

**RADIATION  
CHEMISTRY**  
of  
**ORGANIC  
COMPOUNDS**

by  
**A. J. SWALLOW**

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COMPOUNDS**

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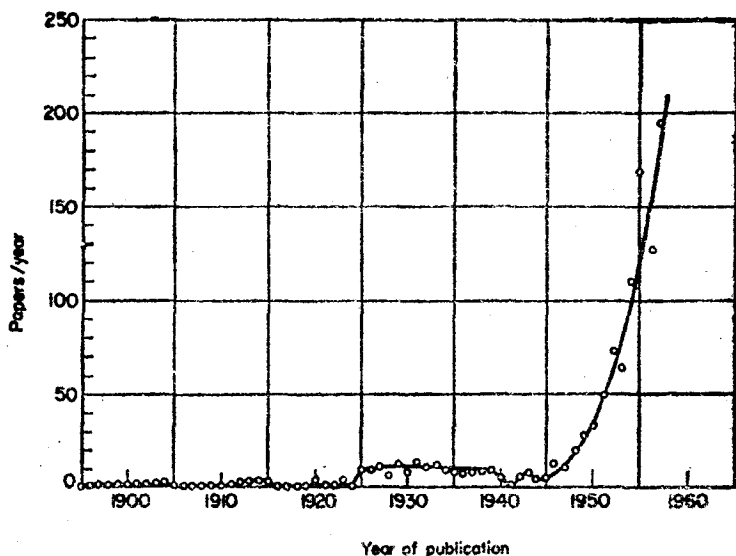
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## PREFACE

PHYSICS has been defined as the subject dealing with energy and its transformations, and chemistry as the subject dealing with matter and its transformations. Physical chemistry deals with the interactions between energy and matter. Radiation chemistry deals with the chemical changes produced by high-energy radiation, and therefore forms an essential part of physico-chemical science. However, although radiation chemistry is of manifest importance it is a subject of remarkably recent origin. This is shown in the graph of numbers of papers on radiation chemistry plotted against year of publication. As radiation chemistry is so new, there have been few attempts to present an overall picture of it, and this book aims to do this, particularly for organic compounds. This book



Development of Radiation Chemistry (based on the Bibliography of this book).

emphasizes what is known rather than what is not known, although a certain amount of speculation is included, and certain gaps in knowledge have been pointed out.

A second aim of the book is to review the published work on the radiation chemistry of organic compounds. All the original work which had been published between 1895 (when high-energy radiation was discovered) and the middle of 1958 has been surveyed for this book and also some of the work which has appeared since then. However, reference to certain publications has been omitted here. In particular, preliminary communications are rarely included if a more complete account of the same work is given elsewhere. Similarly, only the most reliable figures published by a given author are provided in the tables. Work which has been published in essentially the same form in more than one place is only referred to once. There is little or no reference to patents, to dissertations or theses, to reports of commercial organizations, or to atomic energy documents: this entails only slight loss of information because most of the scientific content of work published in this way is also published in the regular journals. There is little or no reference to work published in languages other than English, French, German, Russian or Italian. Work on proteins published before 1936 is not covered exhaustively, but reference is made to reviews of this work. Chapters I and II and sections A and B of Chapter III and sections B, C, D, E and F of Chapter IX contain only key references. Apart from these exceptions the coverage of the literature in the book is comprehensive. In order to ensure that this should be so, a large number of references of possible relevance has been examined, amounting to about twice the number referred to in the Bibliography.

I am very grateful to many friends and colleagues for invaluable help with this book. First, to Professor Arthur Charlesby for suggesting that it should be written, and for helpful criticism, especially of the chapter on polymers. Also to Dr. Edgar Collinson for allowing me to base the book on an article we wrote together for *Chemical Reviews*, and for helpful criticism of the chapter on aromatic compounds. Professor Gabriel Stein deserves particular thanks for reading the whole manuscript and the proofs and for making many valuable suggestions. I am also indebted to several others for reading and advising on parts of the book, and in particular to Dr. B. Coleby, Dr. R. A. Cox, Mr. W. H. T. Davison, Dr. M. Ebert, Mr. J. L. Haybittle, Dr. Barbara Holmes, Mr. S.

Jefferson, Professor H. C. Longuet-Higgins, F.R.S., Mr. H. C. Tresise and Dr. R. Worrall. My special thanks are due to Mr. P. J. Horner for help in correcting proofs. I should also like to thank those who have sent me manuscripts in advance of publication.

A. J. SWALLOW

*Cambridge*  
1960

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## CHAPTER I

# GENERAL INTRODUCTION

It is important to distinguish between radiation chemistry and radiochemistry. Radiation chemistry is the study of the chemical reactions produced by high-energy radiation; radiochemistry is the study of the radioactive elements. The two subjects are therefore quite different, although there are many points of contact between them.

The high-energy radiations with which radiation chemistry is concerned include electromagnetic radiations of wavelength below 100–1000 Å, i.e. of energy greater than 10–100 eV. They also include corpuscular radiations such as fast neutrons,  $\alpha$ -particles,  $\beta$ -particles, protons and fast fission fragments. Many of the effects produced by such radiations are like those produced by less energetic rays such as ultra-violet or visible light, so that radiation chemistry may be regarded as an extension of photochemistry.

One of the characteristic properties of high-energy radiation is to cause ionization of the medium in which it is absorbed. Hence the term 'ionizing radiation' is sometimes used. Because of the ionization produced, the effects of irradiation often resemble the effects produced by electrical discharges. Similarly, the effects produced by the controlled ionization of molecules in the mass spectrometer may be regarded as radiation-chemical effects in a specialized environment.

High-energy radiation often converts stable molecules into free radicals. Hence radiation chemistry is one aspect of free-radical chemistry and, conversely, free-radical chemistry is the subject dealing with the reactions of one type of species produced by radiation. Because free-radical reactions are often to be understood in terms of the well-established concepts of kinetics, it is possible to regard radiation chemistry as a branch of chemical kinetics.

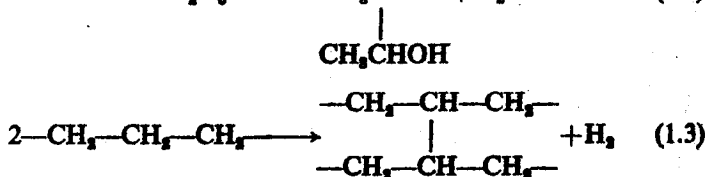
Some day it may be possible to weld all these connected subjects together, and turn them into a single, clearly defined branch of chemistry. Radiation chemistry itself has been dealt with in several places. The earliest work was discussed in a book published in 1928 [L31]. Two review articles published after the Second World War

introduce the subject from a modern point of view [B121, D2]. One book has appeared more recently [M77]. Recent advances in the subject are reviewed regularly in journals, notably in the Annual Reports of the Chemical Society and in the Annual Reviews of Physical Chemistry.

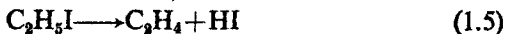
#### A. NET CHEMICAL EFFECTS PRODUCED BY RADIATION

The first step in the study of the chemical reactions induced by radiation is to discover the nature of the overall changes produced. This has now been done for many systems, and for many others not yet studied it is possible to argue by analogy to predict results. Perhaps surprisingly it is found that the reactions induced by high-energy radiation can be as specific as most chemical reactions. This is because the initial energy is rapidly degraded in matter, and much of the *chemical* change produced by radiation is a consequence of the action of electrons of energy less than about 100 eV. Further, the transient species produced by such electrons do not give final products immediately, but take part in various transfer processes in such a way that the molecules finally altered are not necessarily the ones which were affected in the first instance. Such processes are difficult to study, and for many purposes it is better to focus attention on the various categories of overall reactions which occur in radiation chemistry.

One of the commonest reactions is condensation polymerization, otherwise called dimerization or cross-linking, e.g.



This reaction can occur in every phase and in solution, although there are quantitative differences according to the conditions. When both hydrogen atoms are formed from the same molecule, an unsaturated double bond can be formed instead of a cross-link. Unsaturation and cross-links are often formed together. Substances containing iodine do not lose hydrogen, but lose  $\text{I}_2$  or  $\text{HI}$  instead, e.g.



Substances containing chlorine yield HCl, but chlorine cannot be liberated so long as there are hydrogen atoms present.

Another important reaction is degradation, e.g. C—C scission. This is especially important with certain polymers, and in fact many of the physical and chemical effects on such substances as polymers can be explained in terms of the two reactions cross-linking and degradation.

One of the most striking effects in radiation chemistry, especially with the less densely ionizing radiations like X- or  $\gamma$ -rays or fast electrons, is the almost universal influence exerted by oxygen. For example, oxygen causes reaction (1.2) to be replaced by



Owing to the limited solubility of oxygen it is often found that oxidation predominates in the earlier stages of an irradiation and is then replaced by the normal oxygen-free reaction after all the oxygen initially present has been consumed. An oxygen effect is also noted with biological materials, although the two phenomena are not necessarily related. Oxygen is not the only substance which exerts a powerful effect on response to irradiation. The addition to organic compounds of oxidizing agents such as ferric iron or the oxidized form of certain dyestuffs causes their oxidation to be enhanced, the oxidizing agent being simultaneously reduced. Such reactions are called coupled oxidation-reductions.

Coupled oxidation-reductions sometimes proceed with a very high yield for a given energy input and must be chain reactions. For example, a mixture of hydrogen and hydrogen peroxide in aqueous solution is found to react in very good yield when irradiated with  $\gamma$ -rays:



—this reaction is the reverse of reaction (1.1) and in practice an equilibrium is built up. Halogenation may be regarded as a special case of oxidation-reduction. Iodinations proceed only in low yield, but when organic substances are irradiated in the presence of chlorine it is found that chlorination occurs with yields of tens of thousands of molecules changed per 100 eV of energy absorbed, showing that a

chain reaction is taking place. Many other chain reactions can be initiated by radiation, including the polymerization of vinyl monomers and of unsaturated hydrocarbons like ethylene and isobutylene.

It might be thought that high-energy radiation would initiate the explosion of explosives. However, this is not generally so, although the subsequent decomposition can be enhanced. The explosion of nitrogen iodide by  $\alpha$ -particles is the only exception to the general rule, but the mechanism in this case appears to be very untypical. Intense enough beams of electrons can cause the explosion of nitrogen iodide and several other materials, but only because of the heat [B95].

Great progress has been made in understanding the mechanism of the reactions induced by radiation, and this subject will be surveyed in the rest of this chapter.

## B. MECHANISM OF THE INTERACTION OF HIGH-ENERGY RADIATIONS WITH MATTER

The physics of the action of high-energy radiations on matter is quite well understood and has been dealt with fully elsewhere [e.g. F2, G40]. It will be only briefly surveyed here.

### 1. X- and $\gamma$ -rays

Electromagnetic radiations of wavelength below about 100 Å are called X-rays if of extranuclear origin or  $\gamma$ -rays if produced from the atomic nucleus. There are three important ways in which they lose their energy in passing through matter: pair production, Compton scattering and photoelectric absorption. Photonuclear reactions are also possible, but are generally only significant with radiations of energy above 10 MeV, and even then usually dissipate negligible energy in the medium, their only practical consequence being to produce some radioactivity, usually of short half-life. Coherent scattering takes place with low-energy radiations. This is the process used in X-ray crystallography, but it is unimportant in radiation chemistry because the energy transferred to the molecules is not enough to cause chemical change.

(a) **Pair production.** In this process the X- or  $\gamma$ -ray photon produces a positron-electron pair within the medium. It is therefore necessary for the photon energy to be greater than the equivalent of the rest masses of the two particles, i.e. more than about 1 MeV. The electrons and positrons produced are energetic and lose their energy by causing

ionization and excitation (see below). The positron is ultimately destroyed by combining with an electron, usually to give two photons each of energy 0.5 MeV (annihilation radiation).

This radiation will lose its energy by Compton scattering or photoelectric absorption, but, because of the penetrating nature of  $\gamma$ -rays, the processes are likely to occur outside the reaction vessel in which the original event occurred. The cross-section for pair production rises with energy above the 1 MeV threshold and the cross-section per atom is proportional to the square of the atomic number.

**(b) Compton scattering.** In Compton scattering the photons lose part of their energy by ejecting electrons from atoms. The electrons cause ionization and excitation, whilst the scattered photons of reduced energy interact further, either by undergoing Compton scattering themselves or by photoelectric absorption. Compton scattering is a complex function of radiation energy, but as far as the medium is concerned, depends only on the number of electrons present, so that the cross-section per atom is proportional to atomic number.

The Compton scattering process is often the principal effect for X-rays and  $\gamma$ -rays in radiation chemistry: for example, it is the only important process occurring when  $\text{Co}^{60}$   $\gamma$ -rays (1.17 and 1.33 MeV) interact with water or other substances of low atomic number.

**(c) Photoelectric absorption.** In this process the photon is absorbed by an atom with the ejection of a fast electron, usually from one of the inner shells. The electron bears all the energy of the incident photon minus the binding energy. The binding energy can appear as a very soft X-ray, which in turn undergoes photoelectric absorption, but is more likely to be used to eject another electron from the same atom. This latter process is known as the Auger effect and the ejected electron is called an Auger electron.

The photoelectric effect is greatest for radiation of low energy and for material of high atomic number. The photoelectric cross-section per atom is approximately proportional to the third power of the wavelength, and for absorbing medium of high atomic number, to the fourth power of atomic number.

The relative importance of the three scattering processes in water is shown in Fig. 1.1

## 2. Fast Electrons

X- or  $\gamma$ -rays, whether by pair production, Compton scattering or photoelectric absorption, give rise to fast electrons within the medium



irradiated. These electrons have appreciable energy, up to almost the entire energy of the original photon, and as the energy required to

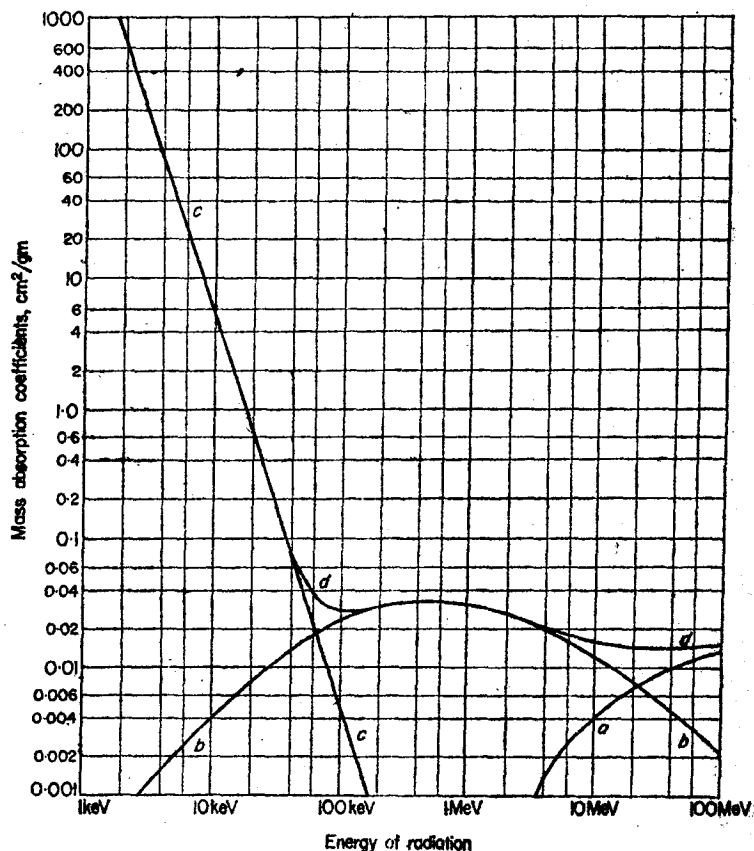


FIG. 1.1. Variation of mass absorption coefficients of water with energy [10]. (a) Part of pair production coefficient corresponding to transfer of energy to positron and electron, (b) part of Compton scattering coefficient corresponding to transfer of energy to electron, (c) photoelectric coefficient, (d) total real absorption coefficient.

produce chemical change is only a few electron volts per molecule, a fast electron is capable of altering several thousand molecules.

Clearly, the chemical change in the single molecule affected by the original event is negligible by comparison, so that the chemical effects of high-energy electromagnetic radiation are due almost entirely to the fast electrons produced within the medium. Fast