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MATRIX-ISOLATION OF FREE RADICALS FROM PURINES AND DERIVATIVES IN AQUEOUS LOW TEMPERATURE GLASSES

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There has been considerable interest recently in the radiation-chemistry of purines both under conditions of direct radiation action and in aqueous solution.[1,2] One of the questions open for discussion concerns the reaction of $H^\cdot$ and $OH^\cdot$ with adenine and guanine bases at sites other than the established carbons C2 and/or C8. Specifically, attack at the C4-C5 double bond has been suggested to occur.[3,4] Another topic of interest is the distribution of reaction sites of $H^\cdot$ and $OH^\cdot$ among the carbons in the sugar(-phosphate) residue of purine nucleosides (-tides).

We have used electron spin resonance (ESR) spectroscopy of matrix-isolated free radicals in low temperature glasses as model for the indirect action system of aqueous solutions to study these questions. For $H^\cdot$-reactions, the Fe^{++}-photolysis in 6 M H_2SO_4/H_2O glasses was employed in which electrons are converted to $H^\cdot$ which are trapped at 77 K. Upon annealing to 110 K ~ 130 K, the $H^\cdot$-atoms form substrate radicals, the secondary reactions of which can be studied upon further warming.[5] For e^- and $OH^\cdot$-reactions, X-irradiated BeF_2/H_2O glasses have been shown to be a suitable system.[6] Comparison of the results of the latter species is made with $OH^\cdot$-reactions in aqueous solution employing the flow-system (Ti^{+++}/H_2O_2).[7,8]

For $H^\cdot$ in acidic glasses, the reaction sequence is fully understood. At the bases, only reaction at the C2 and C8 carbons of adenine and at C8 of guanine takes place leading to the well established $H^\cdot$-addition radicals.[9,10] Reaction at the sugar(-phosphate) group involves abstraction of hydrogen from carbon sites C1′, C2′ or C3′, and C5′ for ribosides (-tides) and C1′, C2′, and C5′ for deoxyribosides (-tides).

In BeF_2-glasses, a more complex overlay of reactions of e^- and OH (together with the formation of $RO_2^\cdot$ and $HO_2^\cdot$) takes place in the annealing sequence. With the base adenine, electron reaction immediately at 77 K leads to the formation of the N3-protonated anion radical giving a 1.1 mT partially resolved doublet spectrum. The anion is stable at least to 150 K; it transforms to a protonated species represented by a broad 1:2:1 triplet of 7.8 mT total splitting which is visible at 190 K. Reaction of $OH^\cdot$ is completed at 150 K and leads to addition at carbon C2 as proved by specific C8-deuteration. Unlike the aqueous flow system where reaction at the C4–C5 double bond cannot be excluded,[7,8] there is no significant contribution of this pathway in the glass.

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