

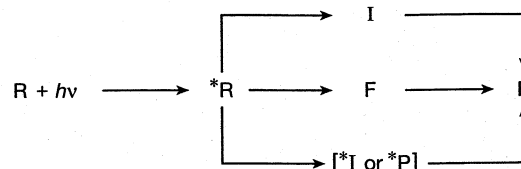
Molecular Photochemistry of Organic Compounds: An Overview

1.1 What Is Molecular Organic Photochemistry?

Molecular organic photochemistry is a science concerned with the structures and dynamic processes that result from the interaction of light with organic molecules. The field of molecular organic photochemistry can be conveniently classified in terms of the *photophysics of organic compounds* (the interactions of light and organic molecules resulting in net physical changes) and the *photochemistry of organic compounds* (the interactions of light and organic molecules resulting in net chemical changes). The molecular photochemistry of organic molecules is a rather broad and interdisciplinary topic embracing the fields of chemical physics, molecular spectroscopy, physical organic chemistry, synthetic organic chemistry, computational organic chemistry, and supramolecular organic chemistry.

In simplest terms (Scheme 1.1), molecular organic *photochemistry* involves the overall process $R + h\nu \rightarrow {}^*R \rightarrow P$, where R is an organic molecule that absorbs a photon ($h\nu$), whose frequency (ν) is correct for light absorption by R; *R is an electronically excited molecule; and P is an isolated product (or products). Organic *photophysics*, on the other hand, involves the overall process $R + h\nu \rightarrow {}^*R \rightarrow R$, where R absorbs a photon, but does not undergo any net chemical change. In general, R will stand not only for the reactant molecule (R) that absorbs the photon, but also any other molecules (M) that are required for production of the product (P). If not stated explicitly, it should be assumed that the reactions described in this text are conducted in a solution of an inert solvent at or near room temperature ($\sim 25^\circ\text{C}$). The electronically excited molecule (*R) is the essential species that is universal to all photochemical and photophysical processes.

The text describes how the overall photochemical process $R + h\nu \rightarrow P$ and the overall photophysical process $R + h\nu \rightarrow R$ can be visualized in structural, mechanistic, theoretical, and experimental terms. For example, Scheme 1.1 describes a global paradigm for understanding the possible paths for the *photochemical* process



Scheme 1.1 A global paradigm for organic photochemical reactions. Photophysical processes that return $*R$ to R are not included at this point, for simplicity. The $*R \rightarrow R$ photophysical processes are shown in Scheme 2.1.

$R + h\nu \rightarrow P$. The holy grail of molecular organic photochemistry uses Scheme 1.1 and its plausible elaborations for *the achievement of a complete structural and dynamic mechanistic description of all of the physical and chemical steps that occur as the result of the absorption of a photon by an organic molecule (R) and eventuate in the formation of an isolated product (P) or the regeneration of the starting material (R)*. The nature of the species I and F will be discussed in Sections 1.9 and 1.10.

Scheme 1.1 and its elaboration for photophysical processes ($R + h\nu \rightarrow R$) provide a *paradigm* of remarkable versatility and scope that serves as a basis for *analyzing all organic photochemical reactions and all photophysical processes*. We shall employ the term “molecular photochemistry” to include *both* the photophysics of $*R$ and the photochemistry of $*R$, since the concepts and laws of photophysics and photochemistry are intimately interwoven. Indeed, we shall see that it is impossible to have a proper understanding of the photochemical processes of $*R$ without a corresponding understanding of the photophysical processes of $*R$.

Scheme 1.1 shows that there are *three* fundamentally distinct pathways, termed *primary photochemical processes*, that $*R$ may follow on the way to P:

1. A pathway, $*R \rightarrow I \rightarrow P$, that leads to the formation of a discrete reactive intermediate (I) that can typically be described as having the characteristics of a radical pair (RP), a biradical (BR), or a zwitterion (Z).
2. A pathway, $*R \rightarrow F \rightarrow P$, that does not involve a discrete reactive intermediate (I), but instead proceeds through a “funnel” (F). This pathway takes R to P and can be described in the language of energy surfaces as a “conical surface intersection” or as a minimum produced by surface-avoided intersections.
3. A pathway, $*R \rightarrow *I \rightarrow P$ or $*R \rightarrow *P \rightarrow P$, that involves the formation of an electronically excited *intermediate* ($*I$) or an electronically excited product ($*P$).

Of these three possibilities, $*R \rightarrow I$ (RP, BR, or Z) is the most commonly observed pathway for organic photochemical reactions.

The “molecular” part of molecular photochemistry emphasizes the use of molecular structure and its implied dynamics (transitions between states) and molecular substructure (electron configuration, nuclear configuration, and spin configuration)

as the crucial and unifying intellectual units for organizing and describing the possible, plausible, and probable pathways of photochemical reactions from “cradle” (the absorption of a photon by a reactant, R, to form $*R$) to “grave” (the isolation of a product, P, produced by one of the three pathways from $*R$ shown in Scheme 1.1).

1.2 Learning Molecular Organic Photochemistry through the Visualization of Molecular Structures and the Dynamics of Their Transformations

This text attempts to teach effective cognitive and contextual strategies for learning molecular organic photochemistry. Physical organic chemistry has thrived and progressed rapidly because of a tradition of correlating molecular structures with reaction mechanisms and with chemical reactivity. Molecular structure provides a powerful and effective visual means of coupling molecular dynamics to the change of molecular structure. We strive to provide an understanding of photochemical reactions through the visualization of molecular structure and the molecular dynamics of the processes described in Scheme 1.1.

1.3 Why Study Molecular Organic Photochemistry?

Scheme 1.1 displays schematically, at an elementary level, the *structural and dynamic content* that is important for the study and understanding of modern molecular organic photochemistry. *Every* organic photochemical reaction can be understood and described in terms of the paradigm of Scheme 1.1 or some plausible and straightforward modification or elaboration of Scheme 1.1. The motivation for studying the molecular photochemistry of organic compounds depends on the *context* in which the student views the content of the field, and many different motivations can provide such a context.

For example, there is the pure intellectual satisfaction of understanding how to visualize the ways in which two of the most fundamental components of the universe, photons ($h\nu$) and molecules (R), interact with one another to produce an electronically excited molecule ($*R$), which eventually is transformed to an isolated product (P). In particular, there can be a special intellectual delight in learning how to integrate different fields, such as spectroscopy, quantum mechanics, reaction mechanisms, molecular structure, magnetic resonance, and chemical dynamics. A qualitative understanding of each of these fields is important for an understanding of molecular organic photochemistry.

The intellectual structure of this field is inherently interdisciplinary and therefore requires a practitioner to seek a commonality and integration of the ideas and methods of many scientific disciplines. Such a process presents a challenge to the student. To a student who starts to learn a scientific subject, theories may appear to be based on disparate and seemingly conflicting concepts and laws, such as the theory of waves and the theory of particles. Molecular organic photochemistry must integrate theories

from different fields. In this text, the required integration of theories and concepts is achieved by providing a visualization of the molecular structures, energetics, and dynamics involved in molecular organic photochemical reactions.

Other motivations for studying organic molecular photochemistry are found in its importance in modern technologies, in molecular and chemical biology, in medical applications, and in solar energy resources. For example, molecular organic photochemistry provides an understanding of the mechanism of photosynthesis, the fundamental process by which nature harnesses the sun's energy by the absorption of solar photons to produce food and energy for our planet. Photosynthesis is initiated by a primary photochemical process involving an electron transfer reaction (Chapter 7). Vision, our most important sense for observing and surviving in the external world, is triggered by a remarkably simple primary process of cis-trans isomerization, which triggers a cascade of physiological events that result in the sensation of vision in the brain.

During the late 1900s, the advent of laser technology revolutionized the field of telecommunications by making it possible to transmit information using light (through glass fibers), rather than electrons (through metal wires). New technologies, termed photonics, employ light to perform tasks that were originally relegated to the domain of electronics. Photochemistry is also attaining an increasingly important role in the health sciences, curing some forms of cancers (through phototherapy), repairing tissues, and performing microsurgery using lasers. Other important applications of photochemistry include the use of photolithography to manufacture computer chips and photopolymerization to produce protective coatings for a variety of high-value materials, such as optical fibers. One of the "holy grails" of photochemistry is the discovery of practical ways to convert sunlight into high-grade fuels to replace fossil fuels. Photophysics, especially the use of fluorescence as a sensor, is currently of enormous importance for applications in the materials sciences and in the biological sciences. All of these applications require an understanding of the essential players in molecular organic photochemistry, namely, the photon ($h\nu$), the molecule (R), and the electronically excited molecule (*R) as outlined in Scheme 1.1.

Among the most exciting developments in photochemistry during the past four decades has been the ever-increasing speed at which "pictures" of reacting molecules, such as *R, can be taken. Lasers can now routinely produce pulses of light whose duration are on the order of a few femtoseconds (fs; $1 \text{ fs} = 10^{-15} \text{ s}$). With such short pulses it is possible to take "snap shots" of actual atomic motions in real time down to periods as short as vibrational time scales. Typical atomic motions (i.e., bond stretching and bending) occur on the scale of $\sim 10^{12} \text{ nm s}^{-1}$ ($10^{13} \text{ \AA s}^{-1}$). Thus, for a bond stretching and breaking of $\sim 1 \text{ nm}$ (10 \AA), the time scale is on the order of 1000 fs. Pulses on the order of 10 fs, therefore, are able to follow such fast atomic processes. Femtosecond lasers are now routine in the laboratories of physicists and chemical physicists.¹

What will be the eventual limit of short laser pulses that will be of interest to chemists? Since chemistry involves the movement of electrons, we can define the time scale for electron motion as the lower limit for events of interest to the chemist.

An electron in a Bohr hydrogen atom makes a complete orbit in $\sim 10^{-16}$ – 10^{-17} s , so we can use this time scale as the ultimate limit of time scales of interest to the chemist. Pulses on the order of 100 as (attoseconds; $1 \text{ as} = 10^{-18} \text{ s}$) have been produced.² If the past is any guide, chemists will someday be taking snap shots of electrons moving in their orbitals. Chemists can probably agree that the zeptosecond (zs) time scale ($1 \text{ zs} = 10^{-21} \text{ s}$) will probably be the exclusive domain of physicists, who will take snap shots of excited nuclei exploding!

A unique property of lasers is the coherence (or phase alignment) of the light that is emitted. This coherence has the promise of controlling the course of chemical reactions by "steering" reactions toward specific pathways.

1.4 The Value of Pictorial Representations and Visualization of Scientific Concepts

Molecular photochemistry employs a number of theories and representations of molecular structure to describe the interaction of light and organic molecules to produce electronically excited states (i.e., $R + h\nu \rightarrow *R$ in Scheme 1.1) and to describe the dynamics of the overall pathways from electronically excited states to products (i.e., $*R \rightarrow P$ in Scheme 1.1). Organic chemists are accustomed to analyzing ground-state, thermally induced reactions of R in terms of molecular structure, molecular energetics, and molecular dynamics. We show that the familiar molecular structural theory of organic chemistry provides an effective and powerful starting point for understanding mechanistic organic photochemistry. However, we have to make some important modifications to the theory of ground-state reactions as we proceed. We need to develop a theory of light and of the interaction of light with molecules where the usual structural theory of organic chemistry is replaced by a theory of interacting waves, and where the classical continuum of states and energies is replaced by quantized states and quantized energies. Consequently, we shall seek to understand and visualize the paradigms of wave and quantum mechanics, which have evolved as an authoritative and powerful means for understanding all structural and dynamic aspects of molecular organic photochemistry.

In order to understand molecular organic photochemistry, in addition to the familiar chemical representations involving molecular structure and dynamics, we must develop an understanding of the concepts of electron spins, electromagnetic radiation, and photons. The latter concepts are described quantitatively and most effectively by the mathematics of wave and quantum mechanics. However, this text is directed at students who do not possess the mathematical background necessary for a quantitative computation of molecular properties through quantum mechanics. Instead, we show that there are classical representations that are readily visualizable and capture the spirit and essence of most of the critical features of quantum mechanics that are needed to understand molecular organic photochemistry. These visualizable classical representations will provide the student with a *quantum intuition* for an understanding of the qualitative details of the pathways given in Scheme 1.1. For those who plan to

proceed more deeply into the mathematics of quantum mechanics, we hope that the pictorial representations will provide a useful framework for the more quantitative mathematical aspects. To delve as deeply into the mathematical aspects as desired, the interested and able student can proceed to standard textbooks and references on quantum mechanics.³

1.5 Scientific Paradigms of Molecular Organic Photochemistry

Consensus exists among scientists on how to perform research and how to describe experimental observations when *authoritative scientific paradigms* exist that provide an accepted process on how to deal with important questions such as What are the fundamental entities that exist in the universe, and what are their properties? and What are the legitimate theoretical concepts and experimental tools that are required to understand and to measure the properties of the entities that exist? Authoritative paradigms allow the practicing scientist to perform everyday research and enable a student to be readily initiated into a mature field of science by studying, learning, and mastering the paradigms of the field.

Now, we examine briefly the concept of scientific paradigms and how it relates to the development of a paradigm for molecular organic photochemistry. The simple paradigm of modern molecular photochemistry shown in Scheme 1.1 helps answer the question What are the fundamental entities that exist along a photochemical or photophysical pathway? We will also answer questions, such as What are the structural, energetic, and dynamic properties of the entities shown in Scheme 1.1? and What are the legitimate theoretical concepts and experimental tools that are required to understand and to measure the properties of these entities? We use the word "paradigm" throughout the text because of its importance in science. We digress briefly now to describe how the word has evolved in the scientific community.

In a book entitled *The Structure of Scientific Revolutions*,⁴ Thomas Kuhn, a philosopher of science, defined a *scientific paradigm* as a complex set of intellectual and experimental structures consisting of assumptions, concepts, strategies, methods, and techniques that provide a framework for performing scientific research in a field and for organizing and interpreting observable phenomena of the universe in a systematic and organized manner. According to Kuhn, *the accepted paradigms of a field provide the authority to which scientists appeal in deciding on the course of everyday, normal scientific activities and in recognizing expected results, exceptional results, and likely errors or artifacts*. A scientific paradigm sets the expectations and coordinates the benchmarks for what a scientific community considers legitimate concepts, laws, theories, and research within the field over which the paradigm governs. In effect, a scientific community is defined by the paradigm that directs the everyday research efforts of the practitioners. *This text is concerned with the description and development of the scientific paradigms of modern molecular organic photochemistry.*

The authority of the currently reigning paradigm prevents practitioners in a field from wasting time arguing over fundamentals, irrelevancies, errors, or artifacts. *Because they share the same paradigm, practitioners can proceed rapidly to advanced levels of inquiry without arguing over fundamental issues.* For example, the paradigm of atomic and molecular structure is so authoritative and widely accepted that no modern chemist or physicist argues whether molecules can be usefully represented by three-dimensional (3D) models of atoms connected by bonds that result from the interactions of electrons and nuclei. However, a little over 150 years ago the paradigm of describing molecular structures in terms of 3D geometry was hotly debated by the scientific community, and before 1955, there were no authoritative paradigms governing the description of organic photochemical reactions. Yet, today photochemists are convinced that all observable photochemical phenomena, no matter how complex, can be understood and investigated based on the paradigm of molecular structure and dynamics implied in Scheme 1.1 and its plausible elaborations. The paradigm of organic photochemistry is now considered to be mature.

Because of the maturity of the paradigms of modern molecular photochemistry, organic photochemists do not argue whether the paradigm of Scheme 1.1 is correct in any essential way. Thus, the critical entities of interest to the organic photochemist are immediately defined by Scheme 1.1 as R, *hν*, *R, I, F, *I, *P, and P. The structures, energetics, and dynamics of these entities are therefore of vital interest to the photochemist. This text will help to develop an understanding of the structures, energetics, and dynamics of these entities and the dynamics of their transformations through the paradigms that currently are the basis of modern molecular organic photochemistry.

In closing this section on paradigms, the student must be warned that the ruling paradigms are by no means permanent but are always subject to change. This is true for at least three reasons, namely, the tentative nature of theories, the incompleteness of experimental information, and the inevitable possibility of completely novel and unanticipated results that may be observed in the future as new techniques are developed and perfected. The history of science over the past two centuries has shown that paradigms that were considered to be absolute and indisputable authorities were eventually overturned as paradigm shifts occurred and the once reigning paradigms were replaced by new governing paradigms. For example, the classical paradigm of light as an electromagnetic wave has been replaced by the quantum mechanical paradigm in which light is viewed as a quantized entity possessing both wave and particle characteristics. The electron, considered a classical particle at the turn of the nineteenth century, is now considered a quantized entity with both wave and particle characteristics (both paradigm shifts are described in Sections 4.2–4.5).

1.6 Exemplars as Guides to the Experimental Study and Understanding of Molecular Organic Photochemistry

Typically, a textbook will describe the paradigms that constitute the assumptions, concepts, strategies, methods, and techniques of the field of interest. An important

cognitive tool in learning a field's paradigms is the explicit consideration of specific informative and well-tested examples called *exemplars*. Exemplars provide pedagogical tools that introduce students to new fields of science. For example, in organic chemistry the concept of functional groups provides a familiar set of exemplars for the understanding of organic structures, organic mechanisms, and organic syntheses. The carbonyl, olefinic, enone, aromatic, and other functional groups are all exemplars of a broad scope of chemical and physical properties that can be extended broadly to cover many actual examples. Thus, we can use a functional group as an exemplar to predict the types of reactions and the properties of an extremely wide range of molecules.

An exemplar can also be loosely defined as a universally recognized scientific accomplishment or a set of accomplishments that for a time provides a theoretical and experimental framework for the scientist on how to investigate a new system. For example, the photoreaction of benzophenone with alcohols has served as an exemplar of how to investigate the mechanisms of organic photochemical reactions. Exemplars of the entities and processes shown in Scheme 1.1 are widely used in this text and they provide a basis for the understanding of molecular organic photochemistry.

1.7 The Paradigms of Molecular Organic Photochemistry

Molecular organic photochemistry integrates the paradigms of structure–energy–reactivity correlations, which are the domain of physical organic chemistry, with the paradigms describing the interaction of electromagnetic radiation (photons) with matter (the electrons and nuclei of organic molecules). The paradigm of organic chemistry employs the structure of the molecule (with its implied electronic, nuclear, and spin configurations) as the key organizing concept; the paradigm of electromagnetic radiation employs photons or oscillating electromagnetic waves as the key organizing concept. Thus, *the field of molecular photochemistry is concerned with the interactions of light (represented by photons or oscillating electromagnetic waves) and matter (represented by the electrons and nuclei of molecules) that lead to the formation of *R and its eventual conversion to P (photochemistry) or R (photophysics) through pathways that are elaborations of Scheme 1.1.*

1.8 Paradigms as Guides for Proceeding from the Possible to the Plausible to the Probable Photochemical Processes

The paradigm of Scheme 1.1 provides the organic photochemist with guides for proceeding from the *possible*, to the *plausible*, to the *probable* when considering how to study and interpret photochemical and photophysical processes. How do you characterize a reaction pathway, such as $*R \rightarrow P$? For any reaction pathway to be *possible*, molecules (and their vibrational and spin substructures) must obey *all* four

of the conservation laws of chemical reactions: (1) the conservation of energy, (2) the conservation of momentum (linear and angular), (3) the conservation of mass (the number and kinds of atoms), and (4) the conservation of charge. As we shall see, these conservation laws place considerable restrictions on the number of *a priori possible* structures ($*R$, I , $*I$, P , $*P$, and F) and *a priori possible* pathways (Scheme 1.1) that a photochemical reaction can follow. *Only the set of structures and pathways that obeys the conservation laws is considered possible and all others are ruled out, absolutely, with no exceptions!*

However, even when the conservation laws are fully obeyed, the paradigm constrains the actual number of *plausible* pathways for a photochemical reaction by the consideration of the details of molecular structure and implied energies and reorganization associated with structural transformations, by the consideration of available interactions that couple structures, and by the consideration of the available mechanisms of momentum and energy exchange. These considerations lead to a set of “selection rules” that indicate the *plausible* (at some assumed level of approximation) reactions that should be considered from the initial set of *possible* reactions.

To move from the *plausible* to the *probable*, you must consider specific details of the structure and the available interactions, reorganization energy, and time scales available to the *plausible* structures. These considerations determine the *kinetics* (or rates) of each of the steps in Scheme 1.1. After eliminating pathways based on kinetic considerations, the remaining (much smaller) set of *plausible* pathways, which occur at the fastest rates, is considered to be the *set of most probable reaction pathways* of the *plausible* processes—that is, those that proceed at the fastest rates will win the race from $*R$ to P and are therefore the most *probable*. We present paradigms that show how to generate selection rules for *plausible* sets of pathways by employing structures, energetics, and interactions that cause transitions between structures to decide whether a pathway is *possible*, *plausible*, or *probable*. We also describe the experimental and computational methods available to photochemists to experimentally “prove” which of the *probable* pathways is actually the one that occurs under a given set of conditions.

In attempting to understand an overall photochemical transformation, $R + h\nu \rightarrow P$, it is very useful first to list *all of the plausible pathways* that are available to $*R$ after the absorption of a photon by R (e.g., from Scheme 1.1, the formation of I , the passage through a funnel F , or the formation of $*I$ or $*P$) and then to qualitatively predict, based on selection rules described in Section 4.13, the relative rates of the *plausible* pathway(s) to P compared to the rate of all other *plausible* pathways available to $*R$ that do not lead to P . Predicting an observed or most *probable* pathway of a photochemical reaction under a given set of conditions requires the ability to use the paradigm of molecular organic photochemistry shown in Scheme 1.1 to make informed judgments based on a knowledge of known, measured rates, exemplars, or theoretically estimated rates based on structure, interactions, energy, and dynamics for a given set of conditions.

The goal of this text is to teach, and for the student to learn, the global and everyday working paradigms that relate, from cradle to grave, the structure, energetics, and

dynamics of molecules and photons to photochemical transformations, such as the overall photochemical process $R + h\nu \rightarrow P$ and the overall photophysical process $R + h\nu \rightarrow R$.

1.9 Some Important Questions that Will Be Answered by the Paradigms of Molecular Organic Photochemistry

Now, let us consider in detail one of the possible paths of the global paradigm given in Scheme 1.1, the $*R \rightarrow I \rightarrow P$ sequence, which involves the following steps:

1. The *absorption of a photon* ($h\nu$) by a reactant molecule (R) to produce an electronically excited state ($*R$).
2. The *primary photochemical reaction* of the electronically excited state ($*R$) to produce a thermally equilibrated ground-state reactive intermediate (I).
3. The *thermally induced reaction* of I to produce the observed product(s) (P).

The paradigm of Scheme 1.1 suggests that a photochemist should always ask and attempt to answer a number of standard questions concerning the details of an overall photochemical reaction, $R + h\nu \rightarrow P$. For example,

1. How do we visualize a photon interacting with the electrons of R to induce absorption of a photon to produce $*R$, and how does this interaction of a photon and the electrons of R relate to theoretical and experimental quantities, such as extinction coefficients, radiative lifetimes, and radiative efficiencies?
2. What are the possible and plausible *structures, energetics, and dynamics* available to $*R$ and I that occur along the reaction pathway from $*R \rightarrow P$?
3. What are the *possible and plausible* sets of *primary photochemical processes* corresponding to the $*R \rightarrow I$ process?
4. What are the legitimate *theoretical approaches, experimental design strategies, experimental techniques, and computational strategies* for experimentally "observing" or validating the occurrence of the species $*R$ and I that are postulated to occur along the reaction pathway from $*R \rightarrow P$?
5. What is the most *probable* pathway from $*R \rightarrow I$?
6. How is the most probable pathway determined by the competing *kinetic* pathways for the photophysics and photochemistry of $*R$?
7. What are the absolute rates (rate constants) at which each elementary step occurs along the reaction pathway from $*R \rightarrow P$?
8. What sorts of *structures, energetics, and dynamics* correspond to $*R$ and I in typical organic photoreactions?

Questions such as these and many more that are implicitly posed by the paradigm of Scheme 1.1 (and its elaborations) can be handled by establishing a more detailed working paradigm and by referencing exemplars that serve as benchmarks for the analysis of photochemical reactions.

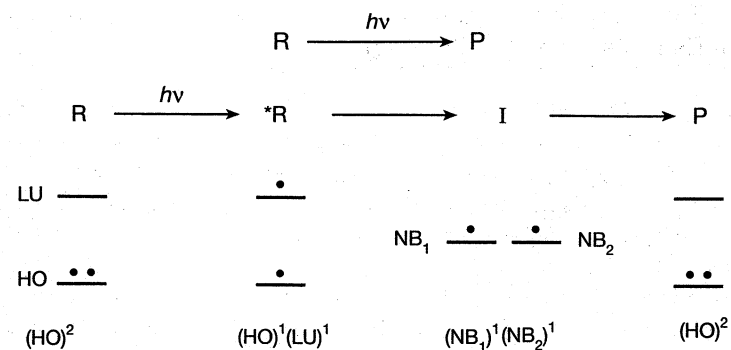
1.10 From a Global Paradigm to the Everyday Working Paradigm

In solving normal scientific puzzles, we save a great deal of time by employing an "everyday working paradigm" that is based on considerable experience or precedent and that is found to be generally applicable to a wide range of commonly encountered situations. This shortcut of using a working paradigm is a sort of mechanistic "Occam's razor," relieving the photochemist from always starting from scratch and examining a large number of hypothetically plausible, but historically improbable, situations each time a photochemical reaction is analyzed, an experiment is designed, or a theoretical point is discussed. The paradigm discourages the scientist from wasting time by considering theoretical or experimental situations that are expected to be outside the paradigm. In our study of molecular organic photochemistry, we shall always start with Scheme 1.1 as the global paradigm and determine how we can continuously elaborate it into an ever more specific everyday working paradigm for molecular organic photochemistry. A very effective method for refining Scheme 1.1 is the appeal to exemplars.

As mentioned in Section 1.6, students of organic chemistry are familiar with the effectiveness of the exemplar approach through the study of *functional groups*, where a functional group is an atom or group of atoms that possess qualitatively similar reactivities, spectroscopic properties, and physical properties that are independent of the molecule in which the functional group is found.

Coupling the functional group approach with exemplars from molecular orbital (MO) theory provides a powerful means of predicting chemical reactivity at a qualitative level and will be used extensively in this text to advance an understanding of the photochemistry of exemplar systems. We show that, to a good starting approximation, having an understanding of the photochemistry of the common functional groups of organic chemistry (carbonyl, olefinic, enone, aromatic compounds, etc.) means the working paradigm needs only to consider two things: (1) the electron configurations of two MOs [the highest occupied molecular orbital (HOMO), abbreviated as HO, and the lowest unoccupied molecular orbital (LUMO), abbreviated as LU] and (2) the electron spin configurations of the electrons in the HO and LU for the key structures (i.e., R, $*R$, I, and P) shown in Scheme 1.1.

Scheme 1.2, an elaboration of Scheme 1.1, includes the energy levels of the HO and LU of R, $*R$, I, and P as a working paradigm for the examination of molecular organic photochemical reactions that proceed through the path $R + h\nu \rightarrow *R \rightarrow I \rightarrow P$. Scheme 1.2 displays qualitatively the energies of the HO and LU, and at this level, electron spin is not explicitly considered. The energies of the HO and LU for R, $*R$, and P are assumed to be far apart (typically $> 40 \text{ kcal/mol}^{-1}$), whereas the *energies of the HO and LU molecular orbitals for I are assumed to be very similar and may often be approximated as nonbonding (NB) orbitals*. It is assumed in the working paradigm of Scheme 1.2 that all of the remaining electrons that are not shown in this scheme are spin paired (according to the aufbau and Pauli exclusion principles) in orbitals of lower energy and are of secondary importance in determining the course of



Scheme 1.2 The global paradigm of organic photochemical reactions displaying orbital configurations of R, *R, I, and P.

the photochemical and photophysical processes (because these lower-energy electrons are difficult to perturb, even in photochemical processes).

The starting point for the analysis of a photochemical or photophysical process is the assignment of the electronic nature of the HO and LU for R and *R. This amounts to assigning a specific electron configuration to $R(\text{HO})^2$ and ${}^*R(\text{HO})(\text{LU})$. The reactive intermediate I is generally a species possessing two nonbonding orbitals that are produced by the primary photochemical process ${}^*R \rightarrow I(\text{NB})^1(\text{NB})^1$. There are no HO or LU of very different energies in the latter case, but instead there are two NB orbitals of similar energy. Thus, the chemistry of I will be determined by the electronic configuration of two electrons in two NB orbitals (and, as we shall see in Section 1.11, by the spin configuration of the two electrons, too).

When the two NB orbitals are located mainly on carbon atoms, the lowest-energy orbital configuration of I corresponds to one electron in each NB orbital [i.e., $I(\text{NB})^1(\text{NB})^1$], thus producing a radical pair I(RP) or biradical (BR). (The terms “biradical” and “diradical” are sometimes used interchangeably in the photochemical literature, but we use the term “biradical” solely for the situation in which two NB orbitals each contain one electron and both NB orbitals are contained in the same molecular structure. We use the symbol D to mean a more general “diradicaloid” species that could be a RP, BR, or some related structure. The definition of a diradicaloid is discussed in detail in Chapter 6.)

In some cases, when the energies of the NB orbitals are significantly different, the reactive intermediate I may possess an electron configuration that places both electrons in the lower-energy orbital, a situation that requires the two electrons to be spin paired. Such electronic configurations correspond to species called *zwitterions*, $Z(\text{NB})^2$, which for simplicity we are ignoring at this point.

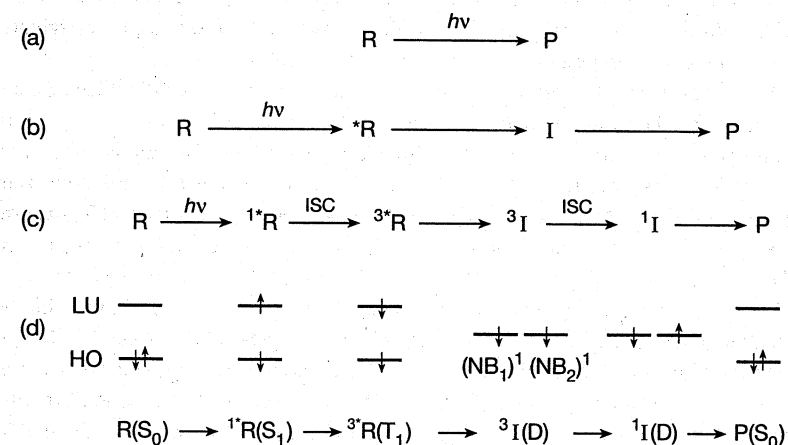
In all cases the orbitals assigned to the HO and LU will be simple one-electron orbitals that are familiar to the student from courses in organic and physical chemistry.

In this approximation, moreover, we ignore electron–electron repulsions that would lead to different energies of the HO and LU in R and *R. This approximation is discussed in more detail in Chapter 2 and is employed throughout the text.

The working paradigm of Scheme 1.2 suggests a number of questions that need to be answered when studying or analyzing any organic photochemical reaction:

1. What are the electronic characteristics of the HO and LU involved in the $R + h\nu \rightarrow {}^*R$ process?
2. What is the electronic configuration of *R (i.e., the orbital occupancy of the HO and LU)?
3. What are the plausible primary photochemical and photophysical processes typical of *R based on its electron configuration $(\text{HO})^1(\text{LU})^1$?
4. What are the electronic natures of the NB orbitals of I?
5. What are the plausible secondary thermal reactions of I that lead to P?

Scheme 1.2 requires one more level of structural elaboration before it can be employed as an everyday working paradigm. (For simplicity, at this stage, we are ignoring both the ${}^*R \rightarrow F$ processes and the ${}^*R \rightarrow {}^*I$ processes.) The nature of the funnel (F) will be considered in detail in Chapter 6. This final level of detail includes not only the electronic configurations of *R and I but also the electronic *spin* configurations of *R and I, as shown in Scheme 1.3. Now, we consider the role of spin in a photochemical reaction of the type ${}^*R \rightarrow I \rightarrow P$.



Scheme 1.3 Exemplar paradigm for an organic photochemical reaction that proceeds through a triplet state.

1.11 Singlet States, Triplet States, Diradicals, and Zwitterions: Key Structures Along a Photochemical Pathway from *R to P

Scheme 1.3 describes an elaboration of the orbital and spin structural detail for the exemplar photochemical reaction $R + h\nu \rightarrow {}^*R \rightarrow I(D) \rightarrow P$. First, we consider the elaboration of the orbital description of the species along the reaction path (b), then we consider an elaboration of the spin description of the species along the reaction path (c).

The electronic configurations of the ground states of R and P are generally $(HO)^2(LU)^0$ for ordinary organic molecules. According to the Pauli exclusion principle, the spins of two electrons in the same orbital must be paired (the spins will be symbolized as $\uparrow\downarrow$, termed “antiparallel spins,” and correspond to a singlet spin configuration or a singlet state). The electronic configuration of *R and I, both of which typically possess one electron in each of the two key orbitals (HO and LU or the two NB orbitals) shown in Scheme 1.3d, are not required by the Pauli exclusion principle to be spin paired, so the two key electrons in the half-filled orbitals can be either paired ($\uparrow\downarrow$, singlet states) or unpaired (symbolized as $\uparrow\uparrow$ and referred to as “parallel spins,” corresponding to a triplet spin configuration or a triplet state).

The *singlet states* of a molecule are given the symbol S_n , where the subscript n ranks the energy of the singlet state. The subscript 0 is reserved for the lowest-energy electronic ground state, which is always a singlet state (i.e., S_0) for ordinary organic molecules. The first excited singlet state is S_1 , the second excited singlet state is S_2 , and so on. When *R (or I) possesses two orbitally unpaired electrons and the electron spins are spin unpaired ($\uparrow\uparrow$), the structure is termed a *triplet state* and labeled T_n , where the subscript n ranks the energy of the triplet state. [Since the subscript 0 is reserved for the lowest-energy electronic ground state (i.e., S_0), $n = 1, 2, \dots$ for triplet states, and the lowest energy triplet state is T_1 .] The terms “singlet” and “triplet” originate from the magnetic properties of electron spins (Chapter 2).

In general, R and P represent the singlet ground states of organic molecules, so they are given the symbols $R(S_0)$ and $P(S_0)$. If the electrons are spin paired ($\uparrow\downarrow$) in *R, this is a singlet *excited* state and it is labeled S_1 , where the subscript indicates that the state is the *first excited* singlet state [i.e., *R(S_1) in Scheme 1.3]. If the electron spins are parallel ($\uparrow\uparrow$) in *R, this is a triplet *excited* state and it is labeled T_1 , where the subscript indicates that the state is the *first triplet excited* state [i.e., *R(T_1) in Scheme 1.3].

Likewise, the reactive intermediate I with one electron in each of two orbitals of similar energy (e.g., two nonbonding orbitals) may be either a singlet ${}^1I(\uparrow\downarrow)$ or a triplet ${}^3I(\uparrow\uparrow)$. We use the symbol D (for diradical) as a general label for a reactive intermediate (I) produced from *R that possesses two half-filled orbitals (typically both nonbonding) of comparable energy. The symbol D represents *both* RP, species in which one radical center is located on each of two molecular fragments, and BR, species in which the two radical centers are located on a single molecular structure. Thus, the symbol I(D) refers to a reactive intermediate that possesses

diradical character and for which the two half-filled orbitals are of similar energy. The I(D) species differ from *R, because *R species possess two half-filled orbitals that are of *very different energies*. This distinction will be of particular importance when we consider the role of electron–electron interactions in changing the energies of orbitals from the values for one-electron orbitals.

The symbols ${}^1I(D)$ and ${}^3I(D)$ represent singlet and triplet diradical intermediates, respectively. The superscript indicates the spin state of the intermediate, and the D means the intermediate possesses two electrons in half-filled orbitals. Then, it follows that the symbols ${}^1I(RP)$ and ${}^3I(RP)$ represent singlet and triplet radical pairs, respectively, and the symbols ${}^1I(BR)$ and ${}^3I(BR)$ represent singlet and triplet biradicals, respectively.

If I is in a singlet state, it is also possible for the two electrons to be in *one* NB orbital, and for no electrons to be in the other, that is, $I(NB)^2(NB)^0$. Such a species is referred to as a *zwitterion* and given the symbol I(Z). The I(Z) species are involved in the ${}^1R \rightarrow {}^1I(Z)$ and the ${}^1R \rightarrow F$ steps of photoreactions involving certain singlet states, whereas D species are always involved in the ${}^3R \rightarrow {}^3I(D)$ step of photochemical reactions involving photochemical processes initiated in 3R . The rules for D or Z formation and the chemical properties of these species are described in Chapter 6.

Scheme 1.3 represents a working *exemplar paradigm* for all photochemical reactions of organic molecules that proceed through a triplet excited state, *R(T_1). For any given reaction, R may be a carbonyl, an olefinic, an enone, an aromatic compound, or so on. We need to know the nature of the HO and LU of each of these structures to deduce the electronic configuration of *R. Given the electronic configuration of *R, we can generate “selection rules” for the plausible *primary photochemical reactions* *R \rightarrow I. Predicting and understanding photochemical reactions requires a knowledge of the structures of the entities shown in Scheme 1.3, namely, $R(S_0)$, *R(S_1), *R(T_1), 3I , 1I , and $P(S_0)$, and of the probabilities of the transitions between the structures connected by the pathways shown in Scheme 1.3(c).

In Chapter 6, we see that when the electronic configuration of T_1 is $HO = n$ (i.e., a nonbonding MO) and $LU = \pi^*$ (i.e., an antibonding MO), which is the case for acetone, benzophenone, and many other ketones, there is only a small set of primary photochemical processes of the type *R(T_1) \rightarrow ${}^3I(D)$ that are plausible. The important role of electron spin rears its head in the overall reaction because (Scheme 1.3) the reactive intermediate ${}^3I(D)$ must be converted to a singlet intermediate, ${}^1I(D)$, before the final product $P(S_0)$, which is a singlet state, can be formed.

How do the ISC processes *R(S_0) \rightarrow *R(T_1) and ${}^3I(D) \rightarrow$ ${}^1I(D)$, which require a change in electron spin, occur? A useful vector representation of electron spin is presented in Chapter 2 to describe how electron spin operates to control the steps that interconvert singlets and triplets. In Chapters 3 and 6, this vectorial representation of electron spin is used to answer questions pertaining to the interconversion of spin states. Now that we have introduced the important global and exemplar paradigms for analyzing organic photochemical reactions, we can develop the *state energy diagram*, which makes it possible to use and manipulate the working and exemplar paradigms.

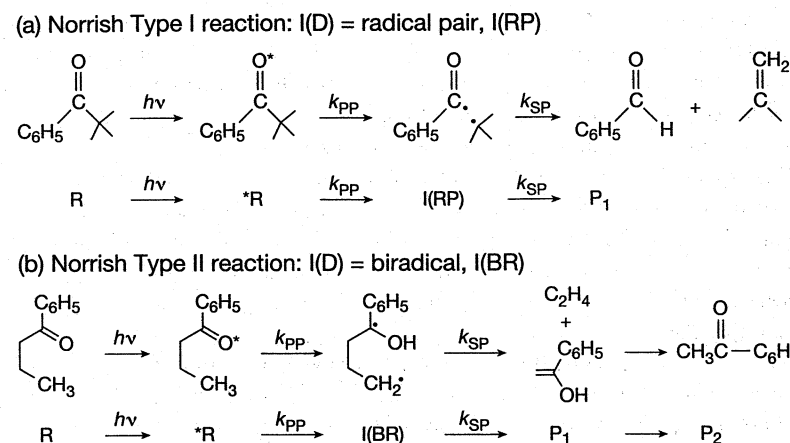
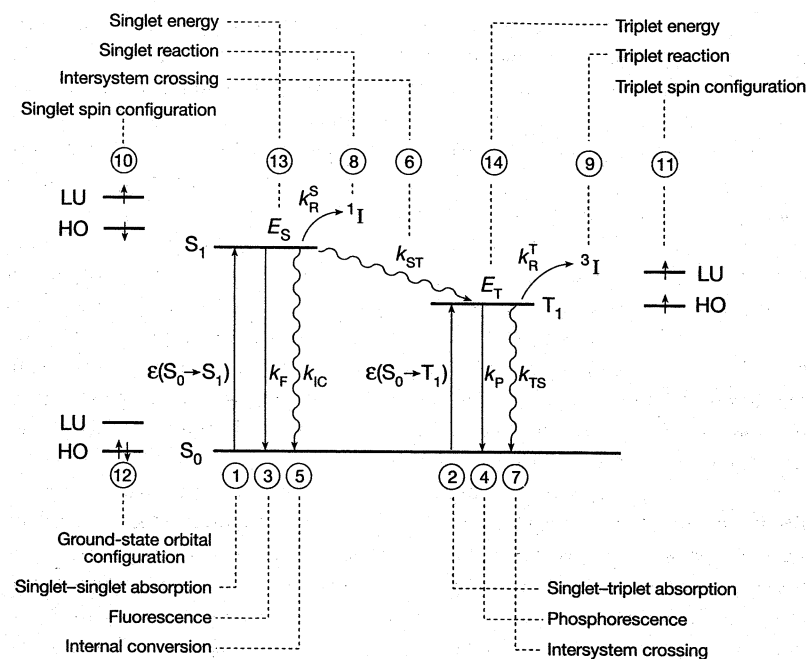


Figure 1.1 (a) An example of a primary photochemical $*R \rightarrow I(\text{RP})$ process, the “Type I” α -cleavage of ketones. (b) An example of a primary photochemical $*R \rightarrow I(\text{BR})$ process, the “Type II” intramolecular hydrogen abstraction of ketones with alkyl side chains.

Figure 1.1 presents two concrete exemplars of $*R \rightarrow I(\text{D})$ primary photochemical processes. In the first example, the Norrish Type I reaction, $*R$ undergoes an α -cleavage of the C—C bond of the C=O function to produce a radical pair, I(RP). In the second example, the Norrish Type II reaction, $*R$ undergoes an intramolecular hydrogen abstraction to produce a biradical, I(BR). These two types of $*R \rightarrow I(\text{D})$ primary photochemical processes are very common and provide excellent exemplars for the analysis of the photochemical primary processes of a wide range of organic molecules.

1.12 State Energy Diagrams: Electronic and Spin Isomers

According to Scheme 1.3, our exemplar paradigm of organic photochemistry, there are three important molecular states, $R(S_0)$, $*R(S_1)$, and $*R(T_1)$, that must always be considered when starting an analysis of a photochemical reaction involving organic molecules. A *state energy diagram* (Scheme 1.4) provides a compact working exemplar for displaying the relative energies and keeping track of the ground state (S_0), the lowest-energy excited singlet state (S_1), and the lowest-energy triplet state (T_1) of an organic molecule (where E_S is the energy of S_1 and E_T is the energy of T_1). The electronic configurations of the S_0 , S_1 , and T_1 states are also shown. Higher-energy singlet states (S_2 , S_3 , etc.) and higher-energy triplet states (T_2 , T_3 , etc.) can also be included as desired, but need not be explicitly included in the working state diagram, because experience has shown that *excitation of these higher-energy excited states generally results in deactivation to S_1 and T_1 faster than any other measurable process* (Kasha’s



Scheme 1.4 The state energy diagram is a fundamental paradigm of modern molecular photochemistry. The intersystem-crossing rate constants k_{ST} and k_{TS} are sometimes referred to as k_{ISC} .

rule, Chapter 4). In a state energy diagram, the y -(vertical) coordinate represents the potential energy (PE) of the system. The x -(horizontal) coordinate has no physical meaning (it is *not* a reaction coordinate or potential energy surface). The lines representing the state energies of S_1 and T_1 are displaced for convenience and to avoid congestion. Thus, a state energy diagram shows the ranking of the energies of the S_0 , T_1 , and S_1 states and is most useful if actual values of these energies can be associated with the T_1 and S_1 states. How the energies of S_1 and T_1 are determined experimentally is described in Chapter 4.

State energy diagrams are sometimes referred to as Jablonski diagrams⁵ in honor of Aleksander Jablonski, a Polish physicist who used a schematic portrayal of the relative positions of the electronic and vibrational levels of R and $*R$ without any attempt to indicate the relative nuclear geometries. For simplicity, vibrational levels are omitted in this introduction to state energy diagrams. Vibrational levels, which are very important in determining the rates of photophysical processes, are introduced into state energy diagrams in Chapter 2.

In state energy diagrams, it is assumed that the equilibrium nuclear geometries of R and $*R$ are similar and that these geometries represent minima of R and $*R$. Since all

of the structures in the state energy diagram have the same composition (i.e., numbers and kinds of atoms) and the same constitution (i.e., atom connectivity) as S_0 , but are chemically different from S_0 , all of the states in the state diagram (S_0 , S_1 , and T_1) are formally isomers of S_0 and also isomers of each other!

What is the basis of the isomerism? The isomerism results from differences in the *electronic configurations* (*electronic isomers*) or in the *spin configurations* (*spin isomers*) between the displayed states. The S_n and T_n states are electronic isomers of each other. The differences in electronic isomers are due to differences in the orbital configurations (i.e., in the different occupancies of the HO or LU) or to differences in the electronic spin configurations of each state (i.e., $\uparrow\downarrow$ or $\uparrow\uparrow$). The S_n and T_n states are related to each other as *spin-electronic isomers*, that is, singlet spin configuration ($\uparrow\downarrow$) or triplet spin configuration ($\uparrow\uparrow$). In addition to the spin-electronic isomerism, the states in the state energy diagram may also be stereoisomers of one another (i.e., they may have the same constitutions and the same spin-electronic configurations, but different spatial arrangements of their atoms).

The state energy diagram provides a handy and useful way to organize and systematize the state electronic structures, the state electronic energies, and the dynamics of interstate transitions corresponding to *all possible* photophysical processes that interconnect S_0 , S_1 , and T_1 . Transitions between any two electronic states in the diagram correspond to the *possible* connections between the states indicated and may be radiative or radiationless processes. The *plausibility* and the *probability* of a transition between any two states, however, requires knowledge of specific molecular structures and reaction conditions, which can be varied at will by the experimenter. The photochemical processes are defined as transitions in the energy diagram that interconvert excited states with each other or that interconvert excited states *R with the ground-state *R . All possible photophysical transitions from S_1 and T_1 must be considered in an overall $^*R \rightarrow R$ photochemical analysis, since photophysical processes will, in principle, be competitive with the photochemical processes from these two key states. If the photophysical processes are very fast compared to the photochemical processes, the competing *photochemical* processes may be plausible, when considered as an isolated process, but will be inefficient and *improbable* because plausible competing photophysical processes occur at a faster rate.

As an exemplar, let us see how the state diagram describes the *possible* photophysical *radiative* processes (processes 1–4 in Scheme 1.4), which involve the absorption or emission of a photon.

1. The spin-allowed singlet–singlet absorption of photons ($S_0 + h\nu \rightarrow S_1$), characterized experimentally by an extinction coefficient $\epsilon(S_0 \rightarrow S_1)$.
2. The spin-forbidden singlet–triplet absorption of photons ($S_0 + h\nu \rightarrow T_1$), characterized experimentally by an extinction coefficient $\epsilon(S_0 \rightarrow T_1)$.
3. The spin-allowed singlet–singlet emission of photons ($S_1 \rightarrow S_0 + h\nu$), called *fluorescence*, characterized by a rate constant, k_F .
4. The spin-forbidden triplet–singlet emission of photons ($T_1 \rightarrow S_0 + h\nu$), called *phosphorescence*, characterized by a rate constant, k_P .

The *plausible* photophysical *radiationless* processes are processes 5–7 in Scheme 1.4:

5. The spin-allowed radiationless transitions between states of the same spin ($S_1 \rightarrow S_0 + \text{heat}$), called *internal conversion*, characterized by a rate constant, k_{IC} .
6. The spin-forbidden radiationless transitions between excited states of different spin ($S_1 \rightarrow T_1 + \text{heat}$), called *intersystem crossing*, characterized by a rate constant, k_{ST} .
7. The spin-forbidden radiationless transitions between the triplet and the ground state ($T_1 \rightarrow S_0 + \text{heat}$), also called intersystem crossing, characterized by a rate constant, k_{TS} .

All of the structures in the state energy diagram refer to a single fixed equilibrium (minimum) nuclear geometry of R ; the geometry of *R is assumed to be very similar to that of R in the state energy diagram. As a useful extension of the state energy diagram, *primary photochemical processes* can be defined as transitions from an electronically excited state $^*R(S_1$ or $T_1)$ that yield molecular structures of different constitution or geometry from that of *R . These chemically different molecular structures are the reactive intermediates I of Schemes 1.1–1.3 and are produced by either process 8 or 9 in Scheme 1.4:

8. A photochemical reaction from S_1 to produce a reactive intermediate, $S_1 \rightarrow ^1I$, called a *primary photochemical reaction*, characterized by a rate constant, k_R^S .
9. A photochemical reaction from T_1 to produce a reactive intermediate, $T_1 \rightarrow ^3I$, also called a primary photochemical reaction, characterized by a rate constant, k_R^T .

The final, isolated product of a photochemical process results from the thermal chemistry of I under the reaction conditions. The thermal $I \rightarrow P$ processes are called *secondary thermal reactions* and are expected to occur in exactly the same manner as when the reactive intermediate $I(D)$ is produced by a ground-state thermolysis. Although not a photochemical process, an understanding of the $I \rightarrow P$ pathway that occurs completely in a ground state is crucial, however, in order to be able to completely describe the overall process $R + h\nu \rightarrow P$. A more complete description of the $^*R \rightarrow P$ process is provided by the working paradigm of a *potential energy surface*, which is described qualitatively in the next sections and in detail in Chapters 3 and 6.

In order to determine which of the *plausible* processes are most *probable* from S_1 or T_1 , we need information on the *relative rates* of all of the plausible photochemical and photophysical processes that compete for deactivation of these states. The values of these rates are available if the *rate constants* (k) for the various processes shown in the energy diagram of Scheme 1.4 are known or can be estimated from experiment, via an appeal to exemplars, or through computation. The relative rates of the transitions from a given state determine the probability of the various plausible processes that can occur from the state. These relative rates depend on a number of structural and energetic

factors that are discussed in Chapters 2–6. At this stage, the exemplar working paradigm is incomplete, since for simplicity we have not explicitly considered other possible, but less common, pathways of Scheme 1.1, such as $*R \rightarrow F \rightarrow P$ or $*R \rightarrow (*I, *P) \rightarrow P$. These possibilities are described in Chapters 4–6.

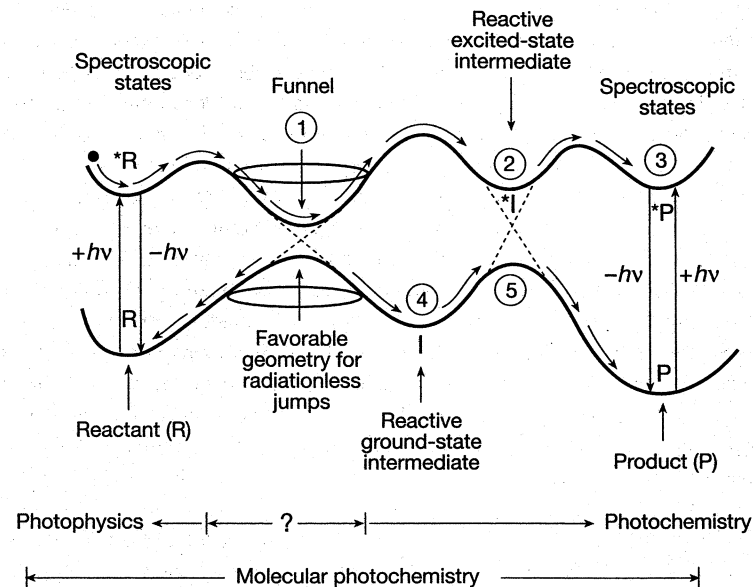
1.13 An Energy Surface Description of Molecular Photochemistry

In proceeding from the state energy diagram (that assumes a fixed nuclear geometry of R) to a complete analysis of a photochemical reaction (that creates a different nuclear geometry than that of R to first form I and then proceed to P), it is necessary to keep track of a number of structures, energies, and dynamics of transitions. Keeping track of all of these features of a photochemical reaction involves a complicated energetic, structural, and dynamic bookkeeping that is nicely handled by the paradigms associated with *potential energy curves and surfaces* (which are discussed in detail in Chapters 3 and 6). For now, we preview how the paradigm of energy surfaces handles the problem of simultaneously integrating the structure, energetics, and transition dynamics involved in photochemical and photophysical processes.

A potential energy (PE) surface displays the PE of a molecular system (the y -coordinate) versus the varying molecular structure of the system (the x -coordinate). The *lowest PE path* along a given potential energy surface is called the *reaction coordinate*. Strictly speaking, PE surfaces are multidimensional mathematical objects that are difficult to visualize. However, as a reasonable “zero-order” (i.e., working) approximation to an energy surface, we can use two-dimensional (2D) “potential energy curves”; for simplicity we use the term “energy surface” to describe these curves.

A PE curve extends the concept of a state energy diagram to describe how the PE of the states of a system changes as the nuclear geometry of $*R$ changes from one that is very similar to that of R to one that begins to resemble the geometry of the possible structures (e.g., I) involved in the photochemical transformation of $*R \rightarrow I \rightarrow P$. Consider the *hypothetical* example of the energy surfaces of the ground and excited states shown in Scheme 1.5. For simplicity, both surfaces are assumed to be singlet states. This exemplar energy surface is intended to display important common features of photochemical reactions but is not representative of any particular class of photoreactions. Whereas in the state energy diagram a nuclear geometry similar to that of the ground state (R) is assumed for all of the structures considered, each point on the PE curve represents a different nuclear geometry (specified on the x -axis) and an associated PE (specified on the y -axis). For a given nuclear configuration, the PE of a molecule is determined mainly by its electronic orbital configuration and its spin configuration.

As an exemplar, the lower-energy curve shown in Scheme 1.5 corresponds to the *reaction coordinate* (the lowest-potential-energy path) for the hypothetical *thermal* transformation $R \rightarrow P$. When more than one energy surface is involved, for simplicity, we assume that the reaction coordinate that refers to the pathway involving the



Scheme 1.5 Schematic representation of a ground-state (R) and excited-state ($*R$) energy surface. The arrows on the surface indicate the motion of a point representing a molecule whose nuclear geometry is moving along the reaction coordinate from left to right. The “?” indicates a “twilight zone” region where the distinction between photochemistry and photophysics is fuzzy.

ground surface starting from R is the same reaction coordinate that $*R$ follows. In general, however, the lowest-energy pathway for the ground-state transformation for the $R \rightarrow P$ process need not be the lowest-energy pathway from $*R \rightarrow P$. In Chapter 6, we discuss the theory of photochemical reactions, which will make it possible to qualitatively predict the reaction coordinates of excited-state reactions.

Scheme 1.5 shows hypothetical surfaces for an overall reaction $*R \rightarrow P$ for two different starting electronic configurations, a ground-state R and an excited-state $*R$. The lower-energy surface is called the *ground-state electronic surface*, and the higher-energy surface is called an *excited-state electronic surface*. Any point, r , of interest on either surface is a *representative point* of the PE (the y -axis) of the system for each nuclear geometry along the reaction coordinate (the x -axis). In this way, we can envision photophysical and photochemical processes in terms of the *motion* of a representative point on a PE curve, where each representative point corresponds to the energy of a specific nuclear configuration on the $R \rightarrow P$ pathway for one surface or the other. Starting from R, we can track the representative point r starting from R and imagine the trajectory of r moving along the excited surface or along the ground surface (propelled along the reaction coordinate by collisions with other molecules in the environment).

The representative point of an electronically excited molecule *R spends its time on either the excited or ground surface on the way from $^*R \rightarrow P$, except for the short periods of time when it finds a "funnel" (F) between the excited- and ground-state surface through which the representative point can "jump" from one surface to the other (the time scales for these jumps are very short for singlet states). To the extent that these hypothetical surfaces are valid, they make it possible to visualize or map *all plausible pathways* for the $^*R \rightarrow P$ transformation. Now, we consider some of the *a priori* plausible pathways for the electronically excited-state *R based on the nuclear-geometry changes that are mapped out by the two curves in Scheme 1.5.

First, consider the important topological (qualitative) features of the two hypothetical surfaces shown in Scheme 1.5. These features include the nuclear geometries for the maxima and minima on each surface, the nuclear geometries for which the surfaces are far apart in energy, the relative disposition of the maxima and minima to each other, and the geometries for which two surfaces come close to one another in energy. We focus on the following important features of the maxima and minima of the two surfaces:

1. *Spectroscopic (Franck-Condon) Minima.* The *absorption* of a photon (the $R + h\nu \rightarrow ^*R$ step) involves a jump from a minimum in the ground state (e.g., R or P) to a minimum on the excited surface (e.g., *R or *P). The *emission* of a photon involves a jump from a minimum on the excited-state surface to a minimum on the ground-state surface (e.g., $^*R \rightarrow R + h\nu$ or $^*P \rightarrow P + h\nu$). In Chapters 3 and 4, we will see that radiative jumps occur with the highest probability between surfaces for which there is a minimum and similar nuclear geometry in *both* the excited- and ground-state surfaces. Such minima are called "spectroscopic" or "Franck-Condon" minima. Small maxima (energy barriers of a few kilocalories per mole) may separate such spectroscopic minima from other regions of the PE surfaces, as shown on the left in Scheme 1.5. If the barriers are small, thermal energy from collisions with neighboring molecules will be sufficient to propel the representative point "to the right" of the energy surface toward region 1. If the barriers are high, then the representative point will be "trapped" in the excited-state minimum for *R until the point returns to R by either emission of a photon (fluorescence) or radiationless deactivation (internal conversion).
2. *Surface-Crossing Minima.* Excited energy surfaces possess minima in energy corresponding to excited-state energy surface crossings with lower-energy surfaces. Crossings of this type, depending on the available electronic interactions, may be true or weakly avoided crossings (the dotted lines in region 1 of Scheme 1.5) or may be strongly avoided crossings (the dotted lines in region 2 of Scheme 1.5). These crossings are described in detail in Chapter 6. If the representative point approaches a weakly avoided crossing, a very fast and therefore probable transition to the ground state will occur. When very fast transitions occur from the excited to the ground surface, a "funnel" is said to exist on the excited surface (region 1). In Chapter 6, we will see that passage

through such funnels can occur on the fastest time scales possible. In addition, we see why such funnels are given the special name of "conical intersections."

3. *Ground-State Maxima Due to Surface Crossings.* Barriers that exist on the ground-state energy surface can often be viewed as having an approximate surface-crossing origin before a weak electronic interaction is taken into account. A surface crossing or a weakly avoided crossing leads to the same result; namely, the excited surface comes close in energy to the ground-state surface at some geometry along the reaction coordinate. Weakly avoided surface crossings may be identified with large barriers along the reaction coordinate in the ground state (excited-state region 1), and strongly avoided surface crossings may be identified with low barriers along the reaction coordinate in the ground state (excited-state region 2). These crossings are described in detail in Chapter 6.

The $R + h\nu \rightarrow ^*R$ process places the system on the excited-state surface, as an electron jumps from a HO to a LU and the electron configuration of negative charges due to the electrons changes "instantaneously" from that of R to that of *R . Consequently, the positively charged nuclei feel a different negative electrical force field whose direction and magnitude are given by the shape (i.e., the gradient) of the excited surface (*R) and no longer by the ground state (R). The new force on the nuclei is due to the different configuration of electrons for *R (i.e., one electron in the HO and one in the LU) compared to R (i.e., two electrons in the HO and none in the LU). The new electrical forces resulting from the HO \rightarrow LU electronic jump cause the nuclei to rearrange to better accommodate the new electronic distribution. The impulse of the newly created electronic distribution causes the nuclei to move, generating kinetic energy of the nuclei (kinetic energy generated in this way is called vibrational energy), which is rapidly transferred intramolecularly and then intermolecularly to the surrounding solvent so that *R reaches the minimum vibrational energy in a few picoseconds (ps). The rates of these vibrational energy-transfer processes are described in Chapter 3 and Chapter 5.

The motion of a representative point, r , on a PE surface completely controls the nuclear motion of molecules, except for regions of the surface that come close to one another. When two surfaces do happen to come close together, each surface has a chance to "compete" for control of the motion of the representative point and, therefore, the control of the nuclear motion of the reacting system. In such regions, the nuclear system is "confused" as to which surface will control its motion.

Let us follow some possible trajectories of a representative point along the energy surfaces of Scheme 1.5. Begin with R on the ground surface (the spectroscopic minimum at the bottom left of Scheme 1.5). Absorption of a photon is extremely fast relative to vibrational motion, and therefore the representative point makes a "vertical jump" (with no change in the nuclear geometry of R) from the ground (R) to the excited-state surface to produce *R , which is assumed to be formed in a relatively shallow energy spectroscopic (Franck-Condon) minimum. A radiative transition is possible for *R , which can emit a photon of fluorescence and return to

the ground state (R). A radiationless path that moves the system toward the structure of P is also possible: As a result of thermal collisions with surrounding molecules, the representative point r corresponding to *R may overcome the small barrier along the excited surface and proceed to region 1, which happens in this hypothetical example to be a weakly avoided "crossing" of the excited- and ground-state surfaces. Such a situation is highly favorable for a very rapid jump from the excited to the ground surface (we explain why this occurs in Chapters 3 and 6), so that such regions on the excited state serve as "funnels" (F), which can take the representative point from the excited to the ground-state surface. These funnels are the same species (F) first encountered in the $^*R \rightarrow F$ processes of Scheme 1.1.

After reaching region 1, the representative point r has two options. First, the point may jump to the ground surface and "spill" into the R minimum (resulting in a net "photophysical" cycle, $R + h\nu \rightarrow ^*R \rightarrow F \rightarrow R$). These jumps are *internal conversions*, since the initial and final states are both singlet states. Internal conversion from $^*R \rightarrow R$ occurs inefficiently when there is a large gap separating the two states, as is the case near region 2 (the rules concerning the factors controlling the rates and efficiencies of internal conversions are explained in Chapter 5), and becomes more and more rapid as the gap between the states undergoing internal conversion decreases.

In the second option, the representative point may jump from region 1 of the *R surface to the right of the maximum on the ground surface and form the reactive intermediate I. Such jumps correspond to *primary photochemical processes* (i.e., $^*R \rightarrow I$ transitions). Since I is a reactive intermediate, it may live long enough to achieve thermal activation and proceed over the barrier (region 5 in Scheme 1.5) to yield the product P. For the pathway $R^* \rightarrow (1) \rightarrow (4) \rightarrow (5) \rightarrow P$, the nuclear motion is controlled by the excited-state surface for part of the reaction, $^*R \rightarrow (1)$, and by the ground-state surface, $(4) \rightarrow (5) \rightarrow P$, for another part of the reaction. This situation, although hypothetical in the example given, is typical of many photoreactions, as described in Chapter 6.

Because of the rapid rate of passing through the funnel (F) to the ground-state surface, only a few, if any, *R molecules moving on the excited surface will be able to gather enough thermal energy and proceed to region 2 of the excited surface, especially if there is a significant barrier for proceeding to *I . The latter is a minimum on the excited surface that corresponds to an *electronically excited reactive intermediate* *I . Note that unlike the weakly avoided surface crossings of region 1, *I is separated from a maximum ground state by a relatively large amount of energy. This sort of minimum-maximum/excited-surface-ground-surface correspondence is a signature of a strongly avoided surface crossing.

In some rare cases, the representative point may make it from region 2 and pass over an energy barrier to region 3, which possesses a minimum that corresponds to *P , an excited state of the product (P). When *I is formed, a true photoreaction has occurred, since a reactive intermediate (I) and its excited state (*I) possess a nuclear geometry that is quite distinct from that of R. Note that the minimum corresponding to *P on the excited surface possesses a corresponding minimum on the ground surface. This means that the nuclear geometries of *P and P are similar, as is the case for *R

and R on the right side of Scheme 1.5. The representative point in region 3 may jump to the ground state with the emission of a photon (fluorescence) or with the release of heat (internal conversion).

As a rule, the absorption and emission of light occur near spectroscopic minima corresponding to the nuclear geometry of the reactants and products. (This rule, called the *Franck-Condon principle*, is discussed in Chapter 4.) Thus, there is both a radiative ($^*R \rightarrow R + h\nu$) and a radiationless ($^*R \rightarrow F \rightarrow R$) pathway for *R to return to R. Pathways that return the system back to R after the absorption of light are called *photophysical* pathways and are of great importance because they generally compete with the *photochemical* pathways that carry *R to I and eventually to P. It is also possible that *R may proceed to an electronically excited *I and *P , although this pathway (called an *adiabatic photoreaction*) is rarely found. Thus, these processes are considered possible, but not plausible, except in special circumstances.

Although Scheme 1.5 represents an arbitrary and hypothetical overall photochemical reaction ($R + h\nu \rightarrow P$), the pathways and processes shown represent an exemplar for most of the important photochemical and photophysical processes and allow the following generalizations to be made based on considerable theoretical and experimental experience:

1. Absorption ($R + h\nu \rightarrow ^*R$) and emission ($^*R \rightarrow R + h\nu$ and $^*P \rightarrow P + h\nu$) of photons tend to occur at nuclear geometries corresponding to *spectroscopic minima* in both the ground and the excited surface.
2. Radiationless jumps from one surface to another are most probable for nuclear geometries at which two surfaces, a minimum and a maximum, come close together in energy ($^*R \rightarrow R$ and $^*R \rightarrow I$).
3. The location and heights of energy barriers on *both* the excited- and ground-state surfaces may determine the specific pathway of a photoreaction.
4. Some minima on excited surfaces (e.g., funnels, F) may not be readily detected by conventional absorption and emission techniques.
5. The course of a photoreaction depends on competing photophysical, as well as photochemical, processes.

In Chapter 3, we explain how to use PE curves to describe photochemical and photophysical transitions, and then apply this knowledge to many situations in the subsequent chapters.

1.14 Structure, Energy, and Time: Molecular-Level Benchmarks and Calibration Points of Photochemical Processes

The most powerful paradigms in all of chemistry are derived from the representation of molecules as particles possessing various levels of internal structure (i.e., atoms, nuclei, electrons, and spins). Both a qualitative and a quantitative appreciation of molecular dimensions, molecular dynamics, and molecular energy are important for

visualizing events and estimating their rates at the electronic and molecular levels. An understanding of the sizes of molecules and the time and energy required for electrons and nuclei to move in space is at the heart of mechanistic descriptions of molecular and spectroscopic phenomena. The ability to achieve a transformation at the molecular level depends on the energy of the initial state, the energy of the final state, the amount of thermal energy available to do work to cause the transition, and the time required to execute the transformation relative to the interactions (forces) that drive the structural changes of interest. Intuitively, the rate of the transformation depends on the efficiency of getting energy into the correct modes or degrees of freedom that cause a motion that can change the structure in the appropriate fashion.

In order to calibrate the energy, distance, and time scales, we now consider some benchmark values of energy and time of great importance to photochemistry.

1.15 Calibration Points and Numerical Benchmarks for Molecular Energetics

Organic chemists are accustomed to counting molecules and using the mole and Avogadro's number (6.02×10^{23}) as a benchmark for the number of molecules contained in 1 mole of molecules. The measurable mass of a pure molecular substance (in grams, g) can be translated into the number of moles of the substance divided by the molecule's molecular weight (in grams per mole, g mol^{-1}).

Photochemists, however, are interested in counting not only molecules but also the number of photons in a light source (the intensity of the light source is the number of photons emitted per second at a specific wavelength, λ). If we consider the photon as a "massless reagent," then the intensity of a light that is absorbed from a source to produce *R in a given volume is related to the concentration of molecules R in a solution. The number of photons absorbed, by a given concentration of molecules through a given path length, is a measure of the "cross section" for absorption (at a given wavelength) that a molecule presents to a stream of passing photons corresponding to the wavelength of absorption (Chapter 4). The number of molecules of I or P produced per photon absorbed is called the *quantum yield* (Φ) of the formation of a reactive intermediate (I) or a product (P).

We now try to understand some of the quantities that are important in all chemical transformations but which are particularly important in photochemical transformations. In this section we consider some *calibration points and numerical benchmarks for molecular and photonic energetics*, and in Section 1.16, we consider some calibration points for molecular and photonic sizes and dynamics.

In general, in photochemistry we are concerned with the *difference in energy of the energy gap*, (ΔE), *between states of a molecule* (Eq. 1.1), rather than the absolute energy of a state.

$$\Delta E = |E_2 - E_1| \quad \text{The energy gap between } E_2 \text{ and } E_1 \quad (1.1)$$

Absorption of a photon by a molecule ($R + h\nu \rightarrow ^*R$) transforms light energy (a photon, $h\nu$) into the electronic excitation energy (*) of a molecule. The photon uses its energy to do work by changing the structure of the orbiting electrons, or vibrating nuclei, or "precessing spins" of a molecule (see Section 2.28). The absorption of light not only provides the molecule with energy that it can employ to make or break chemical bonds but also changes the electronic configuration, and therefore the electronic distribution about the nuclei. The change in the electronic configuration generally promotes a change in the configuration of the positively charged nuclei in response to the change in the electronic distribution. The change in electronic and nuclear configuration may also assist in changing the electron spin configuration.

The energy required to produce an electronically excited state ($R + h\nu \rightarrow ^*R$) is obtained by inspecting the absorption or the emission spectrum of the molecule in question (see Chapter 4), as well as applying Einstein's *resonance condition* for the absorption of light (Eq. 1.2):

$$\Delta E = |E_2 - E_1| = |E_2(^*R) - E_1(R)| = h\nu = hc/\lambda \quad (1.2)$$

where h is Planck's constant ($1.58 \times 10^{-34} \text{ cal s} = 1.58 \times 10^{-37} \text{ kcal s}$), ν is the frequency (commonly given in units of $\text{s}^{-1} = \text{Hz}$), λ is the wavelength at which absorption occurs (commonly given in units of nanometers, nm), c is the speed of light ($3 \times 10^8 \text{ cm s}^{-1}$), and E_2 and E_1 are the energies of a molecule in an excited (*R) and an initial state (R), respectively.

Equation 1.2 is fundamentally important to spectroscopy and photochemistry, since it relates the energy gap (ΔE) between two states to measurable properties, namely, the frequency (ν) and the wavelength (λ) of an absorbed photon. Knowing the absolute energies, E_2 and E_1 , is not required in these kinds of energy analyses, since *it is the difference in energy between the two states that is required when applying Eq. 1.2*.

In the energy diagram of Scheme 1.4, the two most important values of ΔE are the energy gap between S_1 and S_0 (called the singlet energy, E_S) and the energy gap between T_1 and S_0 (called the triplet energy, E_T). These energies reflect the available energy that can serve as a driving force for these two states to do work on the making and breaking of bonds in photochemical processes. Both E_S and E_T correspond to excess electronic energy that can be converted into free energy to drive bond making and breaking in primary photochemical processes. In Chapter 7, for example, the values of E_S and E_T play critical roles in photoinduced electron- and energy-transfer processes. E_S and E_T are similarly important in overcoming thermodynamic endothermicity in bond-breaking processes.

Since photochemistry is concerned with the making and breaking of chemical bonds after the absorption of a photon, it is useful to have calibration points and numerical benchmarks for the energy of absorbed photons and to compare these energies to the energies required to break bonds that commonly occur in organic molecules. It is also important to relate bond energies to the frequency (ν) and

wavelength (λ) of light. In Chapter 4, we develop a model of light as a photon that treats light as consisting of "particles" (or quanta) of energy. Just as a solvent molecule consists of a "field of particles" whose collisions with reactant molecules provide a source of activation energy for a reaction, a beam of light provides a "field of photons" whose collisions with reactant molecules cause the absorption of energy that can serve as activation energy for a reaction.

1.16 Counting Photons

How do photochemists count photons that are emitted from a light source or absorbed by a sample during a photoreaction? Equation 1.3, the second of Einstein's light-energy relationships, relates the energy of a *single* photon to the wavelength (or frequency) of light. Thus, we can use Eq. 1.3 to "count" the photons *emitted* if we know the energy (E) of the light source. Similarly, we can "count" the photons *absorbed* by a sample if we know the energy of the light absorbed by the sample. In other words, a mole of photons of light for a given wavelength (λ) or frequency (ν) corresponds to a definite energy (E), so that if we know the energy contained in the light source at a given ν (or λ), we can compute the number of photons of that ν (or λ) through Eq. 1.3. Since we will be dealing with E in kilocalories per mole, with λ in nanometers, and ν in hertz ($\text{Hz} = \text{s}^{-1}$), we need to use 1.58×10^{-37} kcal s for Planck's constant (h) and 3.00×10^{17} nm s^{-1} for the speed of light (c).

$$E = h\nu = hc/\lambda \quad \text{The energy of a single photon} \quad (1.3)$$

A mole ($N_0 = 6.02 \times 10^{23}$) of photons is called an *einstein* in honor of the intellectual father of the photon. (It is important to distinguish between Eq. 1.3, which relates the energy of a single photon to a light wave's frequency and wavelength, and Eq. 1.1, the resonance condition that relates the energy gap (ΔE) between two states and the frequency of the light wave that corresponds to a photon whose energy is exactly equal to ΔE .) According to Eq. 1.3, the energy contained by an arbitrary number of photons or by an einstein of photons depends on the wavelength (frequency) of the corresponding light wave, which leads directly to Eqs. 1.4a and b, where n is an arbitrary number of photons and N_0 is 1 mol of photons.

$$E = nh\nu = nh(c/\lambda) \quad \text{The energy of } n \text{ photons} \quad (1.4a)$$

$$E = N_0h\nu = N_0h(c/\lambda) \quad \text{The energy of } N_0 \text{ photons (an einstein)} \quad (1.4b)$$

The energy of 1 mol (N_0) of photons given by Eq. 1.4b provides a direct relationship between the amount of light energy absorbed by a system and the number of photons absorbed. Thus, by measuring the energy of light absorbed (E) and knowing the wavelength (or frequency) of the absorbed light, we have a way to count photons!

1.17 Computing the Energy of a Mole of Photons for Light of Wavelength λ and Frequency ν

By using Eq. 1.4b, the energy of 1 mol of photons in kilocalories per mole may be computed from the frequency associated with the photon (Eq. 1.5a), or the wavelength associated with the photon (Eq. 1.5b).

$$E (\text{kcal mol}^{-1}) = (9.52 \times 10^{-14} \text{ kcal mol}^{-1} \text{ s})\nu \quad (1.5a)$$

$$E (\text{kcal mol}^{-1}) = (2.86 \times 10^4 \text{ kcal mol}^{-1} \text{ nm})/\lambda \quad (1.5b)$$

The data in Table 1.1 show how the energy of 1 mol of photons (an einstein) is related to the corresponding wavelength of light (λ in nm) and frequency of light (ν in $\text{s}^{-1} = \text{Hz}$) for the range of wavelengths of greatest photochemical interest ($\lambda = 200\text{--}1000$ nm). These values were calculated using Eqs. 1.5a and b. Historically, because different energy units were used for investigating light in different regions of the electromagnetic spectrum, a number of different energy units are commonly used in both spectroscopy and photochemistry. Values of the energies corresponding to 1 mol of photons of varying ν or λ are commonly given in terms of kilocalories per mole (kcal mol^{-1}), kilojoules per mole (kJ mol^{-1}), reciprocal centimeters (cm^{-1}), and electronvolts (eV). For the most part, however, kilocalories per mole are used in this text, since this unit is commonly employed in chemistry and is associated with bond energies and reaction activation energies.

Table 1.1 Relationship among energy, wavelength, and frequency^a

Type of Radiation	Wavelength ($\lambda = \text{nm}$)	Energy $E = \text{kcal mol}^{-1}$	Frequency ($\nu = \text{Hz} = \text{s}^{-1}$)
Ultraviolet (UV)	200–400	140–70	1.5×10^{15} – 7.50×10^{14}
Violet	ca. 400	70	7.50×10^{14}
Green	ca. 500	60	6.00×10^{14}
Red	ca. 700	40	5.00×10^{14}
Near-Infrared (NIR)	ca. 1000	30	3.00×10^{14}

a. The violet–green–red portion of the spectrum (400–700 nm) corresponds to the visible portion of the spectrum. See Scheme 1.6 for a schematic representation of these data.

1.18 The Range of Photon Energies in the Electromagnetic Spectrum

The range of electromagnetic radiation extends from gamma (γ) rays (the high-frequency, short-wavelength limit) to radiofrequency (rf) waves (the low-frequency, long-wavelength limit). The highest-energy photon in this range corresponds to a γ ray (for $\lambda = 0.0001$ nm and $\nu = 3.0 \times 10^{21} \text{ s}^{-1}$, the energy of an einstein of γ -ray photons $\cong 3 \times 10^8 \text{ kcal mol}^{-1}$). The lowest-energy photons of interest to chemists

correspond to a rf wave (for $\lambda = 1 \times 10^{10}$ nm and $\nu = 3.0 \times 10^6$ s $^{-1}$, the energy of an einstein of radiowave photons $\cong 3 \times 10^{-6}$ kcal mol $^{-1}$). Thus, the range of energies corresponding to 1 mol of photons spans ~ 13 orders of magnitude, from 3×10^8 kcal mol $^{-1}$ for γ rays to 3×10^{-6} kcal mol $^{-1}$ for radio waves!

However, the range of wavelengths (and therefore of energies) of interest to the organic photochemist is just a tiny region of the electromagnetic spectrum, corresponding to ~ 200 – 1000 nm (143 – 30 kcal mol $^{-1}$). This range corresponds to the UV (200 – 400 nm), visible (vis, 400 – 700 nm), and NIR (700 – 1000 nm) regions of the electromagnetic spectrum. The cutoff at short wavelengths (200 nm $\cong 140$ kcal mol $^{-1}$) is determined by practical considerations such as the need for a transparent material (quartz or Pyrex glass) from which to construct photolysis vessels. The most transparent material commonly available is quartz, which becomes strongly absorbing at wavelengths shorter than 200 nm, thereby setting the practical short-wavelength cutoff for organic photochemical reactions at $\lambda > 200$ nm. The cutoff at long wavelengths (1000 nm $\cong 29$ kcal mol $^{-1}$) is somewhat arbitrary and corresponds to the longest practical wavelength for electronic excitation of organic molecules to produce *R. Light with wavelengths longer than 1000 nm tends to excite vibrations rather than electrons.

Equations 1.5a and b offer a convenient formula for the conversion of the wavelength of an electromagnetic wave into the energy (kcal) of 1 mol of photons. Thus, we can use Eq. 1.5a to convert an einstein (1 mol of photons) possessing a wavelength of 700 nm (red light) into its energy equivalent in kilocalories per mole as shown in Eq. 1.6a (Eq. $1.5a \times 6.02 \times 10^{23}$).

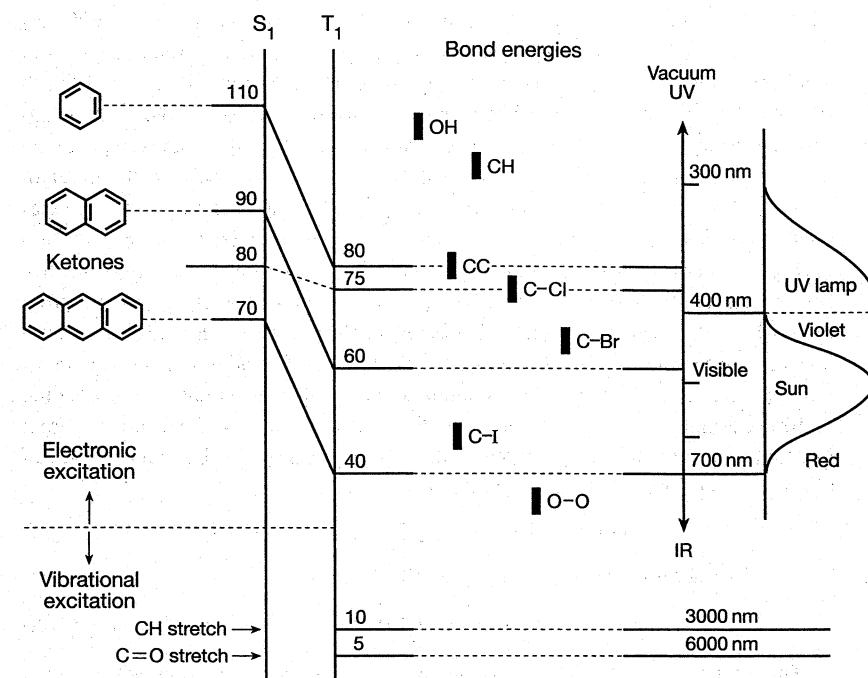
$$E(\text{kcal mol}^{-1} \text{ nm}) = 2.86 \times 10^4 / 700 \text{ nm} = 40.8 \text{ kcal mol}^{-1} \quad (1.6a)$$

Likewise an einstein of light possessing a wavelength of 200 nm (UV light) can be converted into its energy equivalent in kilocalories per mole, as shown in Eq. 1.6b (Eq. $1.5b \times 6.02 \times 10^{23}$).

$$E(\text{kcal mol}^{-1} \text{ nm}) = 2.86 \times 10^4 / 200 \text{ nm} = 143 \text{ kcal mol}^{-1} \quad (1.6b)$$

For comparison with photochemical excitation energies in the UV–vis region, some typical bond energies are shown in Scheme 1.6. The weakest single bonds commonly encountered in organic molecules have strengths of ~ 35 kcal mol $^{-1}$ (e.g., an O–O bond) and the strongest single bonds have strengths on the order of ~ 100 kcal mol $^{-1}$ (e.g., an O–H bond). A photon with a wavelength of ~ 820 nm carries sufficient energy (~ 35 kcal mol $^{-1}$) to break an O–O bond, whereas a photon with a wavelength of ~ 290 nm (~ 100 kcal mol $^{-1}$) would be required to break an O–H bond.

Does absorption of 250 nm light (114 kcal mol $^{-1}$) lead to the random rupture of any of the single bonds of an organic molecule? No, it does not. In fact, many photoreactions proceed with remarkable selectivity, even if UV light corresponding to photons of energy much greater than that of the strongest bonds of organic molecules



Scheme 1.6 A comparison of energies involved in photochemical reactions, bond energies, and the emission of the sun. Vibrational energies are shown for comparison at the bottom of the scheme. Energies of S₁ and T₁ are kcal mol $^{-1}$.

is absorbed. Indeed, only certain bonds are made or broken even when the energy per photon absorbed is higher than the energy of most of the individual bonds of a molecule. The reasons for this selectivity include a combination of the rapid deactivation of excess vibrational energy by electronically excited states, the localization of electronic excitation on certain atoms, and the specificity with which this electronic excitation is employed to make or break bonds. In other words, specific mechanisms exist for the conversion of electronic excitation energy into the nuclear motion that results in a net chemical reaction (e.g., *R → I). In this text, we seek to explain these mechanisms in order to understand photoreactions.

Light of wavelength in the range of 1000 – $10,000$ nm (3×10^{14} – 3×10^{13} s $^{-1}$, 29 – 2.9 kcal mol $^{-1}$) corresponds to photons in the near infra-red (NIR) and the infra-red (IR) region of the electromagnetic spectrum. Photons in this energy region excite fundamental and overtone vibrations (stretches and bends) of organic molecules. For example, a photon corresponding to $\lambda = 3000$ nm corresponds to an energy of ~ 10 kcal mol $^{-1}$ (i.e., the energy required to stretch a C–H bond) and a photon corresponding to $\lambda = 10,000$ nm corresponds to an energy of ~ 3 kcal mol $^{-1}$ (i.e., the energy required to stretch a C–C bond).

Light of wavelength in the region of 1×10^6 nm (1 cm, 3×10^9 s⁻¹, 0.029 kcal mol⁻¹) corresponds to photons in the microwave region of the electromagnetic spectrum, and light of wavelength in the region of 1×10^{10} nm (10 m, 3×10^6 s⁻¹, 0.0000029 kcal mol⁻¹) corresponds to photons in the rf region of the electromagnetic spectrum. The value of ΔE for electron and nuclear spin states depends on the size of the magnetic field in which they are placed. In fields on the order of $\sim 10,000$ G, typical electron spin energies correspond to microwave frequencies ($\sim 10^9$ – 10^{10} s⁻¹), which correspond to energies of $\sim 10^{-4}$ – 10^{-5} kcal mol⁻¹. In a magnetic field of $\sim 10,000$ G, typical nuclear spin energies correspond to radiowave frequencies ($\sim 10^6$ – 10^7 s⁻¹), which correspond, in turn, to energies on the order of $\sim 10^{-6}$ – 10^{-7} kcal mol⁻¹. Finally, it is worthwhile to relate the number of photons (n) and the moles of photons ($N = n/N_0$) that correspond to a given amount of light energy. As an exemplar, let us compute the number of photons corresponding to 100 kcal mol⁻¹ of energy for light of different wavelengths (frequencies). From Eq. 1.4a, the value of n (the number of photons) is given by Eq. 1.7 and the value of N (the moles of photons) is given by Eq. 1.8.

$$n \text{ (number of photons)} = E\lambda/hc \quad (1.7)$$

$$\begin{aligned} N \text{ (moles of photons)} &= n/N_0 = E\lambda/N_0hc \\ &= E\lambda/(2.86 \times 10^4 \text{ kcal mol}^{-1} \text{ nm}) \quad (1.8) \end{aligned}$$

The total energy of 1 mol of photons of 350 nm light is ~ 82 kcal, and the total energy of 2 mol of 700 nm light (the total energy of the photons is ~ 41 kcal mol⁻¹) is also ~ 82 kcal. However, absorption of one photon of 350 nm light instantaneously provides a single molecule with the equivalent of the entire 82 kcal; that is, this energy, in principle, could be employed to break a bond whose energy is ~ 82 kcal mol⁻¹ in a single molecule. Absorption of one photon of 700 nm light provides only the equivalent of ~ 41 kcal of energy to a single molecule. The simultaneous absorption of two photons with ordinary lamps by the same molecule is implausible (having two photons and a molecule together in the same space is analogous to the improbable simultaneous collision or reaction of three molecules), so it would be improbable to efficiently break bonds whose dissociation energy is ~ 82 kcal mol⁻¹ with 700 nm light, no matter how intense the beam. Thus, the total energy is not as important as the energy per photon; that is, an intense red lamp with a large total energy of photons would be useless to efficiently break 82-kcal-mol⁻¹ bonds, but a weak blue lamp could do the job. This relationship, in which a threshold energy is required to break a bond in an organic molecule, is completely analogous to the photoelectric effect (Chapter 4), for which there is a threshold of photon energy to remove an electron from a metal. Indeed, Einstein's interpretation of the photoelectric effect was the first interpretation of light in terms of quantized photons and was made in analogy to Planck's interpretation of the quantization of energy (Chapter 4).

The final calibration point in Table 1.1 is the relationship between the number of photons corresponding to 100 kcal mol⁻¹ of energy for different values of λ or ν . A beam of 0.1 nm (X-ray) light corresponding to this energy contains 3×10^{-4} mol of

photons; a beam of 286 nm light contains 1 mol of photons; a beam of 1000 nm (NIR) light contains 3.5 mol of photons; a beam of 10^8 nm (microwave) light contains 3.3×10^4 photons; and a beam of 10^{10} nm (radiowave) light contains 3.3×10^6 photons.

1.19 Calibration Points and Numerical Benchmarks for Molecular Dimensions and Time Scales

Chemists often think of molecules in terms of "ball-and-stick" models that are useful for evaluating many static (time-independent) properties of molecules, such as molecular geometries (bond lengths and bond angles), but microscopic particles (electrons, nuclei, and spins) are never at rest. Because of the uncertainty principle, nuclei undergo vibrational motions even at temperatures close to 0 K. In addition to vibrating nuclei, electrons in orbits and their electromagnetic spin moments execute characteristic zero-point motions. Indeed, even the electromagnetic field has a zero-point motion (which corresponds to the absence of photons in the field). In Chapter 3, we discuss physical and chemical radiationless transitions, such as the reorganization of the nuclear, electronic, or spin structure of a molecule, may be viewed as changes in zero-point motions. Understanding how this reorganization of structure over distances (on the order of the dimensions of molecules) occurs as a function of time is critical for an understanding of photophysical and photochemical processes. Thus, we need some numerical benchmarks for dimensions and time scales.

First, consider the dimensions of typical *chromophores*, the groups of atoms that are responsible for the absorption of light. The standard functional groups of organic chemistry (carbonyl, olefinic, enone, aromatic, etc.) correspond to simple chromophores. If we consider the typical atoms or groups for organic molecules involved in the absorption of light ($R + h\nu \rightarrow {}^*R$), the "size" of these groups is generally on the order of 2–6 Å (0.2–0.6 nm) and involves a relatively small number of connected atoms. A photon travels at the speed of light ($c = 3 \times 10^{10}$ cm s⁻¹ = 3×10^{17} nm s⁻¹). In other words, a photon travels 1 cm (10^7 nm) in 33×10^{-12} s (33 picoseconds, ps)!

If we associate the wavelength of light (λ) with the "length" or "dimension" (d) of a photon, then photons corresponding to blue light have a dimension on the order of 400 nm (Table 1.1). We may interpret the dimension or length of photons in terms of their ability to collide (interact) with a molecule. Thus, the time it takes a "blue" photon with a wavelength of 400 nm to pass a point is $\tau = d/c = 400 \text{ nm}/3 \times 10^{17} \text{ nm s}^{-1} \sim 10^{-15}$ s, one femtosecond (1 fs). Crudely, this corresponds to an order of magnitude for the "interaction time" available for the absorption of a photon by a molecule. If absorption does not occur in this time period, the photon zips past the chromophore and absorption does not occur.

Can an electron jump from one orbital to another or from one atom to another in this period, or does the photon zip by a molecule too rapidly? Let us use a concrete physical model, the Bohr atom, to estimate the time required for an electron to jump from the orbital of one atom to the orbital of an adjacent atom. The time it takes an

electron to make one complete circuit in the lowest-energy Bohr orbit of a hydrogen atom (the radius of the lowest-energy orbit of a hydrogen atom is ~ 0.05 nm or 0.5 Å) is $\sim 10^{15}$ Å s $^{-1}$. Thus, an electron may move on the order of 0.1 nm in 10^{-16} s and 1 Å in 10^{-15} s. Since 0.1 – 0.3 nm (1 – 3 Å) is on the order of common bond lengths of organic molecules, the orders of magnitude of the time scales of photon interaction and electron motion overlap.

For absorption of light to occur and to cause an electron to jump from one orbital to another (the $R + h\nu \rightarrow {}^*R$ process), the frequency of the light must match a possible frequency of motion of an electron; that is, the resonance condition of Eq. 1.1 ($\Delta E = h\nu$) must be satisfied. Thus, if the resonance condition is met, the energy of the photon may be absorbed and an electron may be excited. In the wave picture, when light is absorbed, energy is transferred from the oscillating electromagnetic field to the electrons, which are simultaneously sent into oscillation due to excitation. In Chapter 4, we discuss the quantum mechanical selection rules that make the absorption of light by a molecule plausible. The time period of $\sim 10^{-15}$ s sets an upper limit to the scale of chemical events, since no chemistry can occur before electron motion has occurred (i.e., before an electron has changed its position in space.) Thus, 10^{-15} s (1 fm) serves as a numerical benchmark time for the fastest events of chemical or photochemical interest. Remarkably, modern laser techniques make it possible to measure processes occurring on the time scale of 10^{-15} s. For his work in developing these techniques, Ahmed Zewail¹ was awarded the Nobel Prize in Chemistry in 1999.

Now, let us obtain a feeling for the magnitudes of the rates (or lifetimes of processes) that can occur during the lifetime of an excited state (*R), that is, the lifetimes of the processes shown in the state energy diagram of Scheme 1.4 and the energy surfaces of Scheme 1.5. What are the calibration points or benchmark rates of the slowest and fastest processes available to *R ? What limits the maximum lifetime of *R ?

*Radiative processes limit the maximum lifetimes of electronically excited states (*R).* In other words, *R cannot live longer than its natural radiative lifetime; if no other process deactivates *R , it will eventually emit a photon, and the ${}^*R \rightarrow R + h\nu$ process will take the excited molecule back to its ground state. Thus, any radiationless transition (photophysical or photochemical) from S_1 or T_1 must occur at a rate faster (in a time scale shorter) than the natural rate of emission, or emission will be the “default” deactivation process. That is, the molecule will deactivate by emitting a photon faster than undergoing a photophysical or photochemical event.

What, then, are the benchmark limits for the fastest and the slowest pure radiative processes? In Chapter 4, we explain that the largest fluorescence ($S_1 \rightarrow S_0 + h\nu_F$) rates of organic molecules are on the order of 10^9 s $^{-1}$ and the smallest fluorescence rate constants are on the order of 10^6 s $^{-1}$. This finding puts the time scale for competitive processes from S_1 in a time period shorter than the range of 10^{-6} – 10^{-9} s. In other words, a radiationless process that takes 10^{-5} s or longer from S_1 will be inefficient, even for the longest-lived S_1 states, and a radiationless process that takes $< 10^{-10}$ s will compete with even the fastest radiative rate.

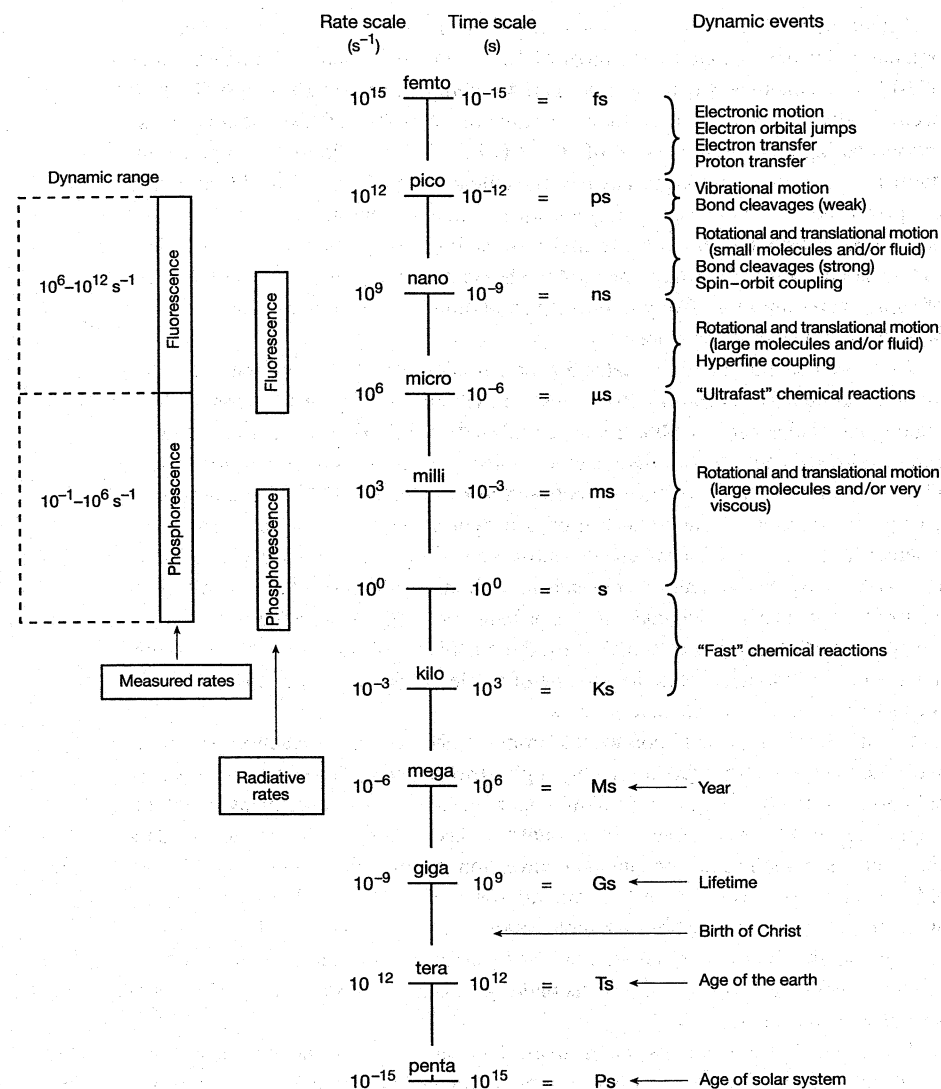
On the other hand, the largest phosphorescence ($T_1 \rightarrow S_0 + h\nu_P$) rate constants for organic molecules, k_P , are on the order of 10^3 s $^{-1}$ and the smallest are on the order of 10^{-2} s $^{-1}$. This means that the time scale for competitive processes from T_1 must occur in a period that is shorter than the range of 10^{-3} – 100 s. Thus, a radiationless process taking place in the period of 10^{-5} s (which is far too long to compete with fluorescence from S_1) or longer may be quite efficient for a T_1 state. The discussion in Chapter 4 shows that the values of k_F and k_P are related to the structure of *R , but for now we have some numerical benchmarks for the limits of the rates of processes that can occur competitively from S_1 or T_1 . All other factors being similar, photoreactions of triplet states are more likely to occur than photoreactions of singlet states, based on lifetime considerations alone.

Now, we compare the time scales for the emission of light to the time scales for the internal nuclear motions of molecules (i.e., vibrations). The fastest vibrations of organic molecules occur with a frequency of 10^{14} s $^{-1}$ (C–H stretching vibrations), and the slowest occur with a frequency of $\sim 10^{12}$ s $^{-1}$ (C–Cl stretching vibrations). This means that it takes somewhere between $\sim 10^{-12}$ and $\sim 10^{-14}$ s to complete a zero-point vibration for the bonded groups in typical organic molecules. Since the inherent lifetime of the fluorescence of most organic molecules falls in the range of 10^{-6} – 10^{-9} s, S_1 states undergo thousands to millions of vibrations before emitting a photon! The T_1 state, which takes 10^{-3} s or longer to emit, can execute $\sim 10^{11}$ – 10^{14} vibrations before emitting photons! Thus, there is plenty of time for nuclear motion to become equilibrated during the lifetime of an electronically excited molecule that is deactivated through a radiative process.

Electron spin plays an important role in many photochemical reaction pathways and is the key structural feature of all singlet–triplet interconversions, radiative or radiationless. In general, the rates of spin interconversions vary over many orders of magnitude but are slow relative to vibrational motions and relatively slow compared to electronic motions. The fastest spin interconversions for organic molecules composed of H and atoms of the elements of the first full row of the periodic table occur at a rate of $\sim 10^{12}$ s $^{-2}$. The slowest spin interconversions occur at a rate of $\sim 10^{-1}$ s $^{-1}$. The rates of spin interconversions are determined by an interaction between an electron’s spin motion and its orbital motion. This interaction is called spin–orbit coupling and is discussed in Chapter 3.

The rates of photoreactions (k_R , Scheme 1.4) vary over enormous ranges, from $\sim 10^{14}$ to $\sim 10^{-2}$ s $^{-1}$. The fastest reactions are limited by vibrational motion (passing through funnels) and electron transfer (ionization), and the slowest reactions are limited by the slowest phosphorescence rates. Whether the photoreaction occurs from S_1 or T_1 depends on both the rate constant (k_R) of the ${}^*R \rightarrow I$ process and Σk (where Σk represents the sum of the rates of all deactivating pathways of the excited state).

Scheme 1.7 compares the spread of time scales for events of photochemical interest, which range from $\sim 10^{-16}$ s ($1/10$ fm) to ~ 1 s, with the same spread of history going back into the past (from ~ 1 – 10^{16} s; 10^{16} s = 10 ps = 3×10^8 years). When compared in this manner, the history of a photoreaction passes through about as many “decades” of time as the history of the earth!



Scheme 1.7 Comparison of time scales.

1.20 Plan of the Text

Now that we have described a broad overview of modern molecular organic photochemistry, indicated the paradigm-and-exemplar approach that is adopted in the text, and reviewed some calibration points and benchmarks for thinking about molecular

organic photochemistry, we conclude this chapter with a review of the plan of the text.

The concepts of structure, energetics, and dynamics are crucial for understanding molecular photochemistry. To get started, in Chapter 1, we need to understand the structures of the species R, *R, I, and P in the paradigms of Schemes 1.1–1.3. Chapter 2 (Electronic, Nuclear, and Spin Configurations of Electronically Excited States) describes how we can visualize the electronic, vibrational, and electronic spin structures of R, *R, I, and P to a zero approximation. Each stable configuration of electrons and electron spins corresponds to a stable nuclear geometry and possesses an associated energy. The enumeration, classification, and visualization of molecular states of electronically excited molecules and their relative energies in terms of orbital configurations, nuclear configurations, and spin configurations are the topics of Chapter 2.

Knowing the plausible structures we will encounter in organic photochemistry, we consider next the problem of the transition of an initial structure into a different final structure, that is, processes, such as $R + h\nu \rightarrow *R$, $*R \rightarrow I$, $I \rightarrow P$, and $*R \rightarrow P$. These issues are addressed in Chapter 3 (Transitions between States: Photophysical Processes), which ties together the concepts of structure, dynamics, and energetics in terms of PE surfaces that allow an effective and concrete visualization of the plausible pathways by which molecular states may be interconverted.

Chapter 4 (Radiative Transitions between Electronic States) describes how radiative transitions (i.e., absorption, $R + h\nu \rightarrow *R$, and emission, $R \rightarrow R + h\nu$) can be understood and visualized, as well as how these radiative transitions are qualitatively and quantitatively related to molecular electronic structure and the structure of the electromagnetic field. Chapter 5 (Photophysical Radiationless Transitions) describes the mechanisms of radiationless transitions between excited states ($*R \rightarrow *R' + \text{heat}$) and each other and between excited and ground states ($*R \rightarrow R + \text{heat}$). The transitions considered in Chapters 4 and 5 are called "photophysical" because they occur between initial and final molecular states of very similar *nuclear geometry* and do not correspond to traditional chemical processes in which bonds are clearly broken or formed to create different nuclear configurations.

In Chapter 6 (A Qualitative Theory of Molecular Photochemistry), we consider radiationless transitions corresponding to chemical reactions, and we develop a theory and paradigms for the understanding and visualization of photochemical reactions in terms of energy surfaces. In addition, we describe the theoretical aspects of photochemical reactions after the electronically excited state (*R) has been formed by the absorption of a photon ($h\nu$). The *primary photochemical* processes $*R \rightarrow I$ and $*R \rightarrow F$ are considered in theoretical terms of orbital interactions and orbital (and state) correlation diagrams.

Chapter 7 (Energy and Electron Transfer) describes the relationship and scope of two closely related and very important processes involving *R. The common orbital interaction relationship between electron and electronic energy transfer is discussed, and a number of exemplars for each process are reviewed within the current paradigms.

To close this chapter, we reference a number of useful sources of information on organic photochemistry.^{5–13}

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