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BOOK REVIEWS

Radical and Radical Ion Reactivity in Nucleic Acid Chemistry. Edited by Marc M. Greenberg (Johns Hopkins University, Baltimore, MD). From the Wiley Series of Reactive Intermediates in Chemistry and Biology. Edited by Steven E. Rokita. John Wiley & Sons, Inc.: Hoboken, NJ. 2009. xii + 458 pp. $125. ISBN 978-0-470-25558-2.

This book focuses on the chemistry of radicals and radical ions of DNA and its constituents. These reactive forms of DNA, nucleobases, and related materials are generated in biological systems by ionizing radiation and are important intermediates in the harmful effects of ionizing radiation on living systems. The goals of the editor are to provide a comprehensive resource for researchers seeking detailed information about new techniques and methodologies used to study these complex systems as well as reviews of the recent results from both computational and experimental studies. In my opinion, he has achieved these goals by assembling an impressive roster of contributors with considerable expertise in this biologically and technologically important area of chemistry and whose contributions collectively make this book well worth reading for others interested in this area.

The first chapter is a description of theoretical results concerning radiation-induced damage to DNA. The chapter is divided into sections that deal with specific topics related to radicals and radical cations in DNA damage. The wide range of such topics allows this first chapter to act as an introduction to the book as a whole. The information is current and includes both experimental and computational results in areas that are less well developed, especially the chemistry of excited-state radical cations of nucleosides and related oligomers.

An overview of the primary reaction pathways initiated in DNA by the direct effect of ionizing radiation is given in the second chapter. It is also very useful as an introduction to the overall field, as the first half nicely summarizes both the structures and reactions of the radical cations and radical anions initially produced by ionizing radiation in well laid out diagrams. In the second half of the chapter, the mobility of the initially produced holes and electrons within the DNA strand as well other fates of the radical cations and anions are described.

The subsequent chapters all focus on more specialized aspects of the effect of ionizing radiation on DNA and, taken together, emphasize clearly the complexity of the related chemistry. Chapters 3−5 each address the reactivity of the oxidized forms of individual constituents of DNA that could be produced by ionizing radiation and include topics such as the mechanisms of reactions of normal and oxidized pyrimidine and purine bases, the reactivity of sugar radicals, and the reactions of pyrimidine nucleobase radicals. All three chapters are very comprehensive and are nice summaries of the wide range of interesting chemistry associated with the reactive radicals and radical cations of the individual constituents of DNA. The next chapter is somewhat related to the previous three but is focused on how degradation of DNA due to the hydrogen abstraction reactions of 5-uracil radicals produced by UV-irradiation of 5-halouracils can be used to help distinguish different DNA structures.

Chapters 7−9 concern yet another element important to the ionization of DNA, namely the mechanisms by which holes and electrons are formed and move within DNA. A detailed description of how initially generated holes migrate is given in Chapter 7, whereas movement of electrons is discussed in the next chapter. Interesting new results are discussed in both chapters, but also, just as importantly, the rather complex approaches needed to examine these problems are described. Similarly, Chapter 9 outlines the experimental techniques needed to study the effect of low-energy electron interactions with DNA and also provides a very extensive compilation of some of the more interesting results obtained using these techniques.

Chapter 10 is perhaps the most unexpected one and deals with reactions of radicals associated with DNA ionization with nitro group-containing electron-affinic radiosensitizers. The topic is introduced by giving a description of electron-affinic radiosensitizers and the radicals derived from them, but the main section focuses on the reactions of such sensitizers with radicals derived from the ionization of DNA. Because much of this chapter covers results that are not new, as the authors admit, the future directions outlined in the conclusions are important to the overall success of the chapter.

Although hydroxyl radicals are regarded as one of the most damaging products from ionizing radiation, other highly reactive small inorganic compounds that might also damage DNA can be produced under ionizing conditions. The chemistry of two of these reactive materials, nitrogen dioxide radicals and carbonate radical anions, is described in Chapter 11, where the authors summarize the mechanisms by which these species can be generated, the wide variety of their reactions with DNA constituents, and the nature of the products arising therefrom.

The last three topics are somewhat different from the previous ones in that they do not primarily focus on ionizing radiation as the source of damaging radicals and radical cations. The electrochemistry of DNA is described in Chapter 12. This chapter provides an introduction to the topic, including a brief description of the electrochemical methods used to examine nucleic acid oxidation. In the main body of the chapter, the authors describe the different elements of DNA oxidation that can be studied using electrochemistry, such as the effects of structure on DNA oxidation and charge transfer through DNA. In the next chapter, the interaction of diradicals generated via the cyclization of enediyne and related antibiotics with DNA is discussed. The chapter begins with a focus on the mechanism by which the diradicals from enediynes induce cleavage of DNA strands and the nature of DNA-diradical adducts. In the second half, related materials that have been specially designed to give diradicals upon cyclization and how effective these diradicals are in causing DNA cleavage are described. The final chapter has a similar theme in that the interaction between phenoxyl radicals and DNA is addressed, with emphasis on reactions that cause DNA damage, especially the formation of phenoxyl radical-DNA adducts.

The apparently divergent topics that make up this book might appear to suggest a lack of focus. However, I would argue that the wide range of topics is necessary for a thorough review of the chemistry of the ionization products from DNA and related materials and that the diversity is a strength. Overall, therefore, this is a valuable publication and is a worthwhile addition to the library of any researcher who has an interest in any one (or more) of the subtopics discussed.

Norman P. Schepp, *Dalhousie University*

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