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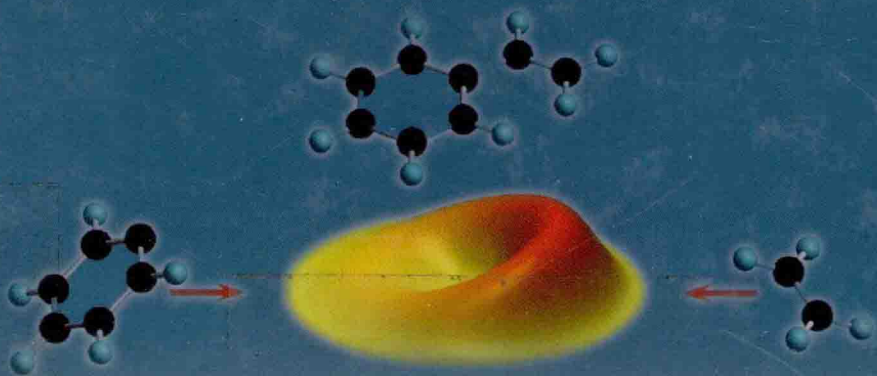
Steven E. Rokita, Series Editor

VOLUME THREE

CARBON-CENTERED FREE RADICALS AND RADICAL CATIONS

STRUCTURE, REACTIVITY, AND DYNAMICS

Malcolm D. E. Forbes, Editor



 WILEY

CARBON-CENTERED FREE RADICALS AND RADICAL CATIONS

Structure, Reactivity, and Dynamics

Edited by

MALCOLM D. E. FORBES



WILEY

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Published by John Wiley & Sons, Inc., Hoboken, New Jersey

Published simultaneously in Canada

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Library of Congress Cataloging-in-Publication Data:

Library of Congress Cataloging-in-Publication Data
Carbon-centered free radicals and radical cations / edited by Malcolm D. E. Forbes.

p. cm.

Includes index.

ISBN 978-0-470-39009-2 (cloth)

1. Free radicals (Chemistry) 2. Carbon, Activated. 3. Reactivity (Chemistry) 4. Cations. I. Forbes, Malcolm D. E., 1960-
QD471.C337 2010
547'.1224-dc22

2009031417

Printed in the United States of America
10 9 8 7 6 5 4 3 2 1

**CARBON-CENTERED
FREE RADICALS AND
RADICAL CATIONS**

Wiley Series of Reactive Intermediates in Chemistry and Biology

Steven E. Rokita, Series Editor

Quinone Methides

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Carbon-Centered Free Radicals and Radical Cations

Edited by Malcolm D. E. Forbes

ABOUT THE VOLUME EDITOR

Born in Belfast, Northern Ireland, and raised in western Massachusetts, Malcolm Forbes completed his university training at the University of Illinois at Chicago, receiving a double major B.S. degree in Chemistry and Mathematics there in 1983. He undertook doctoral studies at the University of Chicago, where he worked with the late Gerhard Closs on the study of unstable spin-polarized biradicals using time-resolved electron paramagnetic resonance spectroscopy. In 1988, his accomplishments in this area were recognized with the Bernard Smaller Prize for Research in Magnetic Resonance. After receiving his doctoral degree, Malcolm was awarded a National Science Foundation Postdoctoral Research Fellowship. From 1988 to 1990 he worked at the California Institute of Technology with Nathan Lewis on interfacial charge transfer kinetics at silicon/liquid junctions.

In July 1990, Malcolm joined the Department of Chemistry at the University of North Carolina at Chapel Hill and was promoted to the position of Professor of Chemistry in 1999. He has received a number of awards: a National Science Foundation Young Investigator Award (1993–1998), a Japan Society for the Promotion of Science Foreign Fellowship Award (1998–1999), the 2000 Sir Harold Thomson Award from Elsevier, and most recently a 2007–2008 J. W. Fulbright Fellowship from the U. S. State Department. Malcolm was co-Chair of the 2008 Gordon Research Conference on Electron Donor–Acceptor Interactions.

Malcolm's research interests span a wide area of physical organic chemistry. His primary focus is studying free radical structure, dynamics and reactivity using a

variety of magnetic resonance techniques. Current projects include the fundamentals of “spin chemistry,” proton-coupled electron transfer reactions, and the photodegradation and chain dynamics of polymers.

Malcolm lives in Chapel Hill with his wife Natalia and sons Matt, Cameron, and Elliot. Together they enjoy swimming, traveling, and home improvement projects.

PREFACE TO SERIES

Most stable compounds and functional groups have benefited from numerous monographs and series devoted to their unique chemistry, and most biological materials and processes have received similar attention. Chemical and biological mechanisms have also been the subject of individual reviews and compilations. When reactive intermediates are given center stage, presentations often focus on the details and approaches of one discipline despite their common prominence in the primary literature of physical, theoretical, organic, inorganic, and biological disciplines. The *Wiley Series on Reactive Intermediates in Chemistry and Biology* is designed to supply a complementary perspective from current publications by focusing each volume on a specific reactive intermediate and endowing it with the broadest possible context and outlook. Individual volumes may serve to supplement an advanced course, sustain a special topics course, and provide a ready resource for the research community. Readers should feel equally reassured by reviews in their speciality, inspired by helpful updates in allied areas and intrigued by topics not yet familiar.

This series revels in the diversity of its perspectives and expertise. Where some books draw strength from their focused details, this series draws strength from the breadth of its presentations. The goal is to illustrate the widest possible range of literature that covers the subject of each volume. When appropriate, topics may span theoretical approaches for predicting reactivity, physical methods of analysis, strategies for generating intermediates, utility for chemical synthesis, applications in biochemistry and medicine, impact on the environmental, occurrence in biology, and more. Experimental systems used to explore these topics may be equally broad and range from simple models to complex arrays and mixtures such as those found in the final frontiers of cells, organisms, earth, and space.

Advances in chemistry and biology gain from a mutual synergy. As new methods are developed for one field, they are often rapidly adapted for application in the other. Biological transformations and pathways often inspire analogous development of new procedures in chemical synthesis, and likewise, chemical characterization and identification of transient intermediates often provide the foundation for understanding the biosynthesis and reactivity of many new biological materials. While individual chapters may draw from a single expertise, the range of contributions contained within each volume should collectively offer readers with a multidisciplinary analysis and exposure to the full range of activities in the field. As this series grows, individualized compilations may also be created through electronic access to highlight a particular approach or application across many volumes that together cover a variety of different reactive intermediates.

Interest in starting this series came easily, but the creation of each volume of this series required vision, hard work, enthusiasm, and persistence. I thank all of the contributors and editors who graciously accepted and will accept the challenge.

STEVEN E. ROKITA

University of Maryland

ABOUT THE SERIES EDITOR

STEVEN E. ROKITA, PhD, is Professor in the Department of Chemistry and Biochemistry at the University of Maryland. His research interests lie in sequence and conformation specific reactions of nucleic acids, enzyme-mediated activation of substrates and coenzymes, halogenation and dehalogenation reactions in biology, and aromatic substitution and quinone methide generation in bioorganic chemistry.

INTRODUCTION

Carbon radicals and radical cations hold central places in modern organic reactivity, from alkene addition reactions in the synthesis of novel polymers to fundamental studies of electronic distribution of spin and charge in the study of donor–acceptor interactions. The importance of free radicals in biological reactions was recognized initially in fields such as photosynthesis, but they are now of interest in areas of research as diverse as tissue damage and the aging process. The field of biological free radicals has grown to the extent that an entire journal is now devoted to the topic: *Free Radicals in Biology and Medicine*. The ubiquity of radical intermediates in chemistry and biology has commanded attention from chemists, biologists, and physicists, across a variety of subdisciplines, who are seeking to understand the structure, reactivity, and dynamics of radicals in magnetic and chemical environments that are often complex.

To this end, high levels of theory have been developed in conjunction with a sophisticated array of experimental techniques that now make it possible to measure the properties of organic reactive intermediates with extraordinary precision. This volume, on carbon-centered free radicals and radical cations, highlights several of the most advanced computational and experimental methods currently available for such investigations. The chapters within are written by a well-rounded group of experts, who have made a strong effort to explain difficult concepts clearly and concisely. The authors were selected with the intention of providing a broad range of material, from small molecule synthesis to polymer degradation, and from computational chemistry to highly detailed experimental work in the solid, liquid, and gaseous states.

Chapter 1 presents a short history of the field of free radical chemistry. Building on a few earlier summaries in monographs that are now a bit dated, this chapter covers more modern developments in radical reactions, mechanisms, and physical methods since

the 1960s. Particular attention is paid to the chemically induced spin polarization phenomena that have a strong presence in this volume. Chapters 2–4 can be considered to have the common theme of mechanistic chemistry, with an emphasis on synthetic utility. Chemists are sometimes surprised to find useful radical reactions in synthesis, and these three chapters summarize many new ideas for the construction of interesting organic structures. In Chapter 2, Wille describes recent experimental and computational results from her laboratory on cascade-type radical additions to alkynes, with mechanistic examples and synthetic applications. Complementary to her work on building carbon skeletons is Poniatowski and Floreancig's description of radical cation fragmentation reactions in Chapter 3, with applications to asymmetric total synthesis. In Chapter 4, Sevov and Wiest discuss chemo-, regio-, and periselectivity trends and solvent effects in radical cation Diels–Alder reactions.

Chapters 5–7 are focused on molecular structure and are therefore mostly from the computational perspective. However, these authors were invited because of their skills in connecting computation to experiment, and they have provided significant insight in many important reactions. In Chapter 5, Coote, Lin, and Zipse provide a summary of stereoelectronic effects governing the stability of carbon-centered radicals, with a detailed discussion of applications to H-atom transfer and olefin addition reactions. Barone, Biczysko, and Cimino present case studies of vibrational and environmental effects on radical stabilities in Chapter 6, with several important biological examples. In Chapter 7, Gescheidt connects the electrochemistry and magnetic resonance of pagodane-type radical cations to their molecular structures. His experimental measurements are strongly supported by computational results.

Chapters 8–11 represent an effort to present the forefront of spectroscopic investigations of radical structure and kinetics. These particular chapters also provide excellent demonstrations of several “spin chemistry” techniques such as CIDNP and magnetic field effects. In this regard, Chapter 8 by Woodward contains an excellent introduction to the physics of geminate radical pair spin state evolution and magnetic field effects, presenting theoretical details clearly and giving numerous experimental examples. Goez, in Chapter 9, also provides background on the radical pair mechanism as applied to the CIDNP experiment. His examples include reactions of radicals, radical ions, and biradicals. This chapter provides a very useful overview of the theory and contains several worthy demonstrations of the mechanistic power of CIDNP spectroscopy. The contributors of Chapter 10, Rawls, Kuprov, Elliot, and Steiner, have combined their experimental and theoretical talents to analyze the magnetic properties of linked donor–acceptor systems that are model systems for artificial photosynthesis, with a particular emphasis on spin relaxation effects. No volume of this type would be complete without a description of modern gas-phase radical reactions. The crossed molecular beam experiments described by Kaiser in Chapter 11 delineate the chemistry of phenyl radicals and other smaller carbon-containing fragments, as related to atmospheric science.

This volume closes with three chapters on different aspects of free radical chemistry in macromolecules. Several photoinitiation reactions that are widely used in polymer synthesis are discussed by Khudyakov and Turro in Chapter 12. This chapter also gives an informative description of how CIDEF can be used to simultaneously study

structure and mechanism in photochemical reactions. The reactions of geminal radical pairs created in bulk polymers are presented by Chesta and Weiss in Chapter 13. Of the many possible chemical reactions for such pairs, they are organized here by polymer and reaction type, and the authors provide solid rationalizations for the observed product yields in terms of cage versus escape processes. Chapter 14 contains a summary of the editor's own work on acrylic polymer degradation in solution. Forbes and Lebedeva show TREPR spectra and simulations for many main-chain acrylic polymer radicals that cannot be observed by steady-state EPR methods. A discussion of conformational dynamics and solvent effects is also included.

On a personal note, I would like to thank the series editor Steven Rokita for the invitation to generate this volume. This was a challenging project and he was always at the ready with good advice during the writing process. Becky Ramos and Anita Lekhwani at Wiley were instrumental in getting this volume off the ground; hands off enough to let me shape the volume the way I wanted, and hands on enough to avoid catastrophe. I am indebted to my editorial assistant (and coauthor) Natalia Lebedeva, without whom I would still be choosing authors and daydreaming about potential topics. I also acknowledge the U.S. Fulbright Scholar Program for a fellowship that gave me substantial time away from everyday duties this year in order to complete this volume.

Finally, no project of this magnitude is ever created without authors who share their commitment and are willing to produce great science within a reasonable time frame. I thank them for their patience with me as the initial deadline slipped past, and for working hard over the holiday break of 2008–2009 to get their manuscripts to me for the final push to production. It is not quite enough to let their efforts shine on the pages within, therefore I close this introduction by stating that the authors' perseverance, diligence, and attention to detail are duly recognized by a most grateful taskmaster.

MALCOLM D. E. FORBES

*Chapel Hill, North Carolina
December 2009*

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