

# Free-radical chemistry

Structure and mechanism

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with a Foreword by

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## Free-radical chemistry

## Foreword

The study of free radicals is the Cinderella of organic chemistry. Students arriving at college in vehicles propelled by internal combustion engines are still taught that alkanes are inert substances. In the majority of text books on organic chemistry free-radical reactions are treated as a special, rather unusual class of reactions despite the fact that in industry and possibly also in nature one-electron transfers are more common than those involving electron pairs. The main reason for this is that the simplest free-radical reactions occur in the gas phase and few organic chemists have the apparatus or the technique to study such processes. The organic chemistry of free radicals in solutions was first fully developed by Kharasch in the United States and by Hey and Waters in Britain. In spite of such a good start free-radical chemistry failed to attract wide-spread interest among organic chemists in general, and very little attempt has been made to correlate the solution-phase work with the extensive kinetic studies in the gas phase. This separation of the 'physical chemistry' of free radicals from the 'organic chemistry' of free radicals has been a major deterrent to advance. The most important feature of this book is that it brings together the physical and organic branches of the subject.

At a time when physical organic chemistry is going through a period of reappraisal the present book emphasizes the important contribution a study of radical reactions can make to the nature of substituent effects. Many of the simple pictures of reactions developed twenty years ago have become clouded by the need to bring the solvent into almost all mechanistic considerations. The present volume shows that radical reactions where solvent effects are minimal, or where the reaction can be carried out in the gas phase, can still be interpreted in the polar and steric terms used by the physical organic chemist. This book arrives at a timely moment and will, I am sure, lead to a wider understanding of the importance of free-radical chemistry.

J. M. TEDDER

## Preface

Free-radical chemistry is a subject which has grown enormously in scope and interest since the advent of the first free radical at the turn of the century. Less than twenty years ago it was possible for a book on mechanistic organic chemistry completely to ignore free radicals. Today radical intermediates are recognized and studied in almost every field of chemical activity, including organic, physical, inorganic and biological systems. There are at least two series of books exclusively devoted to recent advances in various specialized areas of the subject. In this volume we have attempted to bring together experimental results and theories from all these different areas and to show how the concept of free-radical intermediates brings an underlying order and unity to an otherwise complicated and confusing situation. In carrying out this aim we have emphasized the role of free radicals as one of the three major reactive intermediates of organic chemistry. We have sought to demonstrate how the structure and reactivity of free radicals is complementary to that of carbonium ions and carbanions.

The book provides a reasonably comprehensive, though not exhaustive, coverage of the general principles governing the behaviour of free radicals. It is directed primarily towards postgraduate students and chemists wishing to obtain an overall knowledge of free-radical chemistry, though it will also be useful to the more advanced undergraduate. We have attempted to integrate the approaches of the organic and the physical chemist by consideration of kinetic and mechanistic aspects of reactions both in solution and in the gas phase. This emphasis on the more physical aspects of the subject marks a departure from the approach found in most books.

The subject matter of the book falls into two main divisions. The first part, consisting of chapters 1 to 6, is concerned with the general principles and technique of radical chemistry, and deals with methods of production and detection of radicals, and also with their shape and stability. The very widespread use of electron spin resonance spectroscopy justifies the fairly extensive treatment of this topic in chapter 3. A comparison of radical reactions in solution and in the gas phase is

## *Preface*

given in chapter 6. The remainder of the book provides a survey, of as wide a scope as could be encompassed in the space, of all the types of radical reactions which are encountered. In the main, each class of reactions is dealt with in a separate chapter, but we have made a slight departure from this practice for addition, abstraction and combination reactions. It was felt that, since these reactions are so widespread and so characteristic of radical species, a reclassification according to the type of radical involved would lead to a clearer and more interesting presentation. Accordingly chapters 7, 8 and 9 are mainly concerned with these three reaction types for atoms, alkyl radicals and heteroradicals respectively. Prominent sub-headings for each reaction type ensure that there is no difficulty in tracing each subject from one chapter to another. There follows an examination of free-radical oxidation and reduction in chapter 10. This is a large and very important area of radical chemistry which is frequently not given the depth of treatment it merits. Thus the important electrochemical oxidations and reductions, as well as metal- and metal-ion-catalysed reactions and other electron-transfer reactions, are all discussed. Autoxidation is also included in this chapter. Homolytic aromatic substitution is the topic of chapter 11. Radical fragmentations, rearrangements and cyclizations are covered in chapters 12, 13 and 14. The final chapter on radical displacement reactions is also to some extent an innovation, and reflects the growing interest in and importance of this type of reaction. Throughout chapters 7 to 15 we have emphasized, wherever appropriate, the synthetic use of radical reactions. We feel that this is important, as ultimately the chemical industry is concerned with the preparation of compounds and not the study of reaction mechanisms, except where this leads to improved synthetic methods. We have reluctantly omitted the treatment of the most important of all industrial radical reactions, polymerization, because we felt that it was impossible to do this large subject justice in the space available. This subject is also very adequately dealt with in other recent books specifically on polymerization.

We should like to express our heartfelt thanks to Professors Lord Tedder and P. L. Pauson, who have read the bulk of the manuscript and made many invaluable comments. We should also like to thank Professor R. O. C. Norman, Dr J. S. Littler, Dr W. Lawrie and Dr W. I. Bengough, who have read sections of the book and given very valuable advice. We are also indebted to Professor R. O. C. Norman for the provision of spectra for Figures 3-2, 3-4 and 3-9, to Professor W. A.

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Waters for the spectrum for Figure 3-7, to Professor M. J. Perkins for the spectra for Figure 3-10 and to Dr A. R. Forrester for the spectra for Figure 3-11.

Finally, we should like to express our sincere appreciation to Mrs A. Cumming, Miss G. Forrest and Miss B. Martin, who cheerfully typed and not infrequently retyped the manuscript, to Mrs Jane Walton for excellent work in correcting the manuscript and proofs, and also to the staff of Cambridge University Press for their help in proceeding from typescript to printed book.

*Glasgow and St Andrews*  
*December 1972*

D. C. NONHEBEL  
J. C. WALTON

## Note on units

We have written this book at a time when units and the symbols for them are being changed. A new international system is being gradually adopted. Since we are in a period of transition we have used a mixture of SI units and the previously accepted units. The units we have used most frequently, and their relation to other common units, are tabulated below.

### *Thermodynamic data*

Energies in Joules (J) (1 calorie = 4.184 J).

Heats of reaction ( $\Delta H$ ) in kilojoules mole<sup>-1</sup> (kJ mol<sup>-1</sup>).

Entropies ( $S$ ) in joules degree<sup>-1</sup> (J K<sup>-1</sup>).

Entropies of reaction ( $\Delta S$ ) in joules degree<sup>-1</sup> mole<sup>-1</sup> (J K<sup>-1</sup> mol<sup>-1</sup>).

Ionization potentials in electron volts (eV).

Pressure in torr (1 torr = 1 mm Hg).

### *Kinetic data*

Rate constants of first-order reactions in sec<sup>-1</sup> (s<sup>-1</sup>).

Rate constants of second-order reactions in litres mole<sup>-1</sup> sec<sup>-1</sup> (1 mol<sup>-1</sup> s<sup>-1</sup>).

Rate constants of third-order reactions in litres<sup>2</sup> moles<sup>-2</sup> sec<sup>-1</sup> (l<sup>2</sup> mol<sup>-2</sup> s<sup>-1</sup>).

Activation energies in kilojoules mole<sup>-1</sup> (kJ mol<sup>-1</sup>).

*A*-factors have the same units as the rate constants of the reactions from which they are derived.

### *Ultraviolet spectra*

Wavelength in nanometres (1 nm = 10<sup>-9</sup> m).

### *Infrared spectra*

Wavenumber in cm<sup>-1</sup>.

Force constants in mdynes per ångstrom (mdyn Å<sup>-1</sup>).

### *Nuclear magnetic resonance spectra*

Chemical shifts in parts per million (ppm).

Operating frequency in hertz (Hz).

## Note on units

### Electron spin resonance spectra

Coupling constants and magnetic field strengths in millitesla (1 mT = 10 gauss).

### Bond lengths

Lengths in ångströms (1 Å =  $10^{-1}$  nm).

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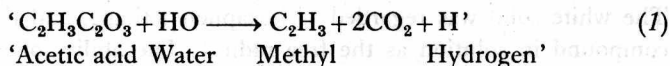
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# Introduction

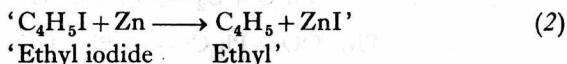
## 1.1 THE HISTORY OF FREE-RADICAL CHEMISTRY

The modern meaning of the term 'radical' has evolved through a series of advances and reverses in the understanding of chemical problems (1). The concept of radicals was introduced by Lavoisier (2) in his theory of acids, which he believed to be compounds of oxygen. He designated the element or group of elements which combined with oxygen in the acid a 'radical'. The oxygen theory of acids soon passed out of favour, but the word 'radical' was still frequently used to signify a group of elements which retained their identity through a series of reactions, e.g. a methyl radical.

The early nineteenth century saw the discovery of numerous 'radicals'. Thus Berzelius and Pontin (3) and Davy prepared the ammonium radical. Cyanogen was separated as an inflammable gas by Gay-Lussac (4), and cacodyl compounds were shown to contain the cacodyl radical  $C_2H_6As$  by Bunsen (5). The radical proved a useful organizing concept in both inorganic and organic chemistry. In the 1840s Kolbe obtained gases, by electrolysis of solutions of fatty acids, which he interpreted as free radicals (6). For example, potassium acetate gave 'free methyl' on electrolysis:



Frankland (7) heated zinc with ethyl iodide in a sealed tube and obtained a gas which he believed to be 'free ethyl':



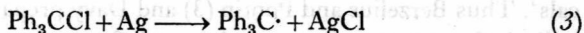
When Cannizzaro placed the measurement of molecular weights on a firm footing by the method of vapour densities it was soon realized that

## Introduction

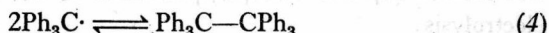
groups such as methyl did not persist in the free state, but combined to form dimers of the radical.

The existence of free organic radicals was also out of harmony with ideas which were developing about structure. The majority of structural formulae could be written by allotting fixed valencies to the elements. Kekulé proved an able supporter of the doctrine of the quadrivalency of carbon which led to rationalization of the formulae of many organic compounds then being studied. This view gained ground until by the beginning of the twentieth century almost all chemists believed carbon to possess the single valency four.

Gomberg's discovery of triphenylmethyl came very unexpectedly in 1900, heralded only by Nef's voice crying in the wilderness (8). Gomberg set out to prepare hexaphenylethane by the reaction of triphenylmethyl chloride with silver in benzene (9). The products of his reaction contained oxygen, and it was only when he carried out the preparation in an atmosphere of carbon dioxide that this was avoided. The product was then a white solid dissolving in benzene to give a yellow solution. The behaviour of the product was very unlike that expected for hexaphenylethane. It rapidly oxidized in air and reacted at once with halogens. On the basis of this evidence Gomberg proposed that the compound was in fact the free triphenylmethyl radical:



This conclusion was not readily accepted by chemists in general, and the free-radical concept came under heavy fire when cryoscopic determinations showed the compound to have a molecular weight close to that of hexaphenylethane. Undeterred, Gomberg explained this observation by postulating an equilibrium mixture in solution:



The white solid was regarded as hexaphenylethane, and the coloured compound in solution as the free radical. The ability of oxygen and halogens to decolorize solutions of 'triphenylmethyl' was explained as involving scavenging reactions of the radical:

