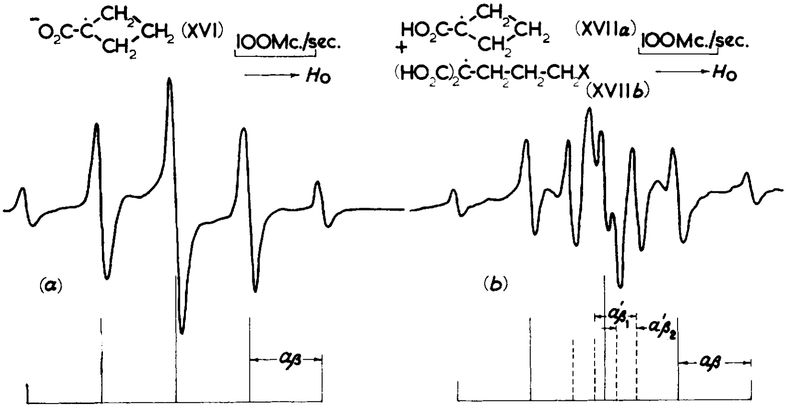

FIG. 5. First derivative spectra of *X*-irradiated (a) polycrystalline sodium cyclobutanecarboxylate (XVI) and (b) single crystal of cyclobutane-1,1-dicarboxylic acid (XVII) (freshly irradiated). Reconstruction: full lines, radical (XVII*a*); dashed lines (XVII*b*).

The more labile radical appeared to give four rather sharp lines of equal intensity, both in the powder and in the single crystal; these lines are shown dashed in the reconstruction of Fig. 5(*b*). They appear to be due to two β-hydrogens with isotropic couplings of 27 and 54 Mc./sec., the splittings being within 3 Mc./sec. of these values for all the crystal orientations studied. The suggested radical is $\cdot C(CO_2H)_2[CH_2]_3X$ (XVII*b*) formed by opening of the ring; X may be a hydrogen atom from another damage site, but there is no definite evidence on this point.

Immediately after *X*-irradiation at room temperature (3 hr.) the spectra indicated that the relative abundance of the radicals (XVII*a*) to (XVII*b*) was 2 : 1; after heating at 100° (10 min.) it was 20 : 1.

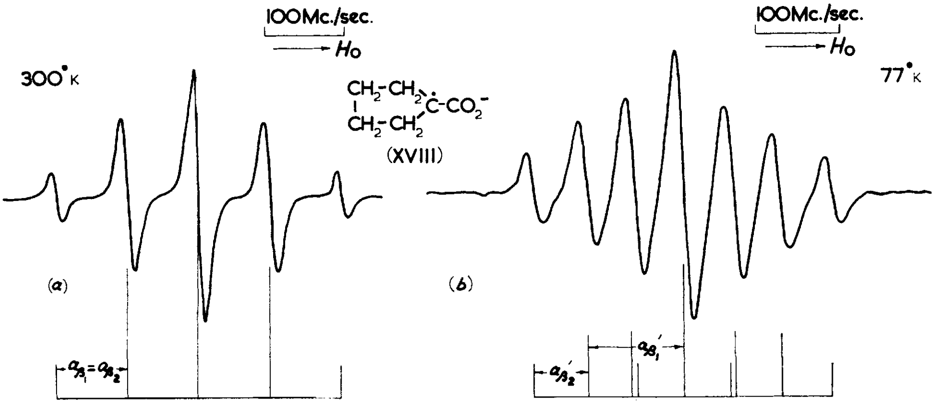

FIG. 6. First derivative spectra of *X*-irradiated polycrystalline sodium cyclopentane carboxylate (XVIII) and their interpretation. The spectra were measured at (a) 300°K, (b) 77°K.

Sodium Cyclopentanecarboxylate (XVIII).—The sodium salt (XVIII) was prepared by neutralising the liquid acid with sodium hydroxide. After *X*-irradiation a polycrystalline sample gave the spectrum of Fig. 6(*a*), when measured at room temperature. The five-line spectrum had a total spread of 356 Mc./sec. and the intensity ratios were 1 : 4 : 6 : 4 : 1, when allowance was made for the differences in line-width. The radical must be $[CH_2]_4 > \dot{C}CO_2^-$ (XVIII) with equal couplings of 89 Mc./sec. to each β-hydrogen. Since this equality is not found in cyclopentyl [13] the spectrum was re-examined at 77°K; the spectrum shown in Fig. 6(*b*) was obtained which is in best accord with two couplings of 118 Mc./sec. and two of 63 Mc./sec., as indicated. Thus there must be a ring-inversion type of motion which makes the β-hydrogens chemically equivalent at room temperature, but which ceases at 77°K or, more strictly, only occurs in a time which is long compared to the reciprocal of the hyperfine-coupling difference of 55 Mc./sec. Heating at 100° caused the radicals to disappear.

trans-*Cyclohexane*-1,4-*dicarboxylic Acid* (XIX).—An *X*-irradiated polycrystalline sample gave [Fig. 7(*a*)] an eight-line symmetrical spectrum with intensity ratios near 1 : 2 : 1 : 2 : 4 : 2 : 1 : 2 : 1 and linewidths of 15 Mc./sec. The analysis is given in terms of two pairs of equivalent β-hydrogens with couplings of 118 and 40 Mc./sec., the radical $\cdot C(CO_2H) < [CH_2]_4 > CHCO_2H$, (XIX) being suggested. The radicals were very stable in the matrix, there being a very small reduction in intensity after heating the sample at 100° (1 hr.).

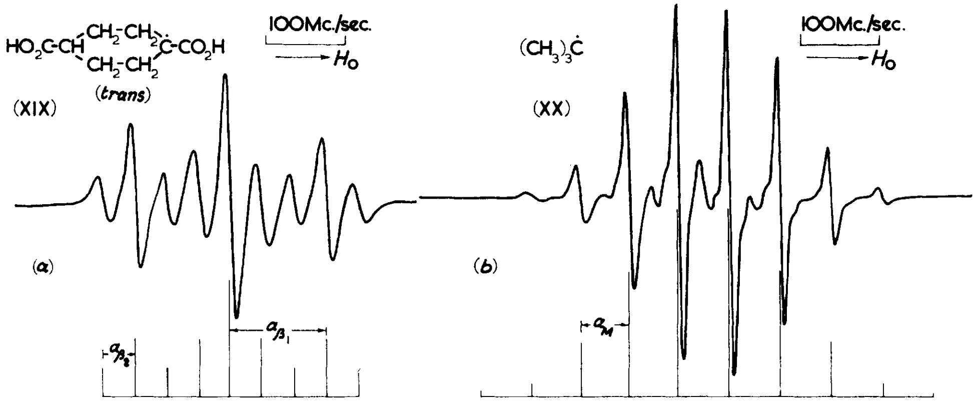

FIG. 7. First derivative spectra of *X*-irradiated (*a*) polycrystalline *trans*-cyclohexane-1,4-dicarboxylic acid (XIX) and (b) polycrystalline ammonium 1,1-dimethyl ethane 1-carboxylate (XX).

Ammonium Pivalate (XX).—The *X*-irradiated polycrystalline ammonium salt, $(CH_3)_3CCO_2^-NH_4^+$, (XX) (ammonium pivalate), gave a clear ten-line spectrum with approximately the binomial distribution of intensities. Fig. 7(*b*) shows the central eight lines; the other two lines were too broad, and thus too weak to be seen at this amplification, but their existence has been verified. The separation of 64·5 Mc./sec. is typical for a methyl group, and the radical must be t-butyl, $\cdot C(CH_3)_3$ (XX). The variations of linewidth [Fig. 7(*b*)] in the spectrum of the polycrystalline sample indicate that there is slight anisotropy. In a single triclinic crystal some slight indications of line doubling and splitting were observed, but there were always less than the line-width of 7 Mc./sec. and could not be analysed. Heating at 70° for 5 min. halved the radical concentration without change in shape of the spectrum. Fig. 7(*b*) also shows some weak lines, not due to t-butyl.

DISCUSSION

The Hyperfine Couplings.—In Table 1 is collected together the results of the present investigation and results, taken from the literature, on related acids. The first column lists the starting material; the italics indicate the atom or group removed ("*CH_2*" implies only the loss of one of the two equivalent hydrogen atoms). The hyperfine couplings are divided into three columns: " α- " for strongly anisotropic couplings attributed to the hydrogen atom attached to the free-radical centre; " β- " for individual couplings to

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[13] Zhidomirov and Bubnov, *Opitika i Spektroskopiya*, 1962, **12**, 445.

hydrogen atoms on an adjacent carbon atom; and " β-methyl " for a rotating methyl group attached to the centre, the equivalent hydrogen atoms of which give a 1 : 3 : 3 : 1 pattern, the coupling quoted being that for each hydrogen.

TABLE 1.

Collected results: roman numerals, this paper; latin letters, reference indicated, bracketed results (from radicals, with α-hydrogens, in polycrystalline samples) are less accurate. The identification of radicals in (III) and (IV) is less certain than in the other cases. Italic letters indicate the group or atom lost on irradiation.

		Hydrogen hyperfine couplings (Mc./sec.)		
Material	Ref.	α-posn.	β-posn.	β-Methyl groups
$\mathit{H}_2\mathrm{C(CO_2H)_2}$	A[a]	−60	—	—
$\mathrm{H_2C}(\mathit{CO_2H})_2$	B[b]	−63 −62	—	—
$\mathrm{CH_3}\mathit{H}\mathrm{C(CO_2H)_2}$	C[3]	—	—	71
$\mathrm{CH_3HC}(\mathit{CO_2H})_2$	D[3]	−55	—	70
$\mathrm{(CH_3)_2C}(\mathit{CO_2H})_2$	(I)	—	—	62, 62
$\mathrm{CH_3CH_2}\mathit{H}\mathrm{C(CO_2H)_2}$	E[c]	—	70, 57	—
$\mathrm{CH_3[CH_2]_2}\mathit{H}\mathrm{C(CO_2H)_2}$	(II)	—	64, 60	—
$\mathrm{(CH_3CH_2CH_2)_2C}(\mathit{CO_2H})_2$	(III)	—	86, 61, 20, 0	—
$\mathrm{(CH_3)_2C}\mathit{H}\mathrm{HC(CO_2H)_2}$	(IV*a*)		66	66, 66
or $\mathrm{(CH_3)_2CH}\mathit{HC}(\mathit{CO_2H})_2$	(IV*b*)	−61		66, 66
$\mathrm{(CH_3)_2C}\mathit{H}\mathrm{HC(CO_2H)_2}$	(IV*c*)		133	66, 66
$\mathrm{HO_2CCH_2C}\mathit{H}_2\mathrm{CO_2H}$	F[d,e]	−60	100, 80	
$\mathrm{HO_2CC}\mathit{H}\mathrm{(CH_3)CH_2CO_2H}$	(V)	—	96, 38	67
$\mathrm{HO_2CC(CH_3)_2C}\mathit{H}_2\mathrm{CO_2H}$	(VI*a*)	−59	—	—
$\mathit{HO_2C}\mathrm{C(CH_3)_2CH_2CO_2H}$	(VI*b*)	—	61, 19	65, 65
$\mathrm{HO_2CC}\mathit{H}\mathrm{(CH_3)CH(CH_3)CO_2H}$ (dl)	(VII)	—	88	66
$\mathrm{HO_2CC}\mathit{H}\mathrm{(CH_3)CH(CH_3)COOH}$ (meso)	(VIII)	—	17	64
$\mathrm{HO_2CCH_2CH_2C}\mathit{H}_2\mathrm{CO_2H}$	G[f]	−56	122, 47	—
$\mathrm{HO_2CCH_2CH_2C}\mathit{H}_2\mathrm{CO_2H}$	H[f]	−51	107, 43	—
$\mathrm{HO_2CCH(CH_3)CH_2C}\mathit{H}_2\mathrm{CO_2H}$	(IX)	(−60)	(130, 65)	—
$\mathrm{HO_2CCH_2CH(CH_3)C}\mathit{H}_2\mathrm{CO_2H}$	(X)	(−60)	(63)	—
$\mathrm{HO_2CC(CH_3)_2CH_2C}\mathit{H}_2\mathrm{CO_2H}$	(XI)	(−60)	(123, 61)	—
$\mathrm{HO_2CCH_2C(CH_3)_2C}\mathit{H}_2\mathrm{CO_2H}$	(XII)	−58	—	—
$\mathrm{HO_2CCH(CH_3)CH_2C}\mathit{H}\mathrm{(CH_3)CO_2H}$	(XIII)	—	68, <17	68
$\mathrm{HO_2CCH_2C{<}[CH_2]_5C}\mathit{H}_2\mathrm{CO_2H}$	(XIV)	−55	—	—
$\mathrm{HO_2CCH_2CH_2CH_2C}\mathit{H}_2\mathrm{CO_2H}$	J[g]	−57	122, 77	—
$\mathrm{HO_2CCH_2CH(CH_3)CH_2C}\mathit{H}_2\mathrm{CO_2H}$	(XV)	(−58)	(124, 62)	—
$\mathrm{[CH_2]_3{>}C}\mathit{H}\mathrm{CO_2^-\ Na^+}$	(XVI)	—	90, 90, 90, 90	—
$\mathrm{[CH_2]_3{>}C}(\mathit{CO_2H})_2$	(XVII*a*)	—	90, 90, 90, 90	—
$\cdot\mathrm{C(CO_2H)_2[CH_2]_3X}$	(XVII*b*)	—	54, 27	—
$\mathrm{[CH_2]_4{>}C}\mathit{H}\mathrm{CO_2^-\ Na^+}$ 300°K	(XVIII)	—	89, 89, 89, 89	—
77°K		—	118, 118, 63, 63	—
$\mathrm{HO_2CHC{<}[CH_2]_4{>}C}\mathit{H}\mathrm{CO_2}$(*trans*)	(XIX)	—	118, 118, 40, 40	—
$\mathrm{(CH_3)_3C}\mathit{CO_2}^-\ \mathrm{NH_4^+}$	(XX)	—	—	64·5, 64·5, 64·5

[a] McConnell, Heller, Cole, and Fessenden, *J. Amer. Chem. Soc.*, 1960, **82**, 766. [b] Horsfield, Morton, and Whiffen, *Mol. Phys.*, 1961, **4**, 327. [c] Rowlands and Whiffen, *Mol. Phys.*, 1961, **4**, 349. [d] Heller and McConnell, *J. Chem. Phys.*, 1960, **32**, 1535. [e] Pooley and Whiffen, *Mol. Phys.*, 1961, **4**, 81. [f] Horsfield, Morton, and Whiffen, *Mol. Phys.*, 1961, **4**, 169. [g] Morton and Horsfield, *Mol. Phys.*, 1961, **4**, 219.

The variation in the α-coupling is scarcely outside the experimental error and it is doubtful if any significance can be attached to the exact values although they are likely to reflect the spin population in the 2*p* half-filled atomic orbital of the free radical.

The methyl couplings are slightly more accurate since they are isotropic, giving sharp lines even in a polycrystalline sample, and the errors of measurement are divided between the three hydrogens. Again the variations are not easily interpreted, though there is a slight tendency[6] for the coupling to be lower if more than one methyl group is attached to the free-radical centre; all values in Table 1 are below the 75 Mc./sec. found for the ethyl radical in liquid ethane.[14]

It is the β-couplings, which can have almost any value from 0 to 135 Mc./sec., which

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[14] Fessenden, *J. Chem. Phys.*, 1962, **37**, 747.

give the most information. Work on non-rotating methyl groups makes it clear [15,16] that the value depends on the molecular geometry. The most important parameter is the angle between the C–H_β bond and the axis of the free radical p orbital, seen in projection on the plane perpendicular to the C–C bond; this angle may be designated θ. The most common formula given for this coupling [17,18] is $B \cos^2 \theta$, with $B \sim 138$ Mc./sec., although the form $B_0 + B_2 \cos^2 \theta$, with $B_0 = 9$, $B_2 = 122$ Mc./sec., has also been suggested.[15] It is not clear if B_0 represents the true direction-independent coupling when the C–H bond is in the nodal plane, or whether the zero-point amplitude of vibration [19] is sufficient to introduce a non-zero effective B_0. The form of the equation is independent of the interpretation of B_0. For cases where there is only one β-hydrogen it is possible to find θ from any such formula, but if there are two β-hydrogens it is probable that the angles are sufficiently regular for the second angle, θ_2, to be $\theta_1 \pm 120°$ which would be required for a regular tetrahedral arrangement at the β-carbon atom. This then provides a form of internal check.

It is possible that the numerical coefficient in such equations may vary with the electronegativity of the substituents and their ability to conjugate with the radical centre. However, as a guide, Table 2 gives the pairs of coupling constants to be expected for the form $124 \cos^2 \theta$ with $(\theta_2 - \theta_1) = 2\pi/3$. The cyclic radicals (XVI), (XVII), and (XVIII) (at 300° K) are expected to have $\theta_1 \sim 30°$, $\theta_2 \sim 150°$, and their coupling of 89—90 Mc./sec., for each hydrogen, is in agreement with this. The four- and five-membered rings give the same value so that there is no strong influence of ring angle, although $B = 120$, rather than 124 Mc./sec., gives perfect agreement.

There are nine radicals, F, G, H, (IX), (XI), J, (XV), (XVIII) (at 77°K), and (XIX), in which one hydrogen atom has a coupling somewhat over 100 Mc./sec., indicating a value of θ_1 in the range $\pm 25°$. θ_2 then has the range from $+95°$ to $+145°$ and the second β-coupling should be within the range 0—80 Mc./sec., as observed. Exact fits with the values in Table 2 are hardly to be expected. The six-membered-ring radical, (XIX), has couplings of 118 and 40 Mc./sec. which suggests a value for θ_1 of about 10°; an exact fit is obtained if $B = 119$ Mc./sec., $\theta_1 = 6°$, and $\theta_2 = 126°$. Such a low value for B is not consistent with the numerous observed couplings of over 120 Mc./sec. or with the methyl group couplings (which should be $B/2$) all of which are greater than 60 Mc./sec. The corresponding figures for an exact fit to (XVIII) at 77°K are: $B = 122$ Mc./sec., $\theta_1 = 15°$, and $\theta_2 = 135°$.

TABLE 2.

Coupling constants, calculated from the form $124 \cos^2 \theta$, for two β-hydrogens, subject to the restriction $(\theta_2 - \theta_1) = 120°$. These figures are merely repeated for values of $\theta_1 > 30°$.

Angles °		Couplings (Mc./sec.)		Angles °		Couplings (Mc./sec.)	
θ_1	θ_2	β_1	β_2	θ_1	θ_2	β_1	β_2
−60	60	31	31	−10	110	120	14
−50	70	52	14	0	120	124	31
−40	80	73	4	10	130	120	52
−30	90	93	0	20	140	105	73
−20	100	105	4	30	150	93	93

Radicals (VI*b*) and (XIII) each have one coupling a little greater than 60 Mc./sec., and one coupling below 20 Mc./sec. Values of $\theta_1 = -45°$ and $\theta_2 = 75°$ are suggested for these cases, although the exact values depend rather critically on the value of the coupling for $\theta = 90°$, if this should not be exactly zero. Radical (III), if it really has the suggested structure, has similar values.

[15] Horsfield, Morton, and Whiffen, *Mol. Phys.*, 1961, **4**, 425.
[16] Miyagawa and Itoh, *J. Chem. Phys.*, 1962, **36**, 2157.
[17] Heller and McConnell, *J. Chem. Phys.*, 1960, **32**, 1535.
[18] Pooley and Whiffen, *Mol. Phys.*, 1961, **4**, 81.
[19] Stone and Maki, *J. Chem. Phys.*, 1962, **37**, 1326.

The couplings of 96 and 38 Mc./sec. for radical (V) are not easily understood with reference to Table 2, but even more anomalous are those for E and (II). The anomalous couplings in E have already been discussed,[20] and, as (II) is very similar, any explanation for one is likely to fit the other. The values in Table 2 suggest that if the couplings are equal they should be either 93 Mc./sec. or 31 Mc./sec. but not the observed 62 Mc./sec. as essentially found for (II). E and (II) each have two carboxyl groups attached to the free-radical centre, a feature found also in A, C, and (XVIIb). The α-hydrogen coupling in A has a normal value of -60 Mc./sec. and the methyl coupling in C, though higher than usual at 71 Mc./sec., is not out of line with those of the other compounds. The couplings in (XVII*b*), of 54 and 27 Mc./sec., are somewhere near those expected for $\theta_1 = -50°$ and $\theta_2 = +70°$, and a non-zero value of B_0 would improve the fit. The effect of delocalisation of the spin on to the carboxyl groups would reduce the expected coupling; although the delocalisation may be a function of the geometry, it is difficult to discuss this in the absence of a known crystal structure. Thus while one may conclude that in (II) either $\theta_1 = -60°$ and $\theta_2 = +60°$, and the coupling is anomalously high or $\theta_1 = 30°$ and $\theta_2 = 150°$, and the coupling is anomalously low, it is difficult to discuss the anomaly without knowing which of these possibilities is correct.

The Damage Centres.—There are two factors governing the selective trapping of radicals at room temperature; the free-radical carbon atom tends to be adjacent to the carboxylic acid group and tends to have as few hydrogens as possible directly attached to it. Apart from radical B which is rather unstable, there is no other radical of the type XCH_2, and in no case has a hydrogen atom been removed from a methyl group, although this does occur in methyl urea.[21] In (XX) the $C-CO_2^-$ bond is broken in preference to a $C-CH_3$ bond and in (XVII) the radical (XVII*a*), formed by breaking a $C-CO_2H$ bond, is more stable than (XVII*b*), formed by breaking a $C-CH_2$ bond. C–H bonds, not in methyl groups, break in preference to C–C bonds in cases such as (XI) and (XII) and tertiary C–H bonds in $(C)_3C-H$ groupings break in preference to C–H bonds in $(C)_2CH_2$ groupings in cases (V), (VII), and (VIII), but not in (XV) where the methylene group only is adjacent to the carboxylic acid.

The heating experiments show that the radicals listed in Table 1 are the most stable in general, except for the cases noted in the text. One of the most striking features observed in acids containing more than two methylene groups is the absence of stable radicals of the type $\cdot CH(CH_2R)CH_2R'$ formed from long-chain hydrocarbons and polymers. It is possible that this type of radical is initially formed but that hydrogen transfer occurs leaving the free-radical centre on a carbon atom bonded to a carboxyl group. Studies at low temperatures and on deuterated samples need to be made in order to solve this problem. It is clear that chemical reactions can occur in the solid, so that the radicals observed at room temperature do not give direct evidence of the original process of radiation damage. The rate of decay of the radicals appears to be related to the difference between the temperature of heating and the crystal melting point; in most cases the radicals disappeared rapidly 20—30° below the melting point.

One of us (Yu. D. S.) wishes to thank the Director for the provision of guest-worker facilities at the National Physical Laboratory. We also acknowledge the assistance of D. E. Henn on crystallographic details and G. O'Neill in chemical preparations.

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[*Received, January 29th,* 1963.]

[20] Rowlands and Whiffen, *Mol. Phys.*, 1961, **4**, 349.

[21] Jaseja and Anderson, *J. Chem. Phys.*, 1961, **35**. 2192.