INDO MO Calculations of the Hydrogen Abstraction Radical Formed by Bombardment of Thymine and Derivatives with Excited Inert Gases

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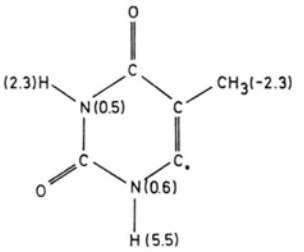
After exposure of dry thymine, thymidine and thymidine-5′-monophosphate to inert gases (*e. g.* argon and helium) excited to metastable states in a glow discharge two types of base radicals have been observed with ESR spectroscopy: 1. A radical formed by CH-bond rupture and 2. the radical resulting from addition to the 5,6 double bond of the hydrogen atoms liberated thereby [1].

While the adduct is readily identified by its characteristic eight line hyperfine spectrum, the identity of the abstraction radical could only be inferred indirectly due to the poorly resolved singlet spectrum underlying this species. Abstraction of hydrogen at carbon C-6 could be shown to be compatible with the experimental results [1]. The present INDO MO calculations were undertaken to confirm that 1. the proposed radical is stable and 2. that it gives rise to a single line of approx. 9 – 12 G line width when ESR observations are performed with the powdered substances of thymine, thymidine and thymidine-5′-monophosphate.

By means of the INDO MO method hyperfine spectra of free radicals can be calculated with good approximation if structure and atomic coordinates of the radicals are known. For the thymine radical (see below) coordinates calculated from the crystallographic data of thymine monohydrate were adopted [3]. The INDO calculations were conducted using program Nr.141 from "Quantum Chemistry Program Exchange" [2]. The following isotropic couplings (in Gauss) were obtained:



Since none of these couplings exceed 5.5 G it can be inferred that in powder form due to anisotropy effects the resultant ESR spectrum is a broad single line. The binding energy of the radical (= energy of its formation from the constituent atoms) is – 3530.32 kcal/mol indicating that the radical is a stable species.

Thus the results of the INDO MO calculations fully support the structure of the abstraction radical as inferred from the experiments [1]. It should be mentioned that the ESR singlet is also a common feature of the spectra obtained after bombardment of the other DNA constituents with excited gases [4, 5]. This suggests that the underlying species might be analogous in structure to the abstraction radical of the thymine derivatives. In fact, the present calculations together with the experimental results [1, 5] strongly support the view of a rather uniform scheme of energy transfer and radical formation after interaction of excited gases with organic material. This is reflected also in the results of inactivation of bacteriophage DNA by means of excited gases [6, 7].

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