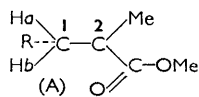


219. *Unstable Intermediates. Part XVIII.* Free Radicals in Poly(methyl Methacrylate).*

By M. C. R. SYMONS.

Thermal loss of radicals trapped in *X*-irradiated poly(methyl methacrylate) has been studied by electron-spin resonance spectroscopy, and it is concluded that a single radical is responsible for the spectrum. An explanation for the alternation in intensities of the nine hyperfine components is offered.

ONE of the earliest studies of electron spin resonance spectra of trapped organic radicals was that of Schneider¹ who obtained a relatively well-resolved spectrum from *X*-irradiated poly(methyl methacrylate) consisting of nine lines with an equal spacing of about 11.5 gauss and a *g*-value close to that of the free-spin. The curious alternation in intensity characteristic of this spectrum (Fig. 1) has been the subject of much discussion,¹⁻⁶ the two major postulates being (a) that a single radical of structure (A) is responsible for the whole spectrum,²⁻⁴ and (b) that there are two trapped radicals, one in high concentration giving a five-line spectrum and the other a four-line spectrum.^{5,6} Although it was possible to account for a nine-line spectrum having an isotropic hyperfine coupling constant of about 11.5 gauss on the former theory,⁴ no convincing explanation of the alternation in intensity was offered. The latter theory, which appears to be currently accepted, is supported by the



* Part XVII, *J.*, 1963, 570.

¹ Schneider, *Discuss. Faraday Soc.*, 1955, **19**, 158.

² Ingram, Symons, and Townsend, *Trans. Faraday Soc.*, 1958, **54**, 409.

³ Abraham, Melville, Ovenall, and Whiffen, *Trans. Faraday Soc.*, 1958, **54**, 1133.

⁴ Symons, *J.*, 1959, 277.

⁵ Piette, "NMR and EPR Spectroscopy," Pergamon Press, Oxford, 1960, p. 218.

⁶ Hotta and Anderson, 4th Internat. Symposium on Free Radicals, 1959.

following observations. (i) Both the five-line and the four-line component have approximately binomial intensity ratios within the groups, and hyperfine coupling constants of about 23 gauss. These results are quite reasonable for trapped aliphatic radicals. (ii) It is claimed that the two radicals have slightly different g -values and hyperfine coupling constants.⁶ (iii) When the solid polymer containing trapped radicals is heated, all nine lines decrease in intensity, but apparently at different rates, the five-line component being lost preferentially.⁵

We shall discuss this evidence in terms of the former postulate (a) and offer an explanation for the alternation in intensities. (1) The theory given earlier⁴ also requires

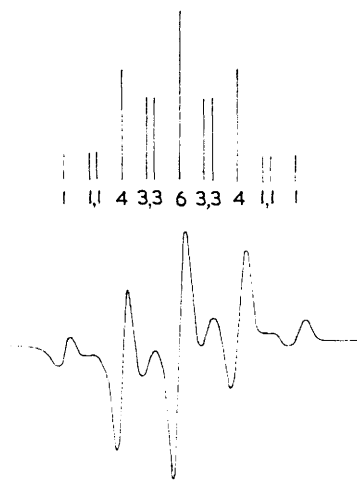


FIG. 1. First derivative of the electron spin resonance absorption spectrum of γ -irradiated poly(methyl methacrylate), together with a suggested reconstruction.

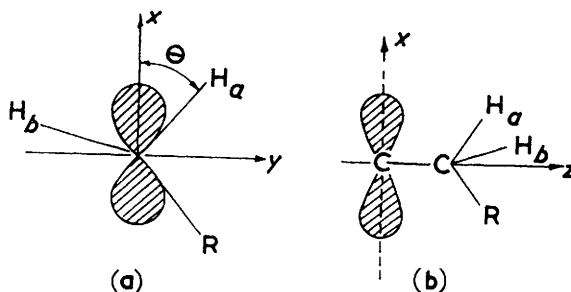


FIG. 2. Orientation of β -protons. (a) Projection in a plane perpendicular to the 1,2-bond. (b) Projection in a plane containing the 1,2-bond and the density axis of the half-filled p -orbital.

that the five-line and the four-line set should have binomial distributions and a hyperfine coupling of 23 gauss. This theory was based upon radicals, having the structure given above, where R is the remainder of the polymer chain, and a preferred conformation in which the bulky group R lies in a plane through C-1 and C-2 at right angles to the radical plane (Fig. 2; $\theta = 60^\circ$). This was found to be the least strained conformation, and such radicals should give rise to a nine-line spectrum having a separation of 11.5 gauss and the intensity distribution 1:2:4:6:6:6:4:2:1. This conclusion results if equation (1)⁴ holds, where $a_{\beta H}$ is the isotropic hyperfine coupling constant to all β -protons.

$$a_{\beta H} = B \cos^2 \theta \quad (1)$$

For a value of 23 gauss from the methyl protons, $B = 46$ gauss and $a_{H_a} = a_{H_b} = 46 \cos^2 60^\circ = 11.5$ gauss.

This intensity distribution is clearly incorrect. The key to the present theory lies in the high-temperature studies by Piette.⁵ Piette's spectra, measured at 80° , consist of nine lines with an intensity distribution far closer to that predicted above. This was taken to mean that one radical was destroyed more rapidly than the other,⁵ but could also mean that some equilibration was occurring rapidly at this temperature. (2) Other workers have not detected the reported⁶ differences in g and a . Careful remeasurement by us showed that, within a rather large experimental error, they are identical. (3) As stated above, this evidence is not compelling. Piette's postulate has been checked by the following experiment.

Poly(methyl methacrylate) was exposed to γ -rays from a ^{60}Co source at room temperature, and then heated at 110° for various periods. Samples were then rapidly cooled and spectra were measured at room temperature. Even after about 80% of the radicals had been lost there was no marked change in the spectrum, the ratio of band intensities remaining constant within experimental error.

Typical results are given in the Table for the central line of the "quintet" and the two more intense lines of the "quartet." It is concluded that the change in the spectrum noted ⁵ at 80° is reversible and not a result of a permanent change in relative concentrations of two radicals.

TABLE.

Relative intensities of the five-component and four-component spectra of γ -irradiated poly(methyl methacrylate) as a function of the time of heating at 110° .

Time (min.)	1	1.5	3	4	5	6
Five-line set	1	0.92	0.75	0.59	0.40	0.31
Four-line set	1	0.93	0.74	0.62	0.50	0.29

Spectra were measured at room temperature. The figures refer to the central line of the five-line spectrum and the average of the two more intense lines of the four-line set. The results are ratios of intensities relative to that after 1 min.

One further argument in favour of the postulate that the spectrum is a property of only one radical is that exactly the same spectrum is obtained under a wide variety of conditions, for example, from irradiated polymer, from radicals occluded in polymer precipitated from solutions of the monomer ^{2,7} and during photo-degradation.⁶ That two radicals should be formed and trapped in the same relative concentrations under these conditions requires a remarkable coincidence.

Line-width Alternation.—It is concluded that only one type of radical is trapped, and the following attempt at interpreting the unusual alternation in intensities is based on the model briefly described above and in more detail in ref. 4.

If all β -protons are equivalent and the single conformation with $\theta = 60^\circ$ is adopted by the trapped radicals, then the alternation in intensities requires that the β -protons, H_a and H_b , are not quite equivalent at room temperature and below (the spectrum is unaltered on cooling to 77°K), but can become equivalent at elevated temperatures. This is shown in Fig. 1, from which it can be seen that the variation in intensity can be a result of variation in line-width, the even-numbered "double" lines being sufficiently close together for them to appear as single broad lines. Whatever be the magnitude of this slight difference between H_a and H_b this theory requires that both the narrow and the broad set of lines have binomial intensity distributions, as is found experimentally.

Unfortunately, overlap between individual lines is so great that it is difficult to estimate the difference between the coupling constants for H_a and H_b . The apparent narrowness of the fourth and the sixth band is a natural consequence of this overlap.

If formula (1) is taken as a projection in the radical plane, then H_a and H_b differ in that one is close to the methyl group and the other to one of the oxygen atoms of the methoxycarbonyl group. It is suggested that these grossly different environments will be sufficient to modify the coupling by the required amount, either directly or as a consequence of a slight distortion of the symmetrical conformation.

However, if there is a sufficiently rapid interchange between the two equivalent conformations having H_a or H_b close to oxygen, their interactions will be averaged and the spectrum will tend to one having equal line widths and the intensity ratio 1 : 2 : 4 : 6 : 6 : 6 : 4 : 2 : 1.

This explanation can be compared with that given by Bolton and Carrington⁸ to explain the alternation in line width found in the electron spin resonance spectrum of

⁷ Bamford, Jenkins, Symons, and Townsend, *J. Polymer. Sci.*, 1959, **34**, 181.

⁸ Bolton and Carrington, *Mol. Phys.*, 1962, **5**, 161.

protonated durosemiquinone, but it contrasts with that proposed to explain the alternation found for n-propyl radicals trapped in solid argon.⁹ In the last case the effect is reversed, the central component from each triplet originating from the two α -protons being narrower than the outer components.

Bamford and Ward¹⁰ have given results which support this conclusion, although the systems studied differ considerably. They also conclude that only one radical is responsible for all the features of their spectra.

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⁹ Cochran, Adrian, and Bowers, *J. Chem. Phys.*, 1961, **34**, 1161.

¹⁰ Bamford and Ward, 5th Internat. Symposium on Free Radicals, 6—1, 1961.
