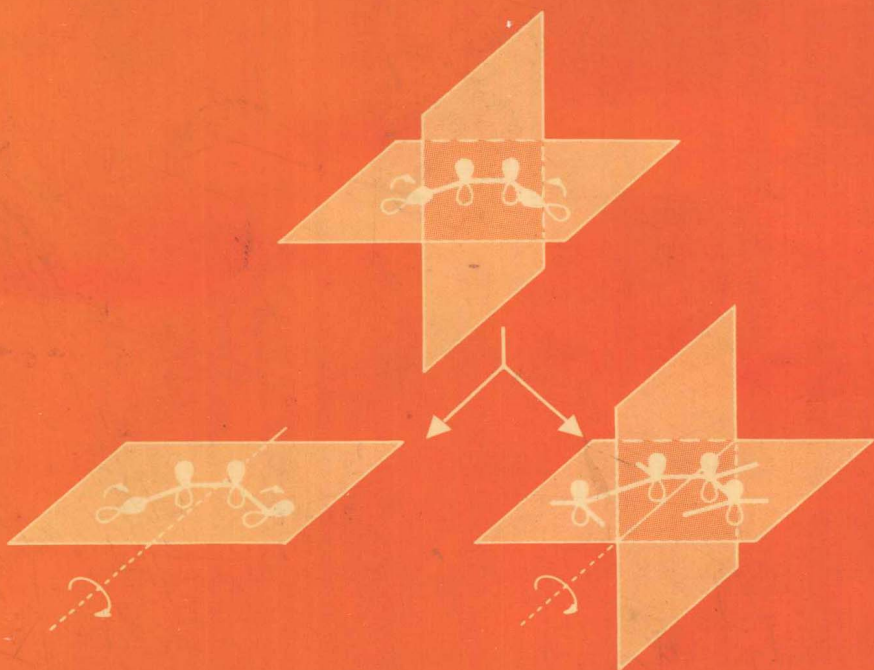


RICHARD P. WAYNE

Principles and Applications of Photochemistry



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Principles and Applications of Photochemistry

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PREFACE

Photochemical processes are of the greatest importance to life on Earth. Photosynthesis harvests the Sun's energy and creates carbohydrate from atmospheric carbon dioxide, as well as liberating oxygen to the atmosphere. Light-induced chemical changes in the gases of the atmosphere and the particles suspended there also modify the chemical composition of the atmosphere and allow it to support life. Indeed, the formation from the simplest elements of the complex organic molecular precursors of life, and then the emergence of life itself, are intimately bound up with photochemical processes. One of the most important senses for Man, and many other species besides, is vision, which is also photochemical in origin. Nature thus relies on light to effect some of her most essential chemistry. Man has also tried to harness light in his service, the applications ranging from the synthesis of new and complex organic species, through numerous kinds of imaging and photographic process, to the gathering and storage of solar energy.

The significance of photochemistry is by no means limited to the use that Nature and Man make of it. Rather, the chemistry itself is of profound interest at the most fundamental level. The reactions, dissociations, isomerizations, and optical emissions of electronically excited species are the central feature of photochemistry. For every atom and molecule known to us in the ground state, there are likely to be one or more excited states. Since these states possess different electronic structures from, and higher energies than, their parents, their chemistry is almost inevitably distinct from that of the ground-state species. Whole new fields of chemistry are thus opened up by allowing light to interact with the elements and their compounds. The motivations for studying photochemistry are as diverse as those for studying chemistry itself. On the one hand, physical chemists may be interested in the detailed dynamics of a photodissociation process and of the progress of the changes on a time scale of less than a picosecond, while on the other, organic chemists may seek an improved understanding, through the examples that photochemistry affords, of the relationships between reactivity and electronic and molecular structure.

In 1970, I wrote a textbook on photochemistry, with the undergraduate or non-specialist research student in mind (*Photochemistry*, Butterworths). At that time, the only available textbooks were twenty years out of date, with the exception of the monumental reference work *Photochemistry* by J. G. Calvert and J. N. Pitts, Jr (John Wiley, New York, 1966). My book was written from the standpoint of physical chemistry, although there was much of organic and

inorganic chemistry within. Since 1970, a steady stream of other excellent books on photochemistry has appeared, but none with quite the same emphasis that I had adopted, and it seemed that the time was now ripe to write a new book along the same lines as my earlier one. The present volume is the result. It is intentionally shorter than the 1970 *Photochemistry*, containing only the most essential material. At the same time as shortening most parts of the book, I have expanded the final chapter on the applications of photochemistry. That chapter was always popular with readers, and many new developments have arisen since 1970. I believe that it is worth weighting the balance of the book towards these practical examples, because they illustrate admirably the fundamental concepts of photochemistry, and because most chemists will ultimately be most involved with photochemistry in the applied context.

Photochemistry has seen an enormous increase of research activity in all areas over the past twenty years. There are now three Photochemical Societies, in Europe, America, and Japan. At least two journals are devoted to photochemistry (the *Journal of Photochemistry* [now *Journal of Photochemistry and Photobiology*], which started in 1970, and *Photochemistry and Photobiology*). There are regular international and informal conferences on photochemistry, together with further photochemical conferences held under the auspices of the International Union of Pure and Applied Chemistry (IUPAC). A series of short reports on the state of knowledge in various parts of photochemistry, written by acknowledged leaders, was edited by Dr John Coyle and myself as *Photochemistry: Past, Present and Future*, a special issue of *Journal of Photochemistry* in celebration of the publication of Volume 25 in 1984.

The huge research effort has led to an explosion of knowledge that has made the task of selecting material for a book even harder than it was in 1970, and the problem is compounded by the numerous new and important techniques used for the study of various aspects of photochemistry that need a mention if the reader is to grasp the nature of modern photochemistry. The increased knowledge makes difficult not so much deciding which principles must be expounded, but rather the choice of examples that will illustrate them. Very often, the simplest examples, and those that are understood in the greatest detail, involve atoms or small molecules in the gas phase. A physical chemist naturally finds such examples appealing, but he must be aware that most chemists work with large molecules in condensed-phase systems. I hope that I have selected my examples in a balanced and sensible way!

The structure of this book is very similar to that of the 1970 *Photochemistry*. Photochemistry is concerned with the chemistry of excited species, and the subject is developed to show the several paths by which an excited species may react or undergo radiative or radiationless decay. Chapters 3–6 describe these paths; Chapter 1 gives a general introduction to the basic

concepts of photochemistry, while Chapter 2 explains briefly the principles of absorption and emission of radiation. Fairly obviously, there are certain experimental techniques peculiar to photochemistry, and the descriptive material is placed in a better context if the reader understands how the experiments were performed. I have explained some of the more important techniques in Chapter 7. I have left this discussion until quite late on in the book, because the theoretical background needs to be developed first. Chapter 7 serves also as a vehicle for a very brief presentation of what has been called 'High-resolution Photochemistry'. This field is concerned with the detailed dynamics of photochemical processes, including the utilization of energy in specific quantum states of the starting species and its disposal in the products. It is proving very successful in probing the intimate nature of photochemical interactions, but does not fit easily into the main development of Chapters 3–8. Since the experimental part of the work is very technique oriented, it seems appropriate to describe the methods in Chapter 7, and to alert the reader here to the existence of the material in Section 7.6, and the later parts of Section 7.5. Chapter 8 concludes the book with the discussion, mentioned earlier, of photochemical processes found in nature and of some commercial and laboratory applications. Incidentally, in this last chapter I have made no effort to stick rigidly to systematic names for chemical compounds, but rather thought it sensible to use the names almost universally employed in industry.

This book is intended primarily for undergraduate readers, although it is hoped that it may prove useful and interesting to graduate students embarking on research in photochemistry. Some knowledge of elementary chemistry (e.g. atomic and molecular structure, spectroscopy, reaction kinetics) is assumed, but the ideas of photochemistry are built up from first principles. Specific literature references are out of place in a book of this kind. Instead, a bibliography is given at the end of each chapter to enable the reader to pursue in greater depth the topics discussed. These bibliographies have deliberately been made more extensive for the later chapters in the book, especially for Chapters 7 and 8. Articles relevant to the overall aims of each chapter are followed by articles on specific topics identified, where possible, by their section numbers. Series of review volumes are an important additional source of information. They include the *Specialist Periodical Reports in Photochemistry* (Royal Society of Chemistry: Senior reporter D. Bryce Smith), *Advances in Photochemistry* (present editors: D. H. Volman, K. Gollnick, and G. S. Hammond), which is biased towards physical chemistry, and *Organic Photochemistry* (present editor: A. Padwa), whose title defines its interests. Excited states are treated specifically in the series *Excited States* (edited by E. C. Lim) from a theoretical and physical point of view, and a whole volume of *Advances in Chemical Physics* (Vol. 50, 1982, edited by K. P. Lawley) was devoted to the dynamics of the excited state. One volume that is particularly

useful for supplementary reading in connection with Chapter 8 is by J. D. Coyle, R. R. Hill, and D. R. Roberts (eds), *Light, Chemical Change and Life*, The Open University Press, Milton Keynes (1982). This book, which was written as a source text for a third-level Open University course in photochemistry, contains fairly short, readable, and authoritative accounts of a wide variety of topics concerning the biological and technological applications of photochemistry.

I recorded, in 1970, my debt of gratitude to Professor R. G. W. Norrish, FRS, who was my first teacher, and to Dr E. J. Bowen. Both were outstanding pioneers in photochemistry, representing the Cambridge and Oxford schools. Sadly, both have died since 1970. Others whose help I acknowledged included Professors C. H. Bamford, FRS, J. N. Pitts, Jr, and B. A. Thrush, FRS, and I should like to reiterate here my appreciation of the help they have always given to me. To their names I should like to add those of Professors W. J. Albery, FRS and R. J. Donovan, Drs N. S. Allen and J. D. Coyle (who are my Associate Editors on the *Journal of Photochemistry and Photobiology*, and who gave me particularly useful advice about Chapter 8), and my Oxford photochemical colleagues, in particular Drs Gus Hancock and Mike Pilling.

Finally, I should like to thank my wife, Brenda, not only for her tolerance while I was writing the book, but also for giving me the benefit of her invaluable editorial skills.

Oxford
October 1987

R. P. W.

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Figure 8.13 is from Eaton, D. F. (1986). Dye sensitized polymerization. In *Advances in photochemistry*, volume 13, (ed. D. H. Volman, G. S. Hammond, and K. Gollnick), pp. 427–487, Copyright © 1986 by John Wiley & Sons, inc., reprinted by permission of John Wiley & Sons, inc.

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Basic principles of photochemistry

1.1 Scope of photochemistry

Man has been aware from the earliest times of the influence that the Sun's radiation has on matter. However, it is during the last seventy years or so that a systematic understanding of photochemical processes has developed. A logical pattern to the interaction between light and matter emerged only after the concept of the quantization of energy was established. It is the purpose of this book to explain the physical foundations on which modern photochemistry is based; the specific examples given in the book are intended to illustrate these principles rather than to provide a comprehensive survey of known photochemical reactions.

'Photochemistry' is a term rather loosely applied. While an important part of photochemistry is concerned with the chemical change that may be brought about by the absorption of light, a number of physical processes that do not involve any overall chemical change lie within the province of the photochemist; processes such as *fluorescence* (in which light is emitted from a species that has absorbed radiation) or *chemiluminescence* (in which light is emitted as a 'product' of a chemical reaction) must be regarded as of a photochemical nature. The word 'light' is also used loosely, since radiation over a far wider range of wavelengths than the visible spectrum is involved in processes that would be accepted as photochemical. The long wavelength limit is probably in the near infrared (say at 2000 nm) and the region of interest extends into the vacuum ultraviolet (see footnote p. 155) and is limited only formally at the wavelengths where radiation becomes appreciably 'penetrating' (X-rays). The essential feature of photochemistry is probably the way in which 'excited' states of atoms or molecules play a part in the processes of interest. It is apparent that absorption or emission of radiation to or from these states is the concern of the spectroscopist as well as of the photochemist, and the photochemist must have at least a background knowledge of spectroscopy. At the same time, the photochemist is frequently interested in the *rates* at which processes occur, so that the concepts of *reaction kinetics* are often employed. It is assumed that the reader of this book has had contact with the ideas of *quantum theory*, *spectroscopy*, and *reaction kinetics*, and that he can obtain

access elsewhere to more detailed discussions of these topics than it is possible to provide here.

1.2 Light and energy

Planck developed his theory of black-body radiation on the basis of a postulate that radiation possessed particulate properties and that the particles, or *photons*, of radiation of specific frequency ν had associated with them a fixed energy ε given by the relation

$$\varepsilon = h\nu \quad (1.1)$$

where h is called Planck's constant. This quantum theory of radiation was then used by Einstein to interpret the photoelectric effect. As early as the beginning of the nineteenth century, Grotthus and Draper had formulated a law of photochemistry which stated that only the light absorbed by a molecule could produce photochemical change in the molecule. The development of the quantum theory led to a realization that the radiation would be absorbed in the quantized energy packets; Stark and Einstein suggested that one, and only one, photon was absorbed by a single particle to cause its photochemical reaction. It is now appreciated that several processes may compete with chemical reaction to be the fate of the species excited by absorption (see Section 1.5) and a more satisfactory version of the Stark–Einstein law states that *if a species absorbs radiation, then one particle is excited for each quantum of radiation absorbed*. Although this law might appear trivial in the present-day climate of acceptance of the quantum theory, the law is of fundamental importance in photochemistry, and the agreement between experiment and predictions based on the law does, in fact, offer substantial evidence in favour of the quantum theory of radiation.[†]

It is now apparent that the energy of excitation of each absorbing particle is the same as the energy of the quantum given by the Planck relation (1.1), and the excitation energy per mole is obtained by multiplying this molecular excitation energy by N , Avogadro's number. A linear relationship exists between energy and frequency, so that frequency characterizes radiation in a particularly direct way. It has been, however, almost universal practice to discuss the visible and ultraviolet regions of the spectrum in terms of *wavelength* of the radiation, and it is therefore convenient to express the molar

[†] A number of photochemical processes are recognized in which more than one quantum of radiation is absorbed by a single molecule. Many such processes do not violate the Stark–Einstein law: they involve excitation to successively higher energy states of the molecule, each step requiring a single quantum. True 'simultaneous' absorption of more than one photon occurs under conditions of intense illumination, as described in Section 3.9. Observation of such multiphoton processes awaited the development of suitably intense sources, especially lasers. Light is still absorbed in quantized packets.

excitation energy, E , in terms of wavelength, λ ,

$$E = Nh\nu = \frac{Nhc}{\lambda} \quad (1.2)$$

where c is the velocity of light. Numerical relationships between E and λ may be derived from the values given for constants in Appendix 1; one particularly useful form is

$$E = \frac{119\,627}{\lambda} \text{ kJ mol}^{-1} \quad (1.3)$$

where λ is in nanometres.

Although the chemist frequently finds thermal energy units (kJ) most useful, it is sometimes convenient to express energies in units such as electron-volts or wavenumber: the conversion factors are given in Appendix 2. The relationships are displayed pictorially inside the front cover. A useful way of remembering the approximate energies of photochemically active radiation is to recall that the wavelength range is roughly 200–600 nm, while the corresponding energies are in the range 600–200 kJ mol⁻¹.

1.3 Excitation by absorption

A molecule that has absorbed a quantum of radiation becomes ‘energy-rich’ or ‘excited’ in the absorption process. Absorption in the wavelength region of photochemical interest leads to *electronic excitation* of the absorber. Absorption at longer wavelengths usually leads to the excitation of vibrations or rotations of a molecule in its ground electronic state. Although it would be a mistake to suppose that the *only* form of excitation that could lead to photochemical change is electronic, it is generally true that electronically excited states are involved in photochemical processes. The importance of electronic excitation is, in part, a result of the energy possessed by the ‘hot’ species, as we shall see in the next section. There is, however, another reason, connected with the nature of the excitation, why electronically excited species exhibit reactivities distinguishable from those of the unexcited species. A simple example will make this clear. The electronic structure of lithium in its ground state is represented in the familiar form Li 1s² 2s¹: the electrons are placed in the lowest orbitals available to them. The configuration Li 1s² 3p¹ lies at a higher energy than the 1s² 2s¹ configuration, and represents an electronically excited state of lithium. Now, this excited lithium atom possesses an electron in a p orbital. Since the chemistry of a species depends to a considerable extent on the electronic structure, the reactivity of the excited lithium atom can be expected to differ from that of the ground-state atom, quite apart from considerations of the extra energy possessed in the excited

configuration. Rather more subtle forms of electronic excitation are possible, and these will be explored further in Chapter 2. For any one atomic or molecular species, a great many electronically excited states may be accessible: for each of these states there may be a distinct chemistry, which is by no means identical with that of the ground state. Thus, it is apparent that the reactions observed in photochemical studies may have little in common with the thermal reactions of the parent, ground-state species.

1.4 Thermal and photochemical reactions

The essential distinction between thermal and photochemical reactions now needs to be explored more fully. Thermal energy may be distributed about all the modes of excitation in a species: in a molecule these modes will include translational, rotational, and vibrational excitation, as well as electronic excitation. However, for species in thermal equilibrium with their surroundings, the Boltzmann distribution law is obeyed. This law states, of course, that the relative numbers of particles, n_1 and n_2 , in two equally degenerate levels 1 and 2, separated by an energy gap ΔE , are given by the expression

$$\frac{n_2}{n_1} = e^{-\Delta E/RT} \quad (1.4)$$

If we take a typical energy of an electronically excited state equivalent in thermal units to 250 kJ mol^{-1} , we can show that at room temperature ($RT \sim 2500 \text{ J mol}^{-1}$) $n_2/n_1 = e^{-100} \sim 4 \times 10^{-46}$, so that a negligible fraction of the species is excited. To achieve a concentration of only 1% of the excited species would require a temperature of around 6800°C , and in the event most *molecular* species would undergo rapid thermal decomposition from the ground electronic state and it would not be possible to produce appreciable concentrations of electronically excited molecules. In contrast, if molecules absorb radiation at a wavelength of about 500 nm as a result of an electronic transition, then electronic excitation certainly *must* occur, and the concentration produced depends on several factors, including the intensity of illumination and the rate of loss of the excited species. That chemical change can follow the production of electronically excited species is not surprising when consideration is given to the energies involved. The very rough wavelength range suggested in Section 1.1 as being of photochemical interest is similar in equivalent energy to the values of chemical bond energies normally encountered. If the electronic excitation energy can in some way be made available for bond rupture, then chemical change may occur. The study of photochemistry is concerned in part with the manner and extent of such energy utilization. Again, the energy of excitation is comparable with the activation energies frequently observed for the reaction of unexcited species: if

the electronic excitation can be used to overcome all or some of the energy of activation, then it may be expected that the excited species will react *more rapidly* than the ground-state species. Thus we see that photochemical reactions are distinguished from thermal reactions, first by the relatively large concentrations of highly excited species, which may react faster than the ground-state species and may even participate isothermally in processes that are endothermic for the latter, and secondly, if the excitation is electronic, by the changes in chemical reactivity that may accompany the new electronic configuration of the species.

A secondary feature of photochemical excitation is that a specific state of the species is formed if the radiation is contained within a sufficiently narrow band: an essentially monoenergetic product can result. It is true that the species may still possess, about its excited level, an energy spread characteristic of the temperature of the surroundings, but at room temperatures the range of energies within which most particles lie is very small compared with the energy of excitation, and even narrower distributions may be achieved at reduced temperatures. The possibility of forming monoenergetic species is of particular concern in connection with theories of reaction kinetics, where it is of fundamental interest to see how rapidly a species possessing a specific amount of energy can participate in a reaction. Monoenergetic species can be produced thermally only by the use of sophisticated methods such as the molecular beam technique, while simple photochemical experiments can achieve a relatively narrow energy distribution for electronically excited species.

1.5 Fates of electronic excitation

Photochemical processes involving the absorption of light can be divided into the act of absorption, which falls within the domain of spectroscopy, and the subsequent fate of the electronically excited species formed. It has been implied, in the discussion of the last few pages, that there are several such fates, and we shall now consider more explicitly what the possibilities are. At this stage a highly simplified picture will be presented: each of the processes mentioned will be explored in greater detail later in the book.

Figure 1.1 represents, in simplified form, the various paths by which an electronically excited species may lose its energy.

Energy transfer, represented by paths (iv) and (v) in the diagram, leads to excited species, which can then participate in any of the general processes. In this preliminary discussion, therefore, energy transfer will not be considered further; instead, this topic is deferred until Chapter 5.

Chemical change can come about either as a result of dissociation of the absorbing molecule into reactive fragments (process i), or as a result of direct reaction of the electronically excited species (process ii); electronically excited

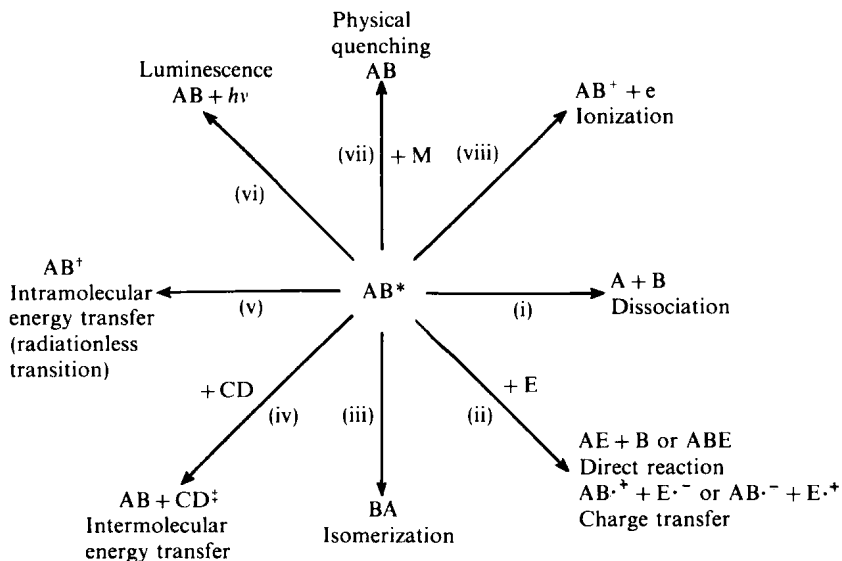
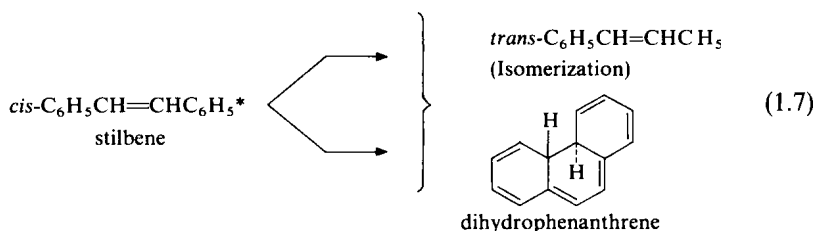
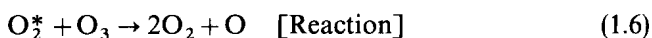
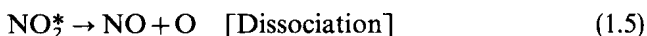


Fig. 1.1 The several routes to loss of electronic excitation. The use of the symbols *, †, and ‡ is only intended to illustrate the presence of electronic excitation and not necessarily differences in states. One or both of the products of processes (i)–(iii) may be excited.

species may also undergo spontaneous isomerization, as indicated by path (iii). Some examples will illustrate these processes; an asterisk is used to denote electronic excitation.



Several mechanisms for dissociation are recognized (they include *optical dissociation*, *predissociation*, *induced predissociation*, and so on), and they are discussed in more detail in Chapter 3. A special case of dissociation is that of ionization, shown as path (viii).