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FREE RADICALS FROM SOLID ORIENTED DNA-FIBERS: FACTS AND FANCY

JÜRGEN HÜTTERMANN

Fachrichtung Biophysik und Phys. Grundlagen der Medizin, Universität des Saarlandes 6650 Homburg/Saar, FRG

Since their introduction in the pioneering work of Ehrenberg *et al.* in 1967,[1] oriented DNA-fibers produced by the wet-spinning method[2] have frequently been employed in electron spin resonance (ESR) studies aiming at elucidating the structural parameters of free radicals formed from irradiation. Due to the high degree of orientation, quasi single-crystal like information is obtained in one direction (H ∥ Z) whereas a planar powder spectrum is obtained along the H I Z-direction. (The axis Z denotes the helix fiber axis).

The resulting potential in structural information has been utilized over the past decade under very diversified experimental conditions concerning the temperature of irradiation, the microwave frequency, the base composition and the conformation of DNA (A-form, B-form), the influence of radiation sensitizers and of chemically modified bases, especially 5-halouracils. The results obtained have led to the development of a two-component model of the primary DNA-radicals, a thymine anion (T^-) and a guanine cation (G^+).[3,4] Most recent results[5] employing thymine deuterated at the 5-methyl and the 6-carbon site strongly indicate that one additional primary radical component is present, the chemical structure of which is still under investigation. The component parameters indicate base radical symmetry and proton interactions which are lost in fully deuterated DNA from algae.

Replacing the thymine residue by 5-halouracils leads to π^*-anions (5-chlorouracil) and π^*-together with σ^*-anions (5-bromo- and 5-iodouracil).[6]

Of the secondary radicals obtained upon warming of the fibers, the well-known 5-yl radical on the thymine base is firmly established since long.[3] More recently, a successor to the G^+ component has been introduced, a radical GN· formed by deprotonation at ~~N1 of the guanine~~ base.[7] Other secondary radicals have been established for 5-halouracil containing DNA-specimen.[8] These involve both base radical analogues of the 5-thymyl species as well as sugar-located free radicals. The latter are currently under active investigation, also in normal, thymine containing DNA.

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