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**Volume 10**

**Free Radical Reactions**

**Edited by W. A. Waters, F.R.S.**



(International Review of Science

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**Volume 10)** :

**Free Radical Reactions**

Edited by **W. A. Waters, F.R.S.**  
University of Oxford

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## Consultant Editor's Note

The ten volumes in Organic Chemistry in the Second Series of the biennial reviews in the International Review of Science follow logically from those of the First Series. No major omissions have come to light in the overall coverage of the First Series. The titles of the ten volumes therefore remain unchanged but there are three new Volume Editors. The volume on Structure Determination in Organic Chemistry has been taken over by Professor Lloyd M. Jackman of Pennsylvania State University, that on Alicyclic Compounds by Professor D. Ginsburg of Technion-Israel Institute of Technology, and that on Amino Acids, Peptides and Related Compounds by Professor H. N. Rydon of the University of Exeter. The international character of the Series is thus strengthened with four Volume Editors from the United Kingdom, two each from Canada and the U.S.A., and one each from Israel and Switzerland. An even wider pattern is shown for the authors, who now come from some sixteen countries. The reviews in the Second Series are mainly intended to cover work published in the years 1972 and 1973, although relevant results published in 1974 and 1975 are included in some cases, and earlier work is also covered where applicable.

It is my pleasure once again to thank all the Volume Editors for their helpful cooperation in this venture.

London

D. H. Hey

## Preface

This second volume of biennial reviews of Free Radical Reactions surveys the literature of the subject from September 1971 to December 1973 in the style chosen for the corresponding volume in Series One.

The ten chapters include contributions from experts in Italy, Malaysia and the U.S.A. as well as from the U.K. and as editor I wish to thank all of them for their thorough appraisal of the current progress in their fields of interest. As the introductory chapter of this book will explain in greater detail, some subjects such as radiation chemistry are not specifically discussed in this volume, but others such as the organic chemistry of molecules in their triplet states and the free radical chemistry of electrode reactions have taken their place. In this way it has been possible to review in a four-year period all major aspects of free radical chemistry in substantial articles of more lasting value than would have resulted from two collections of terse progress reports which could not, in the available space, indicate the more gradual, but basically far more important, evolution of the theories which stimulate original research.

Oxford

W. A. Waters

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# 1

## Introductory Survey: Trends in Free Radical Chemistry

W. A. WATERS

University of Oxford

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If a biennial review of free radical reactions is to be a readable stimulant to research workers and not just a handy compilation of references over its two-year period, then it should deal not only with the steady advancement of knowledge along recognised pathways but should also draw attention to fields of research in physical and even inorganic chemistry which make use of free radical reactions or have theoretical implications of relevance to it.

For this reason, advances in radiation chemistry were reviewed in the Series One volume by Swallow, who clearly explained how the radiolytic decomposition of water and other solvents generated free radicals and solvated electrons active enough to attack most solutes, but has agreed that detailed development of this technique can be better reviewed objectively in a four-year rather than a two-year period. It is proposed therefore to review the radiation chemistry of organic compounds again in the corresponding volume of Series Three.

Again, Series One contained a chapter by Evans and Emes dealing with the production of radical-ions by chemical methods and discussing their structures and reactions. In a wide range of solvents, however, radical-ions are most easily produced by electrolysis and when formed in this way from salts, which often may act merely as 'carrier electrolytes', they can react at or near to an electrode surface with other molecules in a solution. In this volume, therefore, Chapter 10 by Chambers deals with both electrode reactions and radical-ions. To some extent it is complementary to Chapter 8, which deals more broadly with one-electron oxidations and reductions in solution, but the main objective for its inclusion has been to direct attention to the basic implications of using electrolysis as an experimental technique for free radical generation.

As Chambers points out, it is highly probable that *all* the electron transfers which occur at an electrode surface proceed by single electron steps, effecting reduction at a cathode and oxidation at an anode. However, two-electron electrolytic oxidations and reductions of organic compounds which do not produce free radicals are very often observed. In the past these have wrongly

been ascribed to electron-pair transfer reactions, but now it has been realised that in solution a free radical or radical-ion may be metastable with respect to its immediate environment. At least four different mechanisms for apparent two-electron electrolysis have been recognised: (i) in the EE mechanism,  $A \xrightarrow{+e^-} (A\cdot)^- \xrightarrow{+e^-} (A:)^{2-}$ , the second electron transfer occurs so much more rapidly than the first that the transient production of the radical-ion is not detectable by potentiometric methods. Alternatively, (ii) the transient radical-ions may disproportionate or dimerise even on the electrode surface. However, especially in protic solvents, the initially formed radical, free atom or radical-ion may rapidly react chemically with an adjacent molecule before a recognisable product eventuates. In the ECE mechanism (iii) the reaction sequence is (a) a one-electron transfer, (b) a chemical reaction and (c) another one-electron transfer, while in the ECC mechanism (iv) the sequence comprises (a) a one-electron transfer, (b) a chemical reaction with an adjacent molecule and then (c) a rapid reaction between two radicals or radical-ions. Modern electrochemical techniques supported by e.s.r. spectroscopy are now succeeding in distinguishing between these different electrode processes and are providing important new thermodynamic information concerning the stability of free radicals and radical-ions. With this new knowledge the experimental value and also the technical importance of electrochemistry is being enhanced rapidly: today it definitely merits inclusion in the general reading range of any free radical chemist and indeed of everyone who is interested in mechanistic aspects of chemistry.

Photochemistry is another extensive subject of rapidly developing importance. Long ago it was recognised that all natural products originated through photosynthesis and that exposure to visible and still more to u.v. irradiation caused the breakdown of very many coloured and some uncoloured organic substances, but the scientific understanding of photochemical processes had to await the advent of quantum chemistry. Even before this it was realised by Nernst<sup>1</sup> that halogen atoms, capable of initiating chain reactions, resulted from the irradiation of gaseous halogen molecules, but many years elapsed before the inference that absorption of radiant energy could initiate free radical reactions in solution was generally accepted<sup>2</sup>. The favoured earlier view that 'activated molecules' were responsible for photochemically catalysed reactions, however, is still cogent because radiant energy is much more readily absorbed (i.e. extinction coefficients are much greater) by organic molecules containing multiple linkages ( $N=N$ ,  $C=O$ ,  $C=C$ ) than by those comprised only of single bonds and this activation of multiple bonds does not immediately effect molecular dissociation. Instead only one electron pair of a multiple bond is affected and a biradical, described spectroscopically as a molecule in a 'triplet state', is produced. The chemical reactions of these triplet states of molecules are reviewed by Gilbert in Chapter 9.

For the understanding of photochemical reactions it is not sufficient, however, to regard the absorption of radiant energy as being merely one of the many ways by which the homolysis of a covalence can be effected, since whereas thermal homolysis generates a pair of paramagnetic radicals with opposed spins, photochemical homolysis leads to the formation of an 'anti-bonding' or spin parallel radical pair. Until spin inversion takes place, by



energy exchange with surrounding molecules, these radical pairs behave differently, for the anti-bonding radical pair will have a longer free lifetime. Again, the physical interactions between the two paramagnetic fragments of these two types of radical pairs will be different and these interactions can now be studied by magnetic resonance methods.

When chemical evidence for the participation of free radicals in solution was first forthcoming it was thought that many of them, such as free phenyl, were so reactive that they immediately attacked their surrounding solvent molecules, but today we know that this is not the case for some, though often very little, activation energy is needed to bring about radical-molecule reactions. Since radicals are necessarily produced in pairs by single bond homolysis, the surrounding cage of solvent molecules tends, by physical collisions, to promote radical-radical recombination rather more than radical separation. Consequently, when catalysts such as organic peroxides or aliphatic azo compounds are used as 'free' radical initiators of chain reactions, such as olefin polymerisation, it is rarely found that they are more than 70% efficient as free radical sources. Kinetic studies of the 'cage effects' of solvent molecules in preventing the separation of radical pairs have shown that the dominant action of solvents is a function not of their chemical composition but of their bulk viscosity; radical separation becomes more difficult as the solvent viscosity is increased<sup>3</sup>. This cage effect of solvent molecules in promoting the recombination of radical pairs proves to be of more importance than the question of whether radical pairs are first produced in bonding or anti-bonding configurations.

Another question which interests physical chemists is the degree of particle separation that is needed before a radical becomes 'free', i.e. able to move independently through a solution. Cage effects can undoubtedly promote the recombination of even 'free' radicals since the homolytic dissociation of an optically active precursor has often been found to lead to the formation of a mixture of racemic and *meso* recombination products. Again, in solution, radicals like other solute molecules are usually solvated. Consequently their configurations, when investigated by physical methods such as e.s.r., and also their reactivities often differ from solvent to solvent. Detailed consideration of these problems is outside the scope of this review, but many references to them can be found throughout the text. One structural aspect of 'free' radical chemistry, however, needs to be stressed and that is the rather obvious fact that truly free radicals can only exist in a fluid phase, and not in a crystalline solid or a frozen glass. Consequently, computations of the structures of radicals obtained by the irradiation of crystalline or amorphous solids must be treated with caution with reference to structures of free radicals. In particular, 'crystal field theories' are not directly relevant to dilute solutions.

These basic problems concerned with the physical chemistry of free radicals of all types have been mentioned because it is an historic feature of organic chemistry that the discovery of new compounds, or of new reactions, leads, through a phase of rapid qualitative development, to wider quantitative studies of molecular structure and of chemical kinetics. The study of free radical reactions is now entering this latter phase as the following comments on the more conventional chapters of this review will show.

Thus Chapter 2 on homolytic aliphatic substitution deals with a subject that is now of interest mainly to kineticists who have still much to find out about relationships between activation energies and structure in reactions of known types. It therefore includes many tables summarising recent measurements. Homolytic aromatic substitution (Chapter 3), however, has not yet reached this stage of development for it is now apparent that the determination of partial rate factors for the homolytic substitution of a compound  $C_6H_5X$  depend on (a) the rate of formation of the initial radical adduct ( $R-C_6H_5X^\cdot$ ) and (b) on the competing reactions by which these radicals are converted to aromatic molecules  $RC_6H_4X$  by reactions which remove hydrogen, or combine to non-aromatic dimers which later aromatise by hydrogen loss. The fact that early studies of homolytic aromatic substitution were carried out in air now detracts from their value and still more from the value of early theories based upon them. Reactions of heteroaromatic molecules and radicals add further interest to this chapter, for here even qualitative results are still helpful in disclosing new routes for organic synthesis.

Chapter 4 by Davies and Parrott on homolytic addition reactions of radicals of carbon and sulphur again deals with a subject that has been studied intensively for over 30 years. With reference to the olefinic substances themselves the chief interest in this field to organic chemists now concerns the configurations of both the adduct radicals and the final products; homolytic addition is now so versatile that it comprises the easiest route for the production of new free radicals of predictable structure but yet less explored configuration, this being particularly true for additions to cyclic compounds. Advances in knowledge of free radical structure, which was accorded separate treatment in the Series One volume of these reviews, have therefore been included in this chapter.

Chapter 5 on free radicals of nitrogen again deals mainly with structural studies, for in the review period the chemical reactivities of nitrogen radicals has received less attention. Probably this research trend can be ascribed to the extending use of e.s.r. techniques which are particularly helpful in the examination of nitrogen radicals on account of the nuclear spin ( $S=1$ ) of the  $^{14}N$  atom. Somewhat in contrast, Chapter 6 on the free radicals of Groups III-V is preponderately a discussion of the relative stabilities and reactivities of simple radicals of these other elements with respect to corresponding radicals of carbon. It shows how soon searches for new reactions are now supplanted by more precise physicochemical studies. The study of free radicals other than those of carbon is now expanding so rapidly that the authors of both Chapters 5 and 6 have had to be selective in their reviews.

Oxygen chemistry, as such, is, in this volume, reviewed by Hawkins in place of reactions of peroxides. With regard to autoxidations involving normal, i.e. 'triplet', oxygen, scientific interest is increasingly changing to the examination of complex organic molecules and of more specific radical catalysts. Even in chemical technology fewer new developments of importance are being disclosed. The photochemistry of oxygen has been included in this chapter since it involves the production of the more active 'singlet' form of oxygen,  $O=O$ , which is a powerful dienophile that also reacts directly with molecules containing electron-rich isolated double bonds. Autoxidations and

photo-oxidations therefore lead to different peroxides, but these when formed break down by the same routes, which were adequately described in Series One. For those interested in mechanistic theory, Chapter 7 should be read in conjunction with Chapter 9.

One-electron oxidations and reductions involving metal ions now comprise a very extensive subject which exemplifies the value of unifying mechanistic theories in organic and inorganic chemistry. Two specialist authors, Littler and Nonhebel, have collaborated in this wide review. The production of aryloxy radicals by phenol oxidation no longer warrants separate treatment but is included in this chapter together with several aspects of the radical chemistry of nitrogen, such as the oxidation of aromatic amines, which are not to be found in Chapter 5. A uniform picture of the redox chemistry of the transition elements is now emerging, greatly helped by kinetic studies, and the importance of copper compounds in free radical reactions is being increasingly shown, clearly because, as a Group I element, it can form covalent alkyl derivatives and, as a transition element, can participate in one-electron redox reactions. The importance of free radical reactions in the preparation and uses of Grignard reagents also merits special comment.

It has been said that major advances in chemistry depend on the development of new experimental techniques, though these alone can never lead to the discovery of novel reactions, such as the formation of triphenylmethyl or homolytic aromatic substitution. Today new experimental techniques are mainly developed by physical chemists who devise increasingly sophisticated and expensive instruments for separating substances or for exploring implications of the quantum theory of molecular structure. Thus in but 15 years Electron Spin Resonance has transformed free radical chemistry so much that e.s.r. spectrometers are now essential tools in most laboratories. Double resonance spectroscopy (ENDOR and ELDOR) now provides even more refined structural information and new methods, such as INDO, for quantum calculations of radical structures, largely dependent upon the increasing availability of large computers, are now being widely used. These physical developments of e.s.r. have been reviewed elsewhere<sup>4</sup>.

Brief mention has been made already (p. 3) of the use of magnetic resonance for the study of radical-pairs. This Chemically Induced Dynamic Nuclear Polarisation (CIDNP), dating from only 1967, is now being used to show whether or not a chemical reaction produces radicals and to disclose some details of their nature. Several references to the outcome of CIDNP experiments are to be found in following chapters of this volume and it had been hoped to include also a short review of the applicability of this new technique. However, the theoretical principles and scope of CIDNP have been reviewed many times and Dr. J. A. den Hollander of Leiden University has kindly provided the list<sup>8-15</sup> of such articles which is appended to this chapter.

Experimentally, CIDNP experiments need only require the use of an n.m.r. spectrometer, for if a radical-producing reaction is occurring among substances which have been placed in an n.m.r. probe, then a resonance spectrum showing emission lines may be obtained. Positive observations of this are diagnostic of radical-pair formation, but a negative result does not exclude the possibility of occurrence of a free radical reaction in the selected system; for

instance, the reaction may be proceeding far too slowly in the n.m.r. probe. As in the early days of e.s.r., practical improvements of ways of carrying out reactions in strong magnetic fields are needed, for the obvious recourse to heating n.m.r. probes to get faster reactions is impracticable with many existing spectrometers. Though wide developments of CIDNP can be foreseen, many of them may perforce await the time when n.m.r. spectrometers are specifically designed and built to suit the needs of chemists who are interested more in chemical reactions than in chemical structure. Today even e.s.r. studies are too often restricted to those physicochemical experiments that have commended themselves to the instrument manufacturer and not to the research worker with original ideas.

## References

1. Nernst, W. (1916). *Z. Elektrochem.*, **22**, 62; (1918), *ibid.*, **24**, 1916.
2. Waters, W. A. (1946). *The Chemistry of Free Radicals* (Oxford: Clarendon Press).
3. Koenig, T. and Fisher, H. (1973). *Free Radicals*, Vol. 1, Chap. 4 (Kochi, J. K., editor) (New York and London: Wiley).
4. (1972). *Electron Spin Resonance*, Vol. 1 (Norman, R. O. C., editor) (London: The Chemical Society).
5. (1973). *Chemically Induced Magnetic Polarisation* (Lepley, A. R. and Closs, G. L., editors) (New York: Wiley).
6. Fischer, H. (1971). *Fortschr. Chem. Forsch.*, **24**, 1.
7. Fischer, H. (1971). *Ind. Chim. Belge*, **36**, 1054.
8. Closs, G. L. (1971). *23rd International Congress of Pure and Applied Chemistry*, Vol. 4, 19 (London: Butterworths).
9. Buchachenko, A. L. and Zhidomirov, Z. M. (1971). *Usp. Khim.*, **40**, 1729.
10. Ward, H. R. (1972). *Accounts Chem. Res.*, **5**, 18.
11. Lawler, R. G. (1972). *Accounts Chem. Res.*, **5**, 25.
12. Pine, S. H. (1972). *J. Chem. Educ.*, **49**, 664.
13. Roth, H. D. (1973). *Mol. Photochem.*, **5**, 91.
14. Bethell, D. and Brinkman, M. R. (1973). *Adv. Phys. Org. Chem.*, **10**, 53.
15. Ward, H. R. (1973). *Free Radicals*, Vol. 1, 239 (Kochi, J. K., editor) (London and New York: Wiley).

## 2

# Homolytic Aliphatic Substitution

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## 2.1 INTRODUCTION

In this review, reports of halogenation reactions and hydrogen-abstraction reactions are discussed. There has been considerable interest on free energy relationships and their applications to radical reactions. Although halogen-abstraction reactions and some miscellaneous substitution reactions are included, studies involving hot-radical substitution reactions by hydrogen<sup>1,2</sup> deuterium<sup>3</sup>, tritium<sup>4-6</sup>, fluorine<sup>7</sup>, chlorine<sup>7-9</sup>, bromine<sup>7,10,11</sup>, iodine<sup>7</sup> and methyl<sup>12-14</sup> are omitted. A recent review on atom-transfer and substitution reactions covering the literature up to 1972 has appeared<sup>15</sup>.

## 2.2 CHLORINATION

Various aspects of chlorination have been reviewed<sup>16,17</sup>, including allylic chlorination<sup>18</sup> and chlorination by nitrogen cation-radicals<sup>19</sup>.

Linear free energy relationships have been studied in a few systems and the data are collected in Table 2.4. Relative rate constants for hydrogen abstraction from chlorinated ethanes by chlorine atoms are given in Table 2.1.

Table 2.1 Kinetic parameters for hydrogen abstraction\* from chlorinated ethanes by chlorine atoms<sup>20,22</sup>

Substrate	Solvent	Pre-exponential factor	Activation energy cal mol <sup>-1</sup>
1,1-C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub>	neat	$\log A_p/A_t = -0.26 \pm 0.1$	$E_t - E_p = -120 \pm 100$
	CHCl <sub>3</sub>	$\log A_p/A_t = -0.16 \pm 0.01$	$E_t - E_p = -315 \pm 10$
	CHCl <sub>3</sub>	$\log A_p/A_c = -0.13 \pm 0.01$	$E_c - E_p = 1075 \pm 10$
	CHCl <sub>3</sub>	$\log A_t/A_c = 0.03 \pm 0.01$	$E_c - E_t = 1390 \pm 10$
1,2-C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub>	CHCl <sub>3</sub>	$\log A_s/A_c = 0.56 \pm 0.01$	$E_c - E_s = 1280 \pm 10$
1,1,1-C <sub>2</sub> H <sub>3</sub> Cl <sub>3</sub>	CHCl <sub>3</sub>	$\log A_p/A_c = -0.27 \pm 0.01$	$E_c - E_p = -97 \pm 5$
1,1,2-C <sub>2</sub> H <sub>3</sub> Cl <sub>3</sub>	neat	$\log A_s/A_t = 0.09 \pm 0.10$	$E_t - E_s = -100 \pm 100$
	CHCl <sub>3</sub>	$\log A_s/A_t = 0.12 \pm 0.01$	$E_t - E_s = -142 \pm 10$
	CHCl <sub>3</sub>	$\log A_s/A_c = 0.11 \pm 0.01$	$E_c - E_s = 471 \pm 10$
	CHCl <sub>3</sub>	$\log A_t/A_c = -0.01 \pm 0.01$	$E_c - E_t = 613 \pm 10$
1,1,1,2-C <sub>2</sub> H <sub>2</sub> Cl <sub>4</sub>	CHCl <sub>3</sub>	$\log A_s/A_c = -0.03 \pm 0.01$	$E_c - E_s = -60 \pm 10$
1,1,2,2-C <sub>2</sub> H <sub>2</sub> Cl <sub>4</sub>	CHCl <sub>3</sub>	$\log A_t/A_c = 0.24 \pm 0.01$	$E_c - E_t = 90 \pm 5$
C <sub>2</sub> HCl <sub>3</sub>	CHCl <sub>3</sub>	$\log A_t/A_c = -0.25 \pm 0.01$	$E_c - E_t = -129 \pm 10$
C <sub>2</sub> H <sub>2</sub> Cl <sub>4</sub>	CCl <sub>4</sub>	$\log A_s/A_p = 0.21 \pm 0.10$	$E_p - E_s = 86 \pm 100$

\* Subscripts p, s, and t refer respectively to primary, secondary and tertiary hydrogen abstraction. The subscript c refers to hydrogen abstraction from the solvent (CHCl<sub>3</sub>).

The *trans-cis* ratio of 1,2-disubstituted products has been shown to be influenced by the interaction between the half-filled  $\pi$  orbital at the 2-position with a 3p atomic orbital of the substituent<sup>20</sup> in the chlorocyclobutane and methylcyclobutane systems<sup>21</sup> and in 1-cyanobutane and cyanocyclobutane systems<sup>22</sup>. However, a similar observation in the cyclo-octane system has been attributed to steric dipole-dipole interactions<sup>23</sup>.

An earlier report of a displacement reaction between the bromoalkyl radical and a bromoalkane during photochlorination<sup>24</sup> has been substantiated<sup>25</sup>. Studies on the mesomeric effects of substituents<sup>26</sup> and on the effects of neighbouring groups such as Me, CH<sub>2</sub>Cl, CHCl<sub>2</sub> and CCl<sub>3</sub> in the chlorination of alkanes and substituted alkanes were reported<sup>27</sup>.

In the chlorination of methane in the fluidised bed of a catalyst, the fastest reaction step is the formation of CH<sub>2</sub>Cl<sub>2</sub> or that of CCl<sub>4</sub>, depending on the catalyst<sup>28</sup>. The chlorination of a polychloropentane mixture at 60 °C under visible or ionising irradiation is approximately first order in chlorine and dimerisation of chlorohydrocarbon radicals constitutes the major chain-termination step<sup>29</sup>. The rate constant for the reaction of CH<sub>2</sub>ClCHCl $\cdot$  with O<sub>2</sub> to give CH<sub>2</sub>ClCHClO<sub>2</sub> $\cdot$  was determined<sup>30</sup> as  $\log k = 7.8 \text{ l mol}^{-1} \text{ s}^{-1}$ .

Several factors influencing chlorination have been investigated, particularly with the aim of improving the industrial process. These include the

use of radiation<sup>31,32</sup>, the effect of chlorine concentration<sup>33,34</sup>, the effect of added nitric oxide on selectivity of halogenation<sup>35</sup>, the effect of temperature<sup>36</sup>, the flow speed of the gas<sup>37</sup> and the effect of interphase mass transfer<sup>38</sup>.

### 2.2.1 Products of chlorination

Products arising from chlorination of various systems are given in Table 2.2.

Table 2.2

Chlorinating agent	Substrate	Products	Ref.
SO <sub>2</sub> Cl <sub>2</sub> , <i>hν</i>	PhEt	PhCHClMe, PhCHClCH <sub>2</sub> Cl, PhCHClCHCl <sub>2</sub> , PhCCl <sub>2</sub> CH <sub>2</sub> Cl, PhCCl <sub>2</sub> CHCl <sub>2</sub>	41
Cl <sub>2</sub>	CH <sub>3</sub> CHCl <sub>2</sub>	CH <sub>3</sub> CCl <sub>3</sub> (80%), etc.	42
Cl <sub>2</sub>	MeCH=CH <sub>2</sub>	ClCH <sub>2</sub> CH=CHCl Cl <sub>2</sub> CHCH=CH <sub>2</sub>	43
ClSO <sub>3</sub> H	1,3,5-trichloroadamantane	tetrachloroadamantane	44
ClSO <sub>3</sub> H	adamantane	1-chloroadamantane, 1,3-dichloroadamantane, 1,3,5-trichloroadamantane	45
CCl <sub>4</sub>	1-silabicyclo[2,2,1]heptane	1-chloro-1-silabicyclo[2,2,1]heptane	46
Bu <sup>t</sup> OCl, <i>hν</i>	<i>exo</i> -tricyclo[3,2,1,0 <sup>2,4</sup> ]octane	<i>exo</i> -6-chloro-, <i>endo</i> -6-chloro-, 1-chloro- <i>exo</i> -trichloro- [3,2,1,0 <sup>2,4</sup> ]octane (ratio 67:12:17)	47
Bu <sup>t</sup> OCl, <i>hν</i>	<i>endo</i> -tricyclo[3,2,1,0 <sup>2,4</sup> ]octane	<i>anti</i> -8-chloro- <i>endo</i> -tricyclo- [3,2,1,0 <sup>2,4</sup> ]octane, <i>endo</i> -2-chloro- tricyclo[3,3,0,0 <sup>4,6</sup> ]octane and two other monochloro components (ratio: 66:27:5:2)	47

### 2.2.2 Chlorinating agents

The mechanism of chlorination of saturated alkanes by pentachlorobenzene-sulphenyl chloride has been shown to proceed via a free radical chain process in which the pentachlorobenzenethiyl radical is the predominant chain-carrying species<sup>48</sup>. Chlorination of long and intermediate chain fatty acid chlorides in refluxing thionyl chloride exposed to visible and u.v. light results in substitution at the  $\alpha$  position<sup>49</sup>.

1-Chlorobenzotriazole has been used to chlorinate diethyl malonate, cyclohexane, benzene, naphthalene derivatives and the NH group of phthalimide. Chlorination of anisole resulted in substitution at the *ortho* and *para* positions and the predominant formation of the *p*-isomer was suggested as evidence for an ionic mechanism<sup>50</sup>. Several groups of workers have reported on the reactions of the hypochlorites. The study of the kinetics of the radical-chain chlorination of cyclohexane and of toluene by Me<sub>3</sub>COCl in the presence of Cl atom traps revealed that in both cases the predominant termination step is coupling of the hydrocarbon radicals and that the rate-determining propagation step is the abstraction of Cl from the hypochlorite by the hydrocarbon radical<sup>51</sup>. It was found that Me<sub>3</sub>COCl was about 100 times

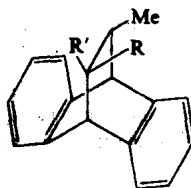
more effective than  $\text{Ph}_3\text{SnH}$  in trapping intermediate oxiranyl radicals<sup>52</sup>. The formation of  $\delta$ -chloro alcohols from suitable tertiary hypochlorites is well known<sup>53</sup>. This intramolecular chlorination has been extended to primary and secondary alkyl hypochlorites made possible by the use of *cis*- or *trans*-dichloroethylene and similar chloro-olefins which act as Cl atom traps<sup>54</sup>.

## 2.3 OTHER HALOGENATIONS

Substitution reactions involving fluorine, bromine and iodine are considered. A recent review on this topic has appeared<sup>55</sup>.

### 2.3.1 Mechanistic aspects

Steric acceleration<sup>56</sup> due to back-strain relief was deduced in a study of the bromination of four bridged polycyclic hydrocarbons (1)–(4) in which (3) and (4) were 15–30 times more reactive than (1) and (2).



- (1)  $\text{R} = \text{R}' = \text{H}$
- (2)  $\text{R} = \text{H}, \text{R}' = \text{Me}$
- (3)  $\text{R} = \text{Me}, \text{R}' = \text{H}$
- (4)  $\text{R} = \text{R}' = \text{Me}$

Polar effects were observed in the transfer reactions with  $\text{BrCCl}_3$  during the radical telomerisation of ethylene and propylene<sup>57</sup>. The kinetic study on the bromination of cyclohexene with and without light and oxygen suggested that a radical-chain mechanism was operating<sup>58</sup>. Bromination of cyanocyclobutane was found to be accompanied by elimination of  $\text{HCN}$ <sup>59</sup>. The rate constants for the bromination of dichloromethane, chlorofluoromethane and dichlorofluoromethane have been determined<sup>61</sup>.

### 2.3.2 Bridged free radicals

An active area of investigation into the mechanism of halogenation is the chemistry of bridged free radicals<sup>62</sup>. Skell has reviewed the subject extensively<sup>63,64</sup>. Further evidence for bridged free radicals has been obtained (i) in the conversion of active 1-bromo-2-methylbutane into 1-bromo-2-deuterio-2-methylbutane when irradiated with a  $\text{Br}_2$ - $\text{DBr}$  mixture<sup>58</sup>, (ii) in the radical-chain halogenation of 2-bromo- and 2-chlorobutanes<sup>65</sup>, (iii) in the photobromination<sup>66</sup> of 1-bromobutane labelled with bromine-82 and (iv) from e.s.r. studies<sup>67</sup>. While there is general agreement on the intermediacy of a bridged free radical in the halogenation of alkyl halides at the carbon next to the halogen, the question of anchimeric assistance has been disputed.



Anchimeric assistance has been reported in the photobromination of alkyl bromides<sup>68-70</sup>, but an alternative explanation has been provided by Tanner<sup>71,72</sup>. Support for this view has come from two other laboratories<sup>73-76</sup>.

### 2.3.3 Radical rearrangement during halogenation

Radical rearrangement has been reported in a few systems. A 1,2-bromine migration in the radical intermediate has been proposed in the photobromination of bromobutane with bromotrichloromethane<sup>77</sup>. In the bromination studies of the benzobicyclo[4,1,0]heptenyl system, the intermediate radical undergoes cyclopropylcarbinyl-allylcarbinyl rearrangement via 1,7 bond cleavage to the primary allylcarbinyl radical species in preference to rearrangement via 1,6 bond cleavage to the corresponding secondary allylcarbinyl radical species<sup>78</sup>. A novel and simple procedure for obtaining tetrahydrofurans from alcohols via the hypochlorite reaction, using silver or mercuric salts and chlorine, has been reported<sup>79</sup>. Another type of radical cyclisation results in the formation of oxetane during the hypiodite reaction of 3 $\beta$ - and 3 $\alpha$ -hydroxy- $\Delta^5$ -steroids<sup>80</sup>.

### 2.3.4 Fluorination

The rate constants for the fluorination of a number of systems are tabulated (see Table 2.3). The kinetic isotope effects for the hydrogen abstraction

Table 2.3 Rate constants for the abstraction reaction\* of fluorine atoms

Substrate	$k/\text{cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	Ref.
H <sub>2</sub>	$1.5 \times 10^{13} (\pm 50\%)$	161
CH <sub>4</sub>	$\geq 6.0 \times 10^{13}$	99
CH <sub>4</sub>	$3.6 \times 10^{13} (\pm 100\%)$	161
CH <sub>3</sub> F	$53 \times 10^{12}$	99
CH <sub>3</sub> F <sub>2</sub>	$11 \times 10^{12}$	99
CHF <sub>3</sub>	$0.19 \times 10^{12}$	99
CHClF <sub>2</sub>	$1.5 \times 10^{12}$	99
CH <sub>3</sub> Cl	$1.4 \times 10^{13} (\pm 30\%)$	161
CH <sub>2</sub> Cl <sub>2</sub>	$5.8 \times 10^{12} (\pm 25\%)$	161
CHCl <sub>3</sub>	$3.2 \times 10^{12} (\pm 25\%)$	161
HCl	$7.3 \times 10^{12}$	99
CBrF <sub>3</sub>	$0.004 \times 10^{12}$	99
NH <sub>3</sub>	$0.55 \times 10^{12}$	99
PH <sub>3</sub>	$\geq 22 \times 10^{12}$	99
Cl <sub>2</sub>	$(6.6 \pm 1.8) \times 10^{13}$	100
CF <sub>3</sub> I	$(7.2 \pm 3.6) \times 10^{13}$	101
CBr <sub>4</sub>	$(5.6 \pm 2.8) \times 10^{13}$	101

\* Atoms abstracted are underlined.

reactions of fluorine atoms with H<sub>2</sub>, CH<sub>4</sub> and CHCl<sub>3</sub> were found to be small and show that hydrogen atom transfer by quantum mechanical tunnelling is unimportant<sup>81</sup>. The effect of an inert gas in fluorination was demonstrated in