Free Rad. Res. Comms., Vol. 6, No. 2-3, pp. 105-106
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Printed in Great Britain

FREE RADICALS IN IRRADIATED ORIENTED DNA FIBERS: RESULTS FROM B-FORM DNA AND FROM DEUTERATED DNA SAMPLES

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The wet spinning method[1] produces oriented fibers of DNA which offer a unique access to structural details resulting from the gain of resolution achieved over polycristalline samples in Electron Spin Resonance (ESR) Spectroscopy. Previous studies[2,3] have reported the existence of two primary components which were assigned to an anion at the thymine base (T^-) and a cation at the guanine base (G^+). For a test of this two component model we have used structurally different samples: DNA in the A-form (Na DNA) and in the B-form (Li DNA) as well as thymine-deuterated (5-CD_3-6-D) and fully deuterated DNA.

The primary components were investigated after irradiation at 77 K. The following results were obtained for H ∥ z:

Undeuterated DNA. The overall structure of the spectrum is, as was previously reported, a doublet with an overlying broader 8 line and a sharp 10 line pattern. The former has been assigned to a radical of the guanine base (G^+) whereas the 10 lines have so far been assigned to an anion at the thymine base (T^-).[2,4]

Thymine-deuterated DNA. The spectrum has the the same structure as in the undeuterated case showing that the 10 line pattern cannot (only) originate from T^- because in this case it should have collapsed into a broad singlet.

Fully deuterated DNA. There are still about 8–10 sharp lines present with similar parameters as before in addition to a singlet and adjacent broader lines. For the latter, the pattern of the assumed G^+ fits well with the nitrogen hyperfine coupling previously estimated from normal DNA. The strong singlet shows that the basic doublet structure of normal DNA was due to a proton, the value and behaviour of which is in line with an assumed pyrimidine base anion. For the sharp 8–10-line pattern we have no proposal presently.

So far we have only indirect evidence for the appearance of anions at the thymine or cytosine bases in irradiated DNA fibers:

1) The appearance of the secondary thymine radical T5yl makes it probable that T^- is found among the primary radicals.

2) Kinetic measurements on normal DNA show a bi-phasic behaviour concerning the decay of lines; the fast component of this decay goes very well together with the appearance of the secondary T5yl.

3) The thymine-deuterated DNA-samples show a gain in spectral resolution after

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warming which can be explained by an underlying component vanishing rapidly by warming which coincides with the fast decaying component of normal DNA.

4) The difference between the spectra of the thymine deuterated and fully deuterated DNA can only be explained by the assumption of at least one primary component which is unaffected by deuteration of the thymine base, but collapse to a more or less unresolved singlet by deuteration of all bases. In normal DNA, the corresponding pattern shows base-radical symmetry.

For a clarification of the anionic primary components as well as of the successor radicals further experiments with ENDOR (Electron Nuclear Double Resonance) and ESE (Electron Spin Echo) are planned in the near future.

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