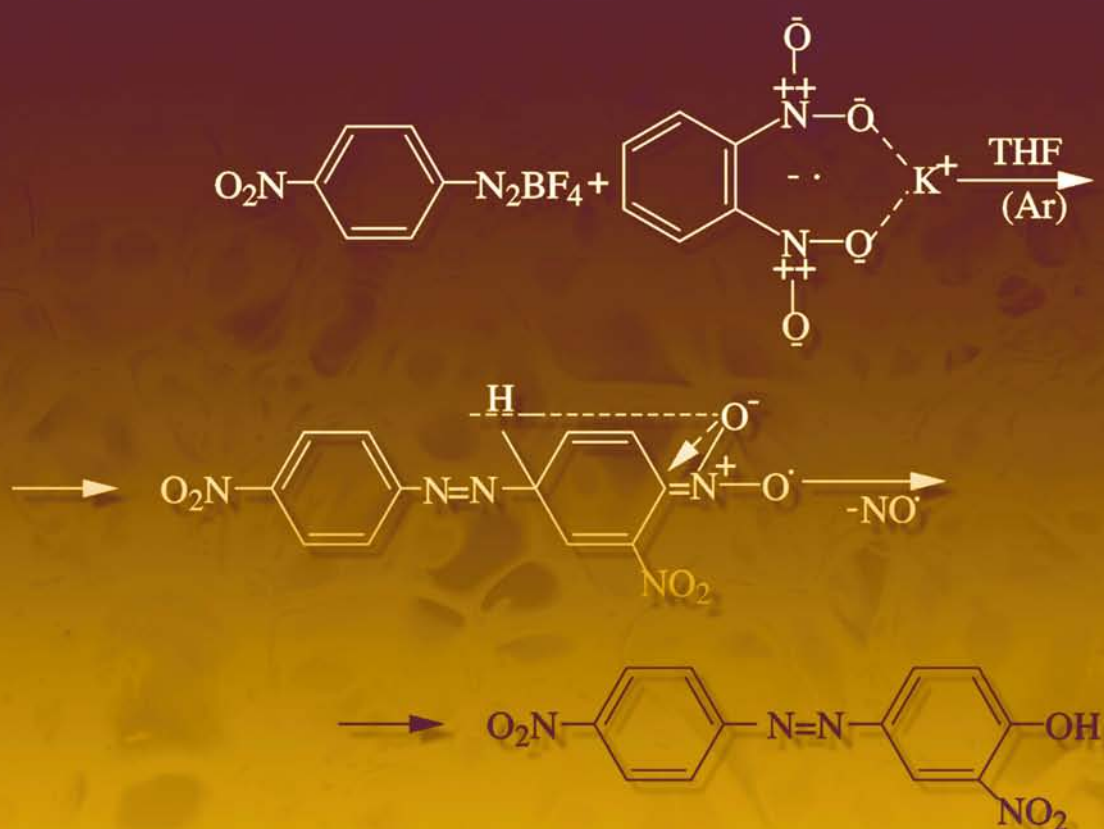


Ion-Radical Organic Chemistry

Principles and Applications

Second Edition



Zory Vlad Todres

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Dedication

To my wife Irina: the cloudless beauty of her heart, profundity of her mind, and depth of her feelings in all times have always provided reliable support to me.

For my children, Vladimir and Ellen, their mother represents a superior, stimulating example.

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Preface

Contemporary organic chemistry lays great emphasis on investigations of the structure and reactivity of intermediate species, originating in the reaction pathway from the starting compounds to the end products. Knowledge of the properties of the intermediary species and insight into the mechanism of reactions open new ways to increase the rates of formation and yields of the desired final products. Until recently, chemists focused their attention on neutral radicals or charged species of the ionic type. Particles having a combined nature of ions and radicals—ion-radicals—were beyond the scope of their investigations. Improved instrumental techniques markedly led to finer experiments. As a result, the species, which were little (if at all) known to the chemists of earlier decades, are now in the forefront.

Currently, the behavior of organic ion-radicals has become an area of interest. Ion-radicals are formed by one-electron oxidation or one-electron reduction of organic compounds in isolated redox processes and as intermediates along the pathways reactions. The conversion of an organic molecule into an ion-radical brings about a significant change in its electronic structure and corresponding alteration in its reactivity. This conversion allows the formation of necessary products under mild conditions with high yields at improved selectivity of transformation. In addition, there are several reactions that can proceed only through the ion-radical pathway and lead to products otherwise unobtainable.

The theme of this book is the formation, transformation, and application of ion-radicals in typical conditions of organic synthesis. Avoiding complex mathematics, this book presents an overview of organic ion-radical reactions and explains the principles of the ion-radical organic chemistry. Methods of determining ion-radical mechanisms and controlling ion-radical reactions are also reviewed.

Wherever applicable, issues relating to ecology and biomedical problems are addressed. The inorganic participants of the ion-radical organic reactions are also considered. Chapter 7 gives representative examples of synthetic procedures and considers the fundamentals of related synthetic approaches.

This book also provides a review of the current practical applications as well as an outlook on those predicted to be important in the near future. The reader will learn of the progress that has been made in technical developments by utilizing the organic ion-radicals. Electronic and optoelectronic devices, organic magnets and conductors, lubricants, other materials, and reactions of industrial or biomedical importance are considered.

Developments in organic chemistry of ion-radicals have been rapid. Thus, new interpretations of scientific data appear frequently in the literature. I have attempted to juxtapose the ideas from various references that complement one another, although the connections between them may not be immediately obvious. (An author index is included to help the readers find such connections in this book.)

Science is a collective affair and its main task is to produce trustworthy and generalized knowledge. My due apologies are to those authors who contributed to the development of this vast field but, for various reasons, have not been cited in this book. The contributors who are cited certainly do not reflect my preferences; their publications have been selected as illustrative examples that will allow the reader to follow the evolution of the corresponding topics.

Every new branch of science passes through several stages of progress, including the latent phase, phase of an increased interest, and phase of blooming and incorporating into its mother science as an integral part. Organic ion-radical chemistry has apparently passed through its initial phases (that spawned decades of heated debates). In recent years, the heat has simmered down. It was a result of the development of this branch of science and technology.

Having become a regular division of scientific knowledge, organic ion-radical chemistry is now entering the stage where the ideas elaborated are being implemented into general operation. It is now necessary to generalize the obtained data and treat them comprehensively. Grafting the new branch to the organic chemistry tree is the aim of this book.

I have worked in the field of organic ion-radicals and their applications for several decades and have become more and more fascinated by the beauty of this area and diversity it presents. Understanding the role of ion-radicals is as difficult as it is interesting. I hope that this attempt to graft this branch to the organic chemistry tree will be useful for both advancing basic research and facilitating new practical applications.

During my entire working life, I, like other researchers, have felt the pressure of the scientific community's judgment. Criticism is crucial! The writing of this book was aided by discussions with my colleagues and friends. I am indebted to all of them for their corrections and polemics. At the same time, their support was a great encouragement. I thank the publishers for initiating to publish the second edition of this book under the title *Ion-Radical Organic Chemistry: Principles and Applications*. The 7-year period after the first edition was so fruitful in terms of publication and has brought so many important benefits that some cardinal renewal of the book's material becomes inevitable. This second edition has been well updated to include the new subject area as well as new developments in the materials covered previously. Appropriate references are provided throughout.

Naturally, the subject development brings about some complications of the topics under consideration. Being concise enough, nonmathematical and not overly technical, the new edition consolidates knowledge from a number of disciplines to present a modern overview on ion-radical organic chemistry. This book is addressed to researchers and technologists who are carrying out syntheses and studying principles, governing the choice of optimal organic reaction conditions. It will be useful for physical organic chemists, ecologists, biologists, and specialists in microelectronics, as well as for professors, researchers, and students. I mean postgraduates, not fainthearted undergraduates (especially those final-year students who are preparing to enter the contemporary job market!).

By and large, people who are engaged in active work on synthetic or mechanistic organic chemistry and its practical applications will hopefully find this treatise informative and, perhaps, somewhat exciting.

Zory V. Todres

Author

Zory Vlad Todres holds an MSc and a PhD in chemistry and technology as well as a doctor habilitas in physical organic chemistry. Formerly, his career was divided between research (as a leading scientist at the Russian Academy of Sciences, Moscow) and delivering of lecture courses (as a professor at higher educational institutions in Russia). Having gained job experience from research organizations and industrial companies in the United States, he, presently, enjoys working as a science analyst at the American Chemical Society. Dr. Todres has been a guest speaker at many international conferences and has worked as a visiting scientist and lecturer for universities in the United States and abroad. His publications consist of 6 single-authored books, approximately 300 original papers and reviews, as well as 10 patents (2 of them in the market). He was awarded with a membership to the World Academy of Letters (the Einsteinian Chair of Science) and is cited in the *who's who* list of the United States and United Kingdom (particularly, in *American Outstanding Professionals*).

His book *Ion-Radical Organic Chemistry: Principles and Applications* (2003), preceding the present issue, gained a good rating in scientific publications. Some quotations from the reviews on the book are as follows:

The book fills an important gap because charged radicals have not had fair share of the press. In its broad scope, it leads you into unfamiliar territory, you find a lot to question, but that itself is stimulating, and you are carried along by its infectious enthusiasm. The book opens up aspects of which you are ignorant, it is a good guide to relevant literature, and above all, the enthusiasm of the author carries through into the text (Alwyn Davies, *Alchemist*, Oct. 2003).

The book's illustrations are mainly chemical formulae and reaction schemes, which are reader-friendly in respect of size and clarity (Laszlo Simandi, *React. Kinet. Catal Lett.* 79 (1), 209, 2003).

The book should be available to students, particularly in a classroom setting, or simply as a resource book to have on their bookshelf. I recommend to purchase the book by libraries, at least (R. Daniel Little, *J. Am. Chem. Soc.* 125 (20), 6338, 2003).

This is a book which, in my opinion, should find a place in the libraries of all universities and research institutes, where people are engaged in active research in synthetic or mechanistic organic chemistry. The task taken by the author was Herculean which the author has carried out with commendable skill, when he could bring in a reasonable amount of space, all the different aspects of ion-radical chemistry. The book is characterized by the lucidity of presentation, which has made it immensely readable (Asish De, *Indian J. Phys.* 77A (4), 401, 2003).

1 Nature of Organic Ion-Radicals and Their Ground-State Electronic Structure

1.1 INTRODUCTION

Organic chemistry represents an extensive volume of facts from which the contemporary doctrine of reactivity is built. The most important basis of this doctrine is the idea of intermediate species that arise along the way from the starting material to the final product. Depending on the nature of chemical transformation, cations, anions, and radicals are created midway. These species are formed mainly as a result of bond rupture. Bond rupture may proceed heterolytically or homolytically: $R-X \rightarrow R^- + X^+$, $R-X \rightarrow R^+ + X^-$, or $R-X \rightarrow R^\bullet + X^\bullet$.

Ions or radicals formed from a substrate further react with other ions or radicals. There are many reactions that include one-electron transfer before the formation of ions or radicals. Sometimes, electron transfer and bond cleavage can take place in a concerted manner. The initial results of one-electron transfer involve the formation of ion-radicals.

This book focuses on species of the type $(RX)^{\pm\bullet}$, that is, on cation- and anion-radicals. These terms were first introduced by Weitz (1928) (“Kationradikale” and “Anionradikale”). Currently, organic chemists differentiate that the anion-radicals originate from π and σ acceptors and the cation-radicals originate from π , σ , or n donors. These species are formed during reactions, when an organic molecule either loses one electron from the action of an electron acceptor or acquires one from the action of an electron donor: $R-X - e \rightarrow (R-X)^{+\bullet}$ or $R-X + e \rightarrow (R-X)^{-\bullet}$.

Ion-radicals differ from starting molecules only in the change of the total number of electrons; no bond rupture or bond formation occurs. From the following chapters, it is seen that after ion-radical formation, cleavage and association reactions often occur. Geometry changes on electron loss or gain can also take place. Reactions with the participation of ion-radicals bring their own, specific opportunities.

The concept of molecular orbitals (MOs) helps to explain the electron structure of ion-radicals. When one electron abandons the highest occupied molecular orbital (HOMO), a cation radical is formed. HOMO is a bonding orbital. If one electron is introduced externally, it takes the lowest unoccupied molecular orbital (LUMO), and the molecule becomes an anion-radical. LUMO is an antibonding orbital. Depending on the HOMO or LUMO involved in the redox reaction, organic donors appear as π , σ , or n species, whereas organic acceptors can be π or σ species. Sometimes, a combination of these functions takes place.

Ion-radicals have a dual character. They contain an unpaired electron and are, therefore, close to radicals. At the same time, they bear a charge and are, naturally, close to ions. This is why the words “ion” and “radical” are connected by a hyphen. Being radicals, ion-radicals are ready to react with strange radicals. Like all other radicals, they can dismutate and recombine. Being ions, ion-radicals are able to react with particles of the opposite charge, and are prone to form ionic aggregates. In contrast to radicals, the ion-radicals are specially sensitive to medium effects.

Equal or nonuniform distribution of spin density can occur among individual atoms of the molecular carcass. This kind of distribution defines the activity of one or another position in an ion-radical. From the point of view of organic synthesis, properties of ion-radicals such as stability, resistance to active medium components, capacity to disintegrate in the required direction, and

the possibility of participating in electron exchange are especially important. All these properties become understandable (or predictable in cases of unknown examples) from the organic ion-radical electronic structure. Therefore, the discussion will be based on the analysis of connections between the structure of ion-radicals and their reactivity or physical properties. This chapter concerns the peculiarities of conjugation, electronic structures, and acid–base properties of ion-radicals originated from molecules of various chemical classes.

1.2 UNUSUAL FEATURES

1.2.1 SUBSTITUENT EFFECTS

This section shows that substituent effects in organic ion-radicals are quite different from those of their parent neutral molecules. Amino and nitro compounds are good examples to show that conventional ideas may not be applicable to the chemistry of ion-radicals.

N,N-dimethylaniline is a molecule with a lone electron pair on the nitrogen atom. Of course, there is a strong interaction between this pair and the π electron system of the benzene ring. We often place the symbol of the cation-radical ($^+\bullet$) on the nitrogen atom. However, according to the *ab initio* Hartree–Fock molecular orbital calculations (Zhang et al. 2000), this nitrogen atom is in fact negatively charged (-0.708) and the positive charge is distributed on the carbon atoms, especially on the two methyl groups ($+0.482$ on each). Influenced by the positive-charge delocalization along the cation-radical, the benzene ring becomes an electron-deficient unit with a positive charge of $+0.744$. Summation yields the total charge of $+1$ for the *N,N*-dimethylaniline cation-radical.

Naturally, the cation-radical of diphenylamine is characterized with an analogous positive-charge delocalization (Liu and Lund 2005). The *N,N'*-diphenyl-*p*-phenylenediamine cation-radical is almost planar and the spin density intrudes outer phenyls. When the outer phenyls contain two methyl groups in ortho positions, the molecule loses planarity. As a result, the spin density concentrates within the inner ring and its adjacent two nitrogen atoms (Nishiumi et al. 2004).

In the trication-triradical of 1,3,5-triaminobenzene, quantum-chemical calculations indicate that the positive charges are very much delocalized into the benzene core, whereas the nitrogen atoms bear negative charges (Nguyen et al. 2005).

In the anion-radicals of nitro compounds, an unpaired electron is localized on the nitro group and this localization depends on the nature of the core molecule bearing this nitro substituent. The value of the hyperfine coupling (HFC) constant in the electron-spin resonance (ESR) spectrum reflects the extent of localization of the unpaired electron; a^N values of several nitro compounds are given in Table 1.1.

Let us compare HFC data from Table 1.1. Aliphatic nitro compounds produce anion-radicals, in which an unpaired electron spends its time on the nitro group completely. In the nitrobenzene

TABLE 1.1
Nitrogen HFC Constants (a^N) from Experimental ESR Spectra
of Nitro Compounds

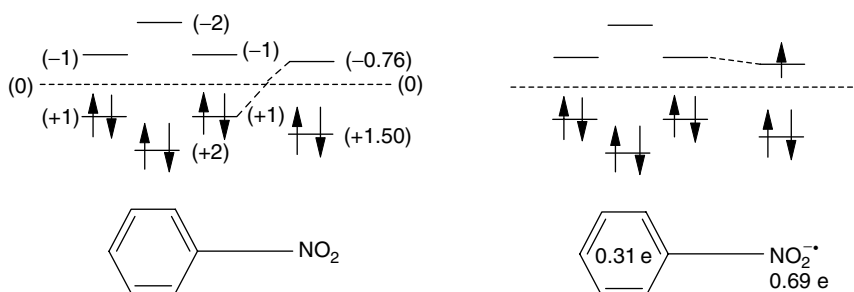
Compounds	Constant a^N (mT)	References
Nitroalkanes	2.4–2.5	Stone and Maki (1962), McKinney and Geske (1967)
Nitrobenzene	1.0	Geske and Maki (1960)
2-Chloronitrobenzene	0.9	Starichenko et al. (2000)
2,6-Dichloronitrobenzene	1.4	Starichenko (2000)
Nitrodurene	2.0	Geske and Ragle (1961)

anion-radical, an unpaired electron is partially delocalized on the aromatic ring due to conjugation. As observed, the HFC constant decreases by a half as compared to the aliphatic counterparts. Diminution of the π conjugation in the PhNO_2 system as a result of the nitro group distortion leads to the localization of the unpaired electron on the nitro group. In the nitrobenzene anion-radical, however, an unpaired electron is not evenly spread between the nitro group and the benzene ring. This anion-radical has most of the spin density (65–70%) localized on the nitro group (Stone and Maki 1962, Kolker and Waters 1964). These values are based on the values of a^{N} and a^{H} constants from the ESR spectrum of the nitrobenzene anion-radical. Molecular orbital calculations within the Hückel approximation predict the same spin distribution: 0.31 of the unit-spin density over the phenyl nucleus and 0.69 on the nitro group (Todres 1981). The recent calculation of the nitrobenzene anion-radical shows that, in terms of Hirshfeld charges, the nitro group bears 0.782 and the phenyl group dissipates 0.218 parts of the unit negative charge (Baik et al. 2002).

Of course, it is the entire molecule that receives an electron on reduction. However, the nitro group is the part where the excess electrons spend the majority of their time. Consideration of quantum-chemical features of the nitrobenzene anion-radical is of particular interest. The model for the calculation includes a combination of fragment orbitals for Ph and NO_2 , and the results are represented in Scheme 1.1. The left part of the scheme refers to the neutral PhNO_2 and the right part refers to the anion-radical, $\text{PhNO}_2^{-\bullet}$ (Todres 1981).

Some changes in the total orbital energy take place on the one-electron placement on the LUMO. According to the calculations, relative energy gaps remain unchanged for the orbitals in the nitrobenzene anion-radical, if compared with those of the parent nitrobenzene. For the sake of graphic clarity, Scheme 1.1 disregards the difference mentioned, keeping the main feature of equality in the energy gaps.

The nitro group in the parent nitrobenzene evidently acts as the π acceptor, which pulls the electron density out of the aromatic ring. An unpaired electron will obviously occupy the first vacant π orbital of the nitro fragment (i.e., the lowest-energy-fragment orbital). Interaction between the occupied orbital and the vacant one (the absolutely empty orbital) is the most favorable. In the nitrobenzene anion-radical, the one-electron-populated fragment orbital of $\text{NO}_2^{-\bullet}$ will send the spin density to the ring. Such an interaction is very advantageous because the lowest vacant ring orbital and the highest occupied orbital of $\text{NO}_2^{-\bullet}$ are close with respect to their energy levels. Therefore, the nitro group can, in fact, act as a π donor in the nitrobenzene anion-radical. This prediction is not self-evident since the nitro group in neutral aromatic nitro compounds is recognized as a strong π acceptor and, in principle, even as a reservoir of four to six additional electrons. Comparing the half-wave potentials of reversible one-electron reduction of *m*-dinitrobenzene and other meta-substituted nitrobenzenes, one can determine the Hammett constant for the $\text{NO}_2^{-\bullet}$ group. When the NO_2 group is transformed into the $\text{NO}_2^{-\bullet}$ group, a change in both the sign and value of the correlation constant is observed (Todres et al. 1972a, 1972b). Formal comparison of the Hammett constants for NO_2 , $\text{NO}_2^{-\bullet}$, and NH_2 groups shows that $\text{NO}_2^{-\bullet}$ is close to NH_2 in terms of donating ability: $\sigma_{\text{m}}(\text{NO}_2) = +0.71$,



SCHEME 1.1