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RADIATION CHEMISTRY OF ADENINE DERIVATIVES FOLLOWING DIRECT IONIZATION IN SOLIDS: ESR AND ENDOR INVESTIGATIONS

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Characterization of radiation-induced radical products of the purine constituents of DNA has developed more slowly than that of the pyrimidine constituents. For this reason, we have undertaken a program of studying in detail the products of purine derivatives irradiated as solids at tempertures from about 10 K to room temperature. Detailed results from several guanine derivatives will be discussed in other presentations at this Symposium. This presentation will discuss results from several adenine derivatives, including adenosine (AR), deoxyadenosine·H_2O (AdR), and adenosine·HCl (AR·HCl). In AR and AdR, the adenine base is present in the neutral form, while in AR·HCl the base is protonated at N1.

Of these, adenine base radicals have been most completely characterized in AR.[1,2] Following irradiation of AR at 10 K, adenine base radicals were the major contributors to the ESR. Investigation with ENDOR revealed two radical products of the adenine base. Radical I was characterized by spin densities at C2 (0.41), C8 (0.18), and N3 (0.12). From these features, Radical I was identified as the N3-protonated product of the base anion. Radical II was characterized by spin densities of 0.42 at N10, the amino nitrogen, and 0.16 at C8. From these features. Radical II was identified as the amino-deprotonated product of the adenine base cation. (The features of both radicals are like those reported previously by Kar and Bernhard[3] for adenine base radicals in adenosine: bromouracil co-crystals.) At about 35 K, Radical I (the anion) abruptly decayed, with no detectable successor; at about 100 K, Radical II (the cation) similarly decayed. At least one other product, probably of the sugar, was present in the AR system, but could not be fully characterized. In particular, no evidence was found for presence of either C2 or C8 hydrogen-addition radicals. However, both forms were found to be present following annealing at room temperature.

In contrast with the case of AR, sugar radicals were the major contributors to the ESR from crystals of AdR irradiated at 10 K. Nevertheless, ENDOR permitted detection of Radical III, a product of the adenine base characterized by spin densities at C2 (0.41), and at C8 (0.12). These features indicate Radical III to be a product of the base anion, perhaps the same as Radical I found in AR. Particularly notable, however, is that no evidence was found for the amino-deprotonated cation, or of any other product of the base cation. On the other hand, evidence appeared in the ESR and ENDOR for presence of C2 and C8 hydrogen addition radicals as primary products. In addition, two different net hydrogen-abstraction radicals of the sugar were identified. Radical IV was the result of abstraction from C5', and Radical V was the result of abstraction from C1'. Radical III was found to abruptly decay at 60–70 K with no detectable successor. After overnight storage of the crystals at room temperature, the concentration of sugar radicals was less, and the concentration of hydrogen-addition radicals (both forms) was greater.

As was the case with AdR, sugar radicals were found to dominate the ESR of AR·HCl crystals irradiated at 10 K. However, base products clearly present in this system were the hydrogen-addition radicals (both forms) and radical VI. Radical VI was characterized by spin densities at N10 (0.42) and at C8 (0.16); these features indicate Radical VI to be the amino-deprotonated product of the (N1-protonated) adenine base. Although the sugar radicals have not yet been definitively identified, qualitative consideration of their features indicate ones formed by net hydrogen abstraction at C1' and at C5'. (In addition, alkoxy radicals were found, as has been previously reported by Bernhard, *et al.*[4]) Radical VI was found to decay at about 200 K, with no detectable successor. Annealing the crystals beyond 250 K led to reduction in intensity of the resonances from sugar radicals, and increase in intensity of the resonances from the hydrogen-addition radicals.

The discussion will consider these results collectively, and possible reaction schemes which can account for them.

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