Chapter 8

Mechanistic Organic Photochemistry

8.1 Mechanisms

In this chapter we are concerned with the mechanisms of organic photochemical reactions. Two important features of mechanisms are the correlation of molecular structure with reactivity and the investigation and establishment of the details of the elementary steps involved in a photochemical process as \(*R\) proceeds to \(P\). We shall be concerned with the experimental tools for characterizing the structure of the reactive intermediates \(*R\) and \(I\) and the kinetics of the primary photochemical processes involved in a photoreaction.

The term “mechanism” is derived from the notion of a “machine” or “contrivance” and the term evokes the image of structures that operate in a cooperative and connected sense. Machines possess components, connections, and can be described in terms of 3D structures. If we saw the "guts" of a machine that is not operating (i.e., a machine in a "static" state), we might deduce from the configuration of the parts how the machine works; that is, we might imagine (or apply our mechanics paradigm), given the "static" forms and their perceived relationships, how the motions of the connected components could create the dynamics of the machine when it is operating. We could then attempt to visualize the forces capable of producing the dynamics of the machine, i.e., the motion sequences of the components in time. Next we might test our conjectures on the interplay of the parts of the machine by getting it to work and beholding the process of the machine in operation. We could then determine the actual forces which provide the energy to operate the machine. If at this stage everything seemed quite natural (i.e., the parts moved as expected and the machine operated as expected, thus fitting our paradigm), we could say that we "understand" the mechanism by which the machine operates.

A similar approach can be applied to the investigation of photochemical mechanisms by applying the paradigms of organic photochemistry to the study of organic photochemical mechanisms. The "components" of a mechanism are the significant structures along the reaction pathway, i.e., structures which correspond to maxima and minima on the ground
and/or excited state energy surfaces. The constitution of a mechanism refers to the relationships of the transition structures, one to another, i.e., how they are connected through elementary steps that consist of plausible radiative transitions, radiationless transitions, or chemical transformations. The "configuration" of a mechanism is the detailed energy surface pathway which is followed starting from an initial excited state to the isolated or detected product. Dynamics tell us how forces operating on transition structures determine the relative probabilities that a specific configuration or pathway will be followed. Thus, a "complete" photochemical mechanism must include a knowledge of (a) all significant transition structures along the reaction pathway, (b) the rate constants for converting one intermediate structure to its successor structure, and (c) the forces and interactions responsible for interconverting structures.

A conventional reaction mechanism for a thermally induced reaction is a paradigm for describing and analyzing a ground state chemical reaction as a finite sequence of elementary physical and chemical steps involving chemical structures which adequately accounts for the conversion of reactant structures (R) to product structures (P). A good chemical mechanism allows us to visualize the succession of key chemical structures (minima and maxima on the energy surface) involved along a chemical pathway and the forces and interactions that cause the transformation of the structures along the reaction pathway. We employ a similar paradigm to that used for ground state mechanisms for describing photochemical reaction mechanisms.

Scheme 8.1 is an exemplar for the most common photochemical reaction pathways followed by excited organic molecules, one involving primary photochemical process \( ^*R \rightarrow I \) (D), where I (D) is a radical pair (RP) or a diradical (DR). The significant chemical structures in this exemplar are R, \(^*R\), I and P. The significant elementary steps that connect these structures are indicated by the arrows in Scheme 8.1. One of the primary goals of mechanistic organic chemistry is the characterization of the structures \(^*R\) and I. A second primary goal of mechanistic organic chemistry is the characterization of the kinetics and efficiencies of each elementary step in Scheme 8.1. The kinetics of each elementary step can be characterized by an experimental rate constant \( k \), and the efficiencies of each elementary step can be characterized by an experimental quantum yield, \( \Phi \). The primary goal of this chapter is to describe the experimental methods and conceptual strategies for determining the mechanism of an overall photochemical reaction \(^*R + hv \rightarrow P\), with Scheme 8.1 as an exemplar. We seek to
answer the questions: (1) How does one experimentally characterize the structures *R and I?; (2) How are the rate constants, \( k_i \), of the elementary steps that characterize the primary photophysical processes of *R (\( k_D \)) and the photochemical processes of *R (\( k_{PP} \)) determined experimentally? (3) How are the efficiencies, \( \Phi_i \), of the photophysical and photochemical processes of *R determined experimentally?; (4) How are the rate constants, \( k_{SP} \), of the steps that characterize the secondary, thermal reactions of I determined experimentally?; (5) How are the efficiencies, \( \Phi_{sp} \), the steps that characterize the secondary, thermal reactions of I determined experimentally?; (6) How are the chemical structures of *R and I correlated with their reactivity and reactions? (7) What are the electronic and spin configurations of *R? (8) What are the photophysical processes from *R that compete with the *R \( \rightarrow \) I step?

Our tactics for obtaining the goals of this chapter will be to employ exemplar photochemical reactions to demonstrate questions such as 1-6 are answered. We shall also provide a range of experimental examples of the values of \( k_i \) and \( \Phi_i \) and discuss how they can be interpreted in terms of mechanism principles that correlate chemical structure with reactivity.
Scheme 8.1. An exemplar for an overall photochemical reaction from *R → P, which involves a *R → I(D) primary photochemical process.

In the context of the paradigms of organic photochemistry, establishing and understanding a photochemical mechanism corresponds to determining, to the best degree possible, of the molecular structures and the dynamics of transformations associated with the arrows in Scheme 8.1. Two concrete exemplars of the general Scheme 8.1 are given in Scheme 8.2 for the photolysis of two ketones, phenyl tert-butyl (1) which undergoes an α-cleavage (termed a Norrish Type I photochemical process) and butyrophenone (2) which undergoes an intramolecular hydrogen abstraction (termed a Norrish Type II photochemical process). The Type I reaction is typical of a *R → I(RP) process in which the intermediate I is a radical pair. The Type II reaction is typical of a *R → I(DR) process in which the intermediate I is a diradical. These two exemplars will typify all of the primary photochemical reactions of n,π* states and most of the primary photochemical reactions of π,π* triplets states. The secondary processes from I are the conventional reactions expected of radical pairs, diradicals and free radicals.

The reactions of S1(π,π*) states may be represented by a separate exemplar for 1,3-butadiene (3), given in Scheme 8.2. In the case of S1(π,π*) states, as discussed in Chapter 6, photochemical primary processes can be dominated by the zwitterionic character that is increased by twisting of C=C bonds along a reaction coordinate. Thus, in the exemplar of Scheme 8.2, we write the primary photochemical process as *R → I(Z) process, i.e., we consider reactions for which *R = S1(π,π*) to be plausibly associated with the formation of a zwitterionic reaction intermediate which then proceeds to product. As indicated in Chapter 6, the possibility of *R → F(AC, CI) → P processes must also be considered for reactions of S1(π,π*) states. These reactions fall into the domain of “concerted” or “intermediateless” photochemical reactions and will be considered separately at the end of this Chapter.
Scheme 8.2. An exemplar for an overall photochemical reaction from $^*R \rightarrow P$, which involves a $^*R \rightarrow I(Z)$ primary photochemical process.

An important aspect of the exemplars of Schemes 8.1 and 8.2 is that they contain mechanistic features which will serve as powerful guides for the experimental approach to establishing the mechanism of the vast array of known organic photochemical reactions.

### 8.2 Some philosophical comments on the fundamental nature of reaction mechanisms.

The student should be alerted to the fact that all reaction mechanisms are both provisional and incomplete. Mechanisms are provisional because one can never conclusively prove a statement with the inferential logic required in scientific inquiry. This lack of a definitive conclusion results from the obvious possibility that an alternate mechanism (possibly not yet thought of) may also be consistent with all known data. Mechanisms are incomplete because experimental data is incomplete and is constantly in various stages of refinement and expansion. Furthermore, there is a practical issue: it is impossible in principle and unnecessary in practice to write all of the physical and chemical steps of a mechanism that can describe an overall chemical or photochemical reaction. In writing a chemical mechanism we use our established paradigms to restrict the number of steps that are considered plausible or probable for a reaction sequence. The rules for these selections were outlines in Chapter 6. Thus, in mechanistic analysis we use the experience of past practitioners in the field to fast-track from numerous possible mechanisms towards a small plausible set. Rarely does that set consist of a unique mechanism. Further, the use of specific exemplars from the working paradigms may direct us towards the selection of the most effective set of experiments that can allow us to select from the set of most plausible mechanisms the most probable mechanism. The upgrade from the status of “probable” to a “proven” mechanism not really possible, since, as mentioned above, it is impossible to know if a new experiment in the future (perhaps utilizing a new
technique not yet invented) will lead to a failure of our mechanism to account for all known facts about the reaction in question. When scientists describe a mechanism as "proven" simply means that it accounts for all known observations for a given reaction at the current time, and usually that it has passed the test of a set of experiments designed to validate the mechanism. In this sense even a "proven" or better, “well established” mechanism may require revisions as new experimental facts are unveiled.

Creation of a standard mechanistic set

Since potential energy is a general property of all chemical systems, we might suppose that we can always describe the conversion of reactants to products in terms of the change in potential energy of the system as the reaction develops. In terms of potential energy surfaces, an analysis should include descriptions of all energy minima which correspond to the structures of reaction intermediates on the ground state surface (or to funnels on an excited state surface which lead to the ground-state surface) and all energy maxima which correspond to the structure of transition states. If possible, the electronic, nuclear, and spin structure of these minima and maxima (and of all important forces which cause structural interconversions) should be clearly identified. Although many mechanisms can be written a priori, we usually find that few (or occasionally only one) are consistent with the known relevant data and theories of chemistry at a given time. Our paradigms allow us to define a standard mechanistic set, which is selected to be analogous to the one under study. Data or theory which are integral to our paradigms is then sought to eliminate each of the members of the standard mechanistic set. After this elimination, three possibilities generally will result (see Scheme 8.3):
**Scheme 8.3:** Flow sheet of the steps involved in establishing a provisional mechanism. members a, b, c, ... represent complete, distinct mechanisms.

1. If every member but one is eliminated, that remaining member provides a provisional *working* mechanism.

2. If more than one member of the standard mechanistic set remains after the elimination, then more than one provisional working mechanism must be considered as validly describing the reaction.

3. If no members of the standard mechanistic set remain, then we must conclude that the reaction involves a "novel" or previously unencountered mechanistic pathway. We should modify our paradigm to accommodate this new knowledge.

We will generally assume that the detailed molecular structure of reactants (R) and products (P) in Schemes 8.1 and 8.2 can be fully established by conventional spectroscopic (NMR, IR, UV, X-Ray, Mass spectrometry) and/or chemical (method of synthesis) methods. The detailed structure of *R* can be established by spectroscopic and/or chemical methods which will be discussed in this Chapter. We note that R represents an ensemble of excited states resulting from direct excitation (R + hv → R) or from interconversions (*R → *R’) within the manifold of excited state surfaces; frequently the bond connectivity in *R* will be
similar to that in R although bond distances and angles can be expected to be different. While
*R may lead directly to the final products of reaction through funnels, in most cases the
mechanism involves one or more reaction intermediates, (I), as shown in scheme Schemes 8.1
and 8.2. These intermediates are normally equilibrated ground state species whose lifetime is
controlled by their intramolecular or intermolecular reactivity in secondary thermal reactions
expected from conventional ground state chemistry of reactive intermediates. As we shall
describe in this Chapter, modern time resolved spectroscopic techniques provide a powerful
means for the direct characterization of the structures and of the reaction kinetics of both *R
and I.

In order to eliminate a member of the standard mechanistic set from consideration, we
must establish a logical inconsistency between this possible mechanism and experimental data
or theoretical laws. For example, any acceptable mechanism should predict correctly the
observed products, including their stereochemistry if applicable. The observed reaction
kinetics provide us with another tool to discriminate among possible mechanisms. Possible
mechanisms are also required to obey energy, momentum and spin conservation laws.

Thus, in moving from a possible to a plausible mechanistic set of primary photochemical
reactions (*R → I), we inspect what is known (if anything) concerning the following criteria
for plausibility:

1. Reaction energetics of the *R → I step: only reactions that are close to being
exothermic are considered plausible since endothermic reactions will require passing through a
significant energy barrier along the reaction pathway and the primary photochemical step will
have to compete with photophysical deactivations of *R. This validity and scope of this
criterion will be discussed in detail in the next section.

2. Reaction kinetics of the photophysical (*R → I) and photophysical (*R → R) steps:
knowledge of or estimation of the rates of these steps will allow an estimation of plausibility of
photoreaction based on competition of competing photophysical pathways for deactivation of
*R.

3. Molecular structure of *R: knowledge of the electronic, geometric and spin
configurations of *R allows the listing of the plausible primary photochemical steps from the
paradigm of frontier molecular orbital interactions discussed in Chapter 6.
Then, after establishing a plausible set of *R → I primary photochemical processes, we may use an additional set of experiment methods to criteria to select from among plausible mechanisms the most probable one. Typically, these criteria will include (if not already established in the photochemical literature):

1. Spectroscopic characterization of the structure of *R and I.
2. Kinetic rate laws for the *R → I and I → P steps.
3. Labeling experiments to differentiate some of the members of the plausible set.
4. Structure-reactivity relationships
5. Trapping of the reactive intermediate I.
6. Quenching of electronically excited states (*R)

We shall describe exemplars which involve each of these criteria in this Chapter.

In addition to the above experimental criteria, computational methods for determining probable overall pathways of photochemical reactions are available and are becoming increasingly powerful with advances in computer performance and algorithms for computation.

### 8.3 Use of Kinetic Plausibility in Quantitative Mechanistic Analyses

From the above discussion, it is clear that in the overall *R → P reaction, the rate of the *R → I must be compared to the rate of other competing deactivation processes of *R. Thus, we the “kinetic plausibility” of the *R → I step is an important issue. The issue of kinetic feasibility can be formulated as: Can an excited molecule *R acquire sufficient activation energy during its lifetime so that the *R → I process occurs at a rate competitive with other modes of excited-state deactivation? The lifetime of *R, τ, is related to the overall rate of decay of *R, k, by Eq. 8.1.

\[ k_d(s^{-1}) = \frac{1}{\tau(s)} \]  

8.1

The rate, k, of an excited state reaction is can be expressed in terms of the Arrhenius expression for a single elemental step, Eq.8.2:

\[ k(s^{-1}) = A e^{-\frac{Ea}{RT}} = A \times 10^{-\frac{Ea}{2.3RT}} \]  

Eq. 8.2 relates the rate constant (k) for reaction at a given temperature to the activation energy (Ea) for reaction and a probability factor (pre-exponential factor) A. E_a is related to the
enthalpic activation energy ($\Delta H^\ddagger$) needed to reorganize the electronic structure of the reactant (*R) to produce a transition state which leads to I. A is related to the entropic activation energy ($\Delta S^\ddagger$) needed to reorganize the reactant structure to produce the transition state which leads to I. We have encountered the notion of an electronic reorganization and an entropic reorganization in the Golden Rule for radiationless transitions and for electron transfer. In the latter cases, the matrix element was a measure of the electronic coupling and can be associated with the A factor of Eq. 8.2 and electronic reorganization (frequency of crossing over a transition state barrier) and the Franck-Condon factor was a measure of the vibrational coupling which can be associated with the activation energy and enthalpic reorganization. As we have seen in Chapter 7, for cases involving highly polar or charged species, such as electron transfer reactions, the enthalpy changes in the solvent need to be considered.

Order of magnitude estimates of the value of $k_r$ may be made by using typical values of A in the range $10^{13}$-$10^{15}$ s$^{-1}$ for first order reactions which do not require much entropic reorganization and $10^6$-$10^8$ s$^{-1}$ for second order reactions (at 1 M of reagent reacting with *R). Table 8.1 lists the relationship of $k_r$ to $E_a$ at three temperatures: 77 K (-196 °C), 300 K (27°C) and 400 K (127°C) for A = $10^{15}$ s$^{-1}$ and A = $10^8$ s$^{-1}$. These values represent the fastest rates expected for unimolecular (A = $10^{15}$ s$^{-1}$) or bimolecular (A = $10^8$ s$^{-1}$) reactions.

Table 8.1

<table>
<thead>
<tr>
<th>T (K)</th>
<th>$A = 10^{12}$, $A = 10^8$</th>
<th>$A = 10^{15}$, $A = 10^8$</th>
<th>$A = 10^{15}$, $A = 10^8$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k$</td>
<td>$E_a$</td>
<td>$E_a$</td>
<td>$E_a$</td>
</tr>
<tr>
<td>---------</td>
<td>---------------------------</td>
<td>---------------------------</td>
<td>---------------------------</td>
</tr>
<tr>
<td>$10^{15}$</td>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$10^{12}$</td>
<td>2</td>
<td>4</td>
<td>5</td>
</tr>
<tr>
<td>$10^9$</td>
<td>3</td>
<td>12</td>
<td>16</td>
</tr>
<tr>
<td>$10^6$</td>
<td>4</td>
<td>16</td>
<td>22</td>
</tr>
<tr>
<td>$10^3$</td>
<td>5</td>
<td>21</td>
<td>27</td>
</tr>
<tr>
<td>$10^{-3}$</td>
<td>6</td>
<td>25</td>
<td>32</td>
</tr>
<tr>
<td>$10^{-6}$</td>
<td>7.5</td>
<td>29</td>
<td>38</td>
</tr>
<tr>
<td>$10^{-9}$</td>
<td>8.5</td>
<td>33</td>
<td>44</td>
</tr>
</tbody>
</table>

Units of k are s$^{-1}$; Units of $E_a$ are kcal/mol

Figure 8.1 shows a series of plots of $\log k$ versus the activation energies for several values of the pre-exponential factor (A) for reactions at 300 K, which is close to typical room
temperature. How do we use this information in determining kinetic plausibility of a *R → I process? Let us use the exemplar provided by the Norrish Type I reaction of tert-butyl phenyl ketone (pivalophenone), which undergoes the Norrish Type I reaction (Scheme 8.1, 1).1,2

![Graph](image_url)

**Figure 8.1:** Calculated rate constants at 300 K for various pre-exponential factors and variable activation energies.

Let us now consider our exemplar, pivalophenone (Scheme 8.1) to see how we can use kinetic data to obtain some feeling for the rates of reaction and deactivation of *R. The α-cleavage of 1 to produce a triplet radical pair is a primary photochemical process which occurs from its n,π* triplet state, i.e., *R(T₁, n,π*) → 3I(RP). The triplet lifetime, τ₂, has been determined experimentally to be ~100 ns at room temperature.2 Thus, from Eq. 8.1, k_r ~ 10⁷ s⁻¹. Acetophenone (CH₃COPh), which is stable towards α-cleavage, is a model for the photophysics of 1. The rate constant for triplet decay of CH₃COPh have been determined to be ca 10⁴ s⁻¹. Thus, we expect that for the chemical reaction of Equation 8.2 to contribute significantly to triplet decay (let’s assume that 1 % triplet decay is due to the Type I reaction). If we set a conservative lower limit of 10⁵ s⁻¹ for the rate constant for the Norrish Type I cleavage, then we calculate that the maximum activation energy is not higher than ~11
kcal/mol (either using Eq. 8.1 or from Figure 8.1). Experimentally the measured values are $A = 2 \times 10^{12} \text{s}^{-1}$ and $E_a = 7.3$ kcal/mol and the cleavage occurs with high quantum yield (i.e., much higher than the 0.01 value assumed as a low limit).

For bimolecular reactions interactions of excited states with stable molecules (M) we need to take into account the concentration of M. Equation 8.3 shows an example where a hypothetical excited reactant $^*R$ is quenched by molecule Q. By quenching we mean a general bimolecular deactivation of $^*R$ as the result of collisions with M.

$$R^* + Q \overset{k_q}{\longrightarrow} \text{quenching of } R^*$$

If the $[Q]$ is adjusted so that $[Q] \gg (^*R)$, then the decay of $^*R$ will follow pseudo-first order kinetics such that the lifetime of $^*R$ will be given by: $(\tau R)^{-1} = k_q[Q]$. Thus the plot of Figure 8.1 can still be employed to estimate the activation energies of bimolecular reactions provided we choose the line on the basis of the product $\log A[Q]$, rather than $\log A$.

Typical activation energies for "thermal reactions" which proceed at convenient rates (~ hours) near room temperature are of the order of 25-35 kcal/mole. For example, the ring opening of cyclobutene to butadiene (reaction exothermic by ~10 kcal/mole) requires an activation energy of 33 kcal/mole and possesses an A factor of $\sim 10^{13} \text{s}^{-1}$. At 300 K (near room temperature) the ring opening rate of cyclobutene is $\sim 10^{-10} \text{s}^{-1}$. (This corresponds to a half-life of hundreds of years!) On the other hand, the photochemical ring closure of 1,3-butadiene to cyclobutene (endothermic by 10 kcal/mole in the ground state) occurs with negligible activation energy and proceeds in $10^{-10} \text{s}$ or less corresponding to a rate of $10^{10} \text{s}^{-1}$ or greater! (Check recent femtosec experiments and add example)

Rate constants, $k$, depend on both enthalpic ($\Delta H^\ddagger$ or $E_a$) and entropic ($\Delta S^\ddagger$ or $A$) factors. Restriction of conformational freedom in reactants can increase the rate of reaction if the restriction also selectively favors the formation of the reaction transition state. This corresponds to an entropic enhancement of the rate constant for reaction, since the entropy change upon going from reactant to transition state is more positive (less ordering is required
to achieve the transition state). As an example of the information which is available from \( \text{Ea} \) and \( A \) but not available from \( k \), consider the data in Table 8.2 for the Norrish Type II hydrogen abstraction (shown for valerophenone in Scheme 8.1). As was the case for the Norrish Type I reaction, the Norrish Type II reaction usually occurs exclusively from \( {^*R(T_1)} \) in alkyl aryl ketones. The rate constants in Table 8.2 correspond to the \( {^*R \rightarrow I} \) reaction (Eq. 8.4). The three reactions of I (Eq. 8.5) reflect the secondary thermal chemistry (and dynamics) of the diradical I, not the triplet state, \( {^*R(T_1)} \). From Eq. 8.5 we see that there are actually \three\ reactions that can result from the \( {^*R \rightarrow I} \) primary photochemical reaction. Eq. 8.5a corresponds to the original Norrish Type II reaction, which is a fragmentation reaction of the diradical, I. In addition, the diradical undergoes both a cyclization reaction to form a cyclobutanol (Eq. 8.5b) and a disproportionation reaction (Eq. 8.5c). Eq. 8.5b has been termed the Yang reaction in honor of its discoverer.\(^3\)

\[
\text{Type II H-abstraction from the triplet state}
\]

\[
\text{Type II 1,4-biradical}
\]

\[
\text{typical lifetimes are}
\]

\[
\text{around 30-100 ns}
\]

\[
\text{Note that reaction path (c) is a chemical process that is similar to a photophysical process in that it returns \( {^*R} \) to \( R \). Thus, this pathway contributes to an inefficiency in the reaction because a photon has been used to generate \( {^*R} \), but by pathway 8.5c, \( R \) is regenerated. This}
\]

\[
(8.4)
\]

\[
(8.5)
\]
pathway is quite important in non-polar media. Reactions of the type shown in Eq. 8.5 are discussed in detail in Chapter 9. There is a variation in rate constant $k_r$ of a factor of ~60 (see Table 8.2) in proceeding from 1 ($k_r \sim 8 \times 10^6 \text{ s}^{-1}$) to 2 ($k_r \sim 1 \times 10^8 \text{ s}^{-1}$) to 3 ($k_r \sim 5 \times 10^8 \text{ s}^{-1}$). From the activation parameters it is seen that the increase in $k_r$ going from 1 to 2 to 3 is due mainly to a decrease in $E_a$; i.e., the A-factor is more or less constant ($10^{12}$) for the series. On the other hand in Table 8.2, the bicyclic ketone 14 undergoes reaction nearly 100 times faster than 2 (a secondary hydrogen is abstracted when both 2 and 14 react). The increase in $k$ on going from 2 to 14 is due mainly to an increase in the A-factor (from $10^{12}$ for 2 to $10^{13}$ for 14).

These results are reasonable when we identify A with $\Delta S^\ddagger$, the activation entropy. As A increases, $\Delta S^\ddagger$ becomes more positive, i.e., the reaction requires less reorganization. Ketones 1, 2, and 3 require similar organization on proceeding from the starting excited state to the transition state; therefore, $\Delta S^\ddagger$ (and A) should be similar. It is thus expected, and found, that the differences in $k$, result from differences in $E_a$ (primary hydrogen is abstracted slower than secondary hydrogen which, in turn, is abstracted slower than tertiary hydrogen). On the other hand, in comparing 2 and 14 the same type of hydrogen atom (secondary) is abstracted, so that comparable values of $E_a$ are expected. However, because of its structure, 14 is locked into a conformation particularly favorable for hydrogen abstraction. As a result, a smaller price in activation entropy must be paid (less organization required) to reach the transition state for hydrogen abstraction. This results in a more positive $\Delta S^\ddagger$ (larger A) for 14 than for 2 and, because of the comparable $E_a$ values, a larger value of $k$ for 14 than for 2.

Table 8.2
The A-factor for intermolecular hydrogen abstraction is typically $10^8$-$10^9 \text{ M}^{-1}\text{s}^{-1}$. Such values are typical of bimolecular reactions requiring a modest amount of structural organization in the transition state.

8.3 Basic introduction to free radical reactions
The exemplars of Scheme 8.1 illustrate the important role played by radical pairs, diradicals and free radicals in many photochemical reactions. Indeed to a good approximation, all organic photochemical reactions of n,π* states and all triplet reactions for π,π* states, the *R → I process produces either a radical pair (RP) or a diradical (DR). Thus, an understanding of the process I → P requires a knowledge of (1) the chemistry of radical pairs and of the free radicals which result from the irreversible separation of the partners of a radical pair and (2) the chemistry of diradicals. Since students do not always receive an extensive background in radical pair, free radical and diradical chemistry in their undergraduate courses and since free radical chemistry is so important in organic photochemistry, this section will provide a brief introduction to the basic paradigms of radical chemistry. These paradigms will help us understand the I → P steps for many photochemical transformations.

We shall be mainly concerned with carbon centered radicals. First lets consider the electronic structure of carbon centered radicals. The simplest exemplar, the methyl radical (CH₃•), is planar, with sp² hybridization at the central carbon; while many radicals approach this hybridization, most are not exactly planar. Even the ethyl radical is slightly pyramidal. On the otherhand, the radical CF₃• is essentially tetrahedral, and the carbon atom approaches sp³ hybridization. The hybridization at the carbon of carbon centered radicals is important because the reactivity of radicals increases as the degree of s character increases in the half filled orbital. This important reactivity characteristic can be related to the energy required to homolytically breaking a bond to carbon in a series of C-X compounds. The more stable the bond to carbon being broken, the less stable the resulting carbon centered radical. Turning the idea around, the less stable the carbon radical, the more reactive the radical for a series of related reactions.

A wide range of time resolved (laser flash photolysis) employing spectroscopic techniques (UV-VIS, IR, EPR) for detection have be employed to detect and characterize radicals (each will be discussed later in the Chapter). These time resolved (TR) techniques complement each other in several ways; for example, laser flash photolysis using UV-VIS detection is most useful for detecting systems with large extinction coefficients, while structural interpretation is easiest in EPR for simple radicals showing a straightforward line splitting pattern.
A vast number of photochemical reactions corresponding to a \( *R \rightarrow I(D) \) process produces radical centers in pairs. This is simply a reflection of the fact that free radicals have an odd number of electrons, while most stable molecules are diamagnetic and have an even number of electrons. Thermal free radical generation normally involves a homolytic bond cleavage, and frequently involves molecules with at least one very weak bond, such as in the case of peroxides and azo compounds illustrated in Scheme 8.3.

\[
\begin{align*}
O & \quad \rightarrow \quad 2 \text{RO}^* \\
N=\text{N} & \quad \rightarrow \quad 2 \text{R}^* + \text{N}_2
\end{align*}
\]

Scheme nn.3

Both reactions in Scheme 8.3 can also be triggered photochemically; in the case of azo compounds photoinduced cis-trans isomerization competes with bond cleavage and leads to reduced efficiency. Thermal radical generation can also involve cleavage of much stronger bonds, such as C-C bonds, however, these processes require elevated temperatures (as in the thermal cracking of petroleum products). In contrast, in the case of photochemical reactions it is possible to cleave relatively strong bonds under mild conditions at room temperature. Figure 8.2 compares common bonds with their bond energies and some representative wavelengths. The wavelength labels have been selected to coincide with a few wavelengths frequently used in photochemical research. Having enough energy is a requirement for the \( *R \rightarrow I(D) \) reaction to be possible (energy conservation), many other considerations are required to establish if the reaction is plausible (accessible kinetic pathway to compete with other modes of deactivation of \( *R \)). The Type I reaction in Scheme 8.1 provides a good example of C-C bond cleavage occurring efficiently through photoexcitation.
Figure 8.2: Energy scale (in kcal/mol) in comparison with typical bond energy and commonly used wavelengths in photochemistry. The visible region (400 to 700 nm) has been identified.
If the $^*R \rightarrow I$ process produces a radical pair, the two radicals that are “born together” are termed a “geminate (born together)” radical pair. The two radical partners of a geminate pair may irreversibly diffuse out of the solvent cage in which they are born and become “free radicals”. Radical pairs that are born in the singlet state ($^1I$) undergo efficient radical-radical reactions in the solvent cage (the fraction of pair which react instead of escaping from the solvent cage is termed the “cage effect”). On the other hand, radical pairs that are born in the triplet state ($^3I$) usually separate efficiently from the solvent cage and form free radicals in high yield (low “cage effect”). Chapter 9 discusses some of the special properties of these pairs.

After initial separation, the "free" radicals can form product (the $I \rightarrow P$ process) by reacting with other free radicals (radical-radical reactions) or with other molecules present (radical-molecule reactions). There are two major radical-radical reactions: combination or disproportionation (Eq. 8.6). Reaction 8.6 illustrates the reactions that occur in the case of two ethyl radicals, where approximately 15% of the products result from radical disproportionation.

$$2 \text{C}_2\text{H}_5^\bullet \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$$

Radical-radical reactions of carbon centered radicals usually occur at close to the diffusion controlled rate when they involve unhindered radical centers leading to the formation of a strong bond (i.e., the reaction is highly exothermic). In solution, the maximum rate constant achievable is one quarter of the diffusion controlled rate constant (see Chapter 7), reflecting spin statistical factors (only one of four random encounters will result in a singlet state). A few representative rate constants for radical recombination in solution at room temperature are given in Table 8.3. Fast reactions such as these examples tend to be sensitive to the solvent viscosity, reflecting its influence on diffusion coefficients (see Chapter 7).

**Table nn.3**: Representative rate constants for radical-radical recombination reactions.

<table>
<thead>
<tr>
<th>Radical</th>
<th>Solvent</th>
<th>Rate constant ($M^{-1} s^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3^\bullet$</td>
<td>cyclohexane</td>
<td>$4.5 \times 10^9$</td>
</tr>
</tbody>
</table>
In addition to radical-radical processes, radical-molecule reactions play an important role in the I → P processes. Radical-molecule reactions always lead to radical products, reflecting that an odd number of electrons participate in the process. Table 8.4 summarizes the most common types of radical-molecule reactions of carbon centered radicals.

<table>
<thead>
<tr>
<th>Reaction type</th>
<th>Characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atom transfer or abstraction</td>
<td>Commonly hydrogen abstraction, also halogen atoms. Hydrogen transfer from a radical to oxygen is common when they are accompanied by an increase in bond order in the donor moiety.</td>
</tr>
<tr>
<td></td>
<td>[ \text{Bu}^\cdot \text{O} + \text{PhCH}_3 \rightarrow \text{Bu}^\cdot \text{OH} + \text{PhCH}_2^\cdot ]</td>
</tr>
<tr>
<td></td>
<td>[ \text{H}_3\text{C} - \text{OH} + \text{O}_2 \rightarrow \text{H}_3\text{C} = \text{O} + \text{HO}_2^\cdot ]</td>
</tr>
<tr>
<td>Addition to $\pi$ systems</td>
<td>Usually to multiple bonds or aromatic rings. Constitutes the basis for vinyl polymerization (see first example). The reaction with molecular oxygen can also be regarded as an addition (see Chapter xx)</td>
</tr>
<tr>
<td></td>
<td>[ \text{CH}_3\text{CH}_2^\cdot + \text{PhCH}=\text{CH}_2 \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2^\cdot \text{CHPh} ]</td>
</tr>
<tr>
<td></td>
<td>[ \text{CH}_3\text{CH}_2^\cdot + \text{O}_2 \rightarrow \text{CH}_3\text{CH}_2\text{OO}^\cdot ]</td>
</tr>
<tr>
<td>Electron transfer</td>
<td>Less common than the types above. Usually occurs with reducing radicals in polar solvents</td>
</tr>
</tbody>
</table>
Homolytic substitution at polyatomic centers

Referred as $S_H^2$ reactions (the name also applies to atom transfer), occur with atoms capable of easily expanding their valence, such as boron.

$$\text{Bu}^1\text{O}^- + \text{B}(\text{C}_2\text{H}_5)_3 \rightarrow \text{Bu}^1\text{OB}(\text{C}_2\text{H}_5)_2 + \text{CH}_3\text{CH}_2^-$$

Bond energies play a dominant role in determining the course of free radical reactions. For example, in the reaction of tert-butoxyl radicals with toluene the O-H bond formed in the product is much stronger than the benzylic C-H bond cleaved in toluene. Thus, the overall reaction is exothermic and therefore energetically possible and kinetically plausible. All the reactions in Table 8.4 can be written as reversible processes, and we are listed in the spontaneous direction, i.e., that for which $\Delta G < 0$. Table 8.5 illustrates some representative rate constants for radical-molecule reactions in solution at room temperature.

Table 8.5: Representative rate constants for radical molecule reactions in solution at room temperature.$^5$-$^10$

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Solvent</th>
<th>Rate constant (M$^{-1}$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Bu}^1\text{O}^- + \text{PhCH}_3 \rightarrow \text{Bu}^1\text{OH} + \text{PhCH}_2^-\bullet$</td>
<td>Benzene/ t-butyl peroxide</td>
<td>$2.3 \times 10^5$</td>
</tr>
<tr>
<td>$\text{Bu}^1\text{O}^- + \text{PhCH}_2\text{CH}_3 \rightarrow \text{Bu}^1\text{OH} + \text{PhCH}(-)\text{CH}_3$</td>
<td>Benzene/ t-butyl peroxide</td>
<td>$1.05 \times 10^6$</td>
</tr>
<tr>
<td>$\text{Bu}^1\text{O}^- + \text{CH}_3\text{CHOHCH}_3 \rightarrow \text{Bu}^1\text{OH} + \text{CH}_3\text{C}(-)\text{OHCH}_3$</td>
<td>Benzene/ t-butyl peroxide</td>
<td>$1.8 \times 10^6$</td>
</tr>
<tr>
<td>$\text{Bu}^1\text{O}^- + \includegraphics[width=0.5cm]{circle.png} \rightarrow \text{Bu}^1\text{OH} + \includegraphics[width=0.5cm]{circle.png}$</td>
<td>Benzene/ t-butyl peroxide</td>
<td>$5.4 \times 10^7$</td>
</tr>
</tbody>
</table>
In addition to the radical-radical and radical-molecule reactions illustrated above, free radicals can undergo a number of unimolecular reactions, such as rearrangements and fragmentations. A rearrangement or fragmentation of a free radical must produce another free radical. Also, one of the radical centers in a diradical may undergo a rearrangement or fragmentation to produce a new diradical. Simple energetic considerations serve as a useful guide to rearrangements and fragmentations of free radicals: they are kinetically plausible if they are exothermic. Scheme 8.4 shows several exemplars of radical rearrangements involving reaction types that can be readily understood within the normal paradigm of radical-molecule reactions (see Table 8.3 above), they are simply their intramolecular analogues.
Scheme 8.4.

Reaction (B) in Scheme 8.4 has found numerous applications in synthetic organic chemistry, and has also been used as a clock to determine the rate constants for radical-molecule reactions employing competitive methods. It occurs with a rate constant of $2.4 \times 10^5 \text{ s}^{-1}$ at room temperature.\(^7\)

Radical fragmentation reactions are usually driven by the strengthening of another bond, such as the formation of a double bond, aromatization of a ring, or elimination of a very stable product, such as CO\(_2\), CO or N\(_2\). Some exemplars of radical fragmentations are shown in Scheme 8.5.

Scheme 8.5
Scheme 8.5 also illustrates a very common feature of radical fragmentations, i.e., the bond cleaved is in the β-position relative to the radical center. This feature is the result of the fact that the β C-C bond can overlap well with the half filled orbital. The driving force for radical fragmentation are either entropic (formation of two particles from one) or enthalpic (formation of a more stable radical) or some combination of both. In the case of reaction (B), the formation of CO₂ provides enough driving force to form the highly unstable phenyl radical; the reaction occurs in solution in about 10⁻⁶ seconds.¹¹

A few carbon centered radicals are highly unreactive, even toward radical-radical reactions of combination and disproportionation. The triphenyl methyl radical is a classic example of a stable carbon centered free radical. If in addition to this the radical is unreactive towards oxygen, it is sometimes possible to isolate these materials under normal laboratory conditions. These radicals are called *persistent radicals*, and sometimes *stable radicals*. The former should be the preferred name, since stabilization (as in resonance stabilization) is not a requirement. In the case of free radicals that are centered on nitrogen or oxygen, the molecules are so stable that they are commercially available products! Two examples are DPPH and Tempo.

\[
\begin{align*}
\text{DPPH} & \quad \text{NO}_{2}N\quad \text{NO}_{2} \\
\text{TEMPO} & \quad \text{NO}^* \\
\end{align*}
\]

(Persistent radicals are unreactive towards each other in radical-radical reactions, but are not necessarily unreactive towards carbon centered radicals. For example, TEMPO reacts readily with carbon centered radicals,⁹,¹⁰ see Table 8.5.

The radical centers of diradicals, such as those illustrated in reactions 8.4 and 8.5 share most of the properties of free radicals. For example, in diradical-molecule reactions the
reaction pathways and rate constants match well those determined for monoradicals. Further, we note that in reaction 8.5 path (a) corresponds to radical fragmentations similar to those in Scheme 8.5. In the case of 1,4-diradicals (Scheme 8.1) there exists a structurally specific reaction: cleavage of the 2,3 bond (which is in the β-position relative to both radical centers) leads to the strongly exothermic formation of two double bonds. Because the reaction is very exothermic the rate of such a fragmentation is generally orders of magnitude faster than the fragmentation reaction of monoradicals, where a radical is formed as a product and only one bond is formed for each one broken so the reaction is generally close to thermally neutral overall. The cyclization of path (b) is the equivalent of radical-radical combination, but now occurs in an intramolecular process, since the molecular frame prevents the separation of the two radical centers. The cyclization reaction it is therefore the diradical analogue of a geminate cage combination reaction of a radical pair. Finally, path (c) yields the starting material and is equivalent to a radical-radical disproportionation. This diradical reaction is the analogue of radical pair disproportionation.

A special and interesting situation arises when a diradical interacts with a paramagnetic substrate, such as oxygen, nitroxides and some transition metals. In this case "normal" free radical process compete with spin interactions characteristic of the spin configuration involved. In this specific case the paradigm for free radical reactions needs to be adjusted to accommodate differences in spin interactions. These effects are presented in chapters xxxxx(discuss spin catalysis here).

The simplest free radical is probably the electron. Solvated electrons are easy to detect spectroscopically and have been extensively studied, particularly using pulse radiolysis techniques (see discussion in Chapter 7). The solvated electron (frequently "hydrated" electron in water) is highly reactive. It adds to almost all molecules having π bonds with rate constants approaching diffusion control.

8.4 The Use of Structural Criteria and the Role of Reactive Intermediates in Mechanistic Analysis
A knowledge of the *structure* is essential for an understanding of the mechanism of the overall photochemical reaction. Molecular structure is at the heart of organic reaction mechanism. Important qualitative arguments and conclusions concerning photochemical reaction mechanisms can be made based on structural considerations alone. It is convenient to consider the structures of Scheme 8.1 in terms of two classifications:

1. Stable and isolable structures: the initial reactants (R) and isolated products (P)
2. Transient structures and metastable *reactive intermediates*: electronically excited states (*R*) and thermally equilibrated reactive intermediates (I).

What can we deduce about the mechanism of a reaction solely from the structure of the ground-state reactants (R) or products (P)? The answer is quite a bit qualitatively. More can be deduced if the electronic nature of the S₁ and T₁ of *R* states is known (e.g., electronic configuration, n,π* or π, π*). Still more can be deduced if it is known whether S₁ or T₁ (or both) undergo the reaction under study, and if the structures of the reactive intermediates (I) in addition to S₁ and T₁ are known. For instance, one of our paradigms may tell us that excited carbonyl compounds (see reactions 8.4-5) have a high reactivity toward hydrogen transfer (intermolecular or intramolecular) for *R(n,π*)), but are far less reactive *R(π,π*). character (see Chapter 6).

We will try to develop the paradigm of molecular organic photochemistry so as to try to have a framework that allows us to propose plausible provisional reaction mechanism(s) with ease. This *mechanistic road map* showing the way from reagents to products will help us define which are the experiments and techniques required to establish if a plausible mechanism is a probable one.

**The Use of Reaction Types and Structural Relationships in Mechanistic Analyses**

The following are typical questions raised in the use of our paradigm. By answering these questions we will be able to start using the vast experience accumulated by past practitioners in the field:

1. Does the overall reaction (R → P) correspond to a standard reaction type or to a sequence of standard reaction types?
2. How does the product atomic composition and connectivity relate to the reactant atomic composition and connectivity?

3. How does the product stereochemistry relate to the reactant stereochemistry?

If the answers to these questions are available, a basis for guessing at a set of plausible mechanisms is available. This procedure is based on the postulate that there are very few fundamentally different reaction mechanism types for an elementary chemical or photochemical step. In effect, we postulate that many reactions, already a part of existing paradigms, are more or less the same with respect to the fundamental chemistry which occurs at a reactive site, and differ in quantitative detail rather than in their qualitative nature. This postulate is the intellectual strategy of the use of functional groups to classify organic reaction types and will be used as the basis for discussing examples of organic photochemical reactions in Chapters 9-12. We will frequently try to identify the business end of a molecule by examination of its structure, using the functional group strategy.

An integral postulate in our paradigm is that reactions (i.e., R → P) can be classified in terms of mechanistic types, and for any given class of reactions only a small set of mechanistic types is likely to be required for a detailed analysis. In other words, in the context of Scheme 8.1, the number of possible primary reaction steps, *R → I, is extremely limited and can be based on the paradigm, derived from past experience, for any given type of reactants if the electronic configuration of *R is known or is assumed.

In ground-state chemistry, most of the fundamental reaction types (e.g., S_N2) can be viewed as proceeding via shifts of pairs of electrons toward or away from carbon as one passes from reactant to product (i.e., pushing electrons). An exception occurs when one (and only one) of the reagents possesses an odd number of electrons, i.e., reactions of monoradicals. In this case the reaction, is usually viewed in terms of single-electron shifts toward or away from carbon.

As we have shown in Chapter 6 from the frontier molecular orbital view, most photoreactions can be described initially as being driven by one-electron shifts characteristic of radical chemistry. This is understandable in terms of electronic excitation, which may be thought of as orbital decoupling of an electron pair to produce a species which possesses two half-filled orbitals. The one-electron behavior is a natural consequence of the high one electron affinity of the lower-energy half-filled orbital and the low one-electron ionization
potential of the higher-energy half-filled orbital. Reactions from \( \text{R}(S_1, \pi, \pi^*) \) may proceed through \( \text{I}(Z) \). In these instances two electron shifts involving carbonium ion and carbanion centers will occur along the \( \text{I}(Z) \rightarrow \text{P} \) pathway. Examples of such reactions are the subject of Chapters 10 and 12 and will not be considered in detail in this Chapter.

The point of these classifications is that each reaction type (for example involving radicals, diradicals or zwitterions) has been established to occur via a relatively small and well-defined set of mechanisms. If a reaction falls into one of the above categories, the paradigm of organic reaction mechanisms automatically provides a standard set of mechanisms available to consider for the steps in an overall reaction path. If a reaction does not fall into one of the above categories, we may assume that the reaction is complex (i.e., involves a sequence of two or more of the above reaction types) or that one has encountered a novel mechanism. The latter is extremely rare!

### An Exemplar of the Use of Structural Relationships in Mechanistic Analysis

The photolysis of aryl alkyl ketones generally results in the formation of products of the type shown in Eqs. 8.4 and 8.5, i.e., methyl aryl ketones, ethylenes and cyclobutanols (termed Type II products). These product structures (P) may be used as a basis to deduce precursor structures (I). The first test is to determine if a single intermediate (i.e, I, as opposed to \( \text{I}_1, \text{I}_2, \text{I}_3 \) …) is sufficient to rationalize all the products of reaction. When more than one product is observed from photoreactions of a single excited state, it is commonly observed that these products can be logically derived from competing pathways for reaction of a single intermediate, I. For example, all the Norrish Type II products are derivable from the common diradical I shown in Eq. 8.5. In other words, three "natural" and logical diradical reactions expected from the paradigm for radical chemistry. They are (a) cleavage of bonds \( \beta \) to the radical center, which for a 1,4-diradical corresponds to the selective cleavage of the 2,3 bond; (b) radical-radical combination which for a diradical is a cyclization and (c) disproportionation, which in the case of the specific radical corresponds to a back reaction to regenerate the starting material. Note that cleavage reaction (a) does not produce directly produce the methyl aryl ketone that is isolated. Rather a short lived enol, reaction 8.5, which tautomerizes to the observed product (i.e, \( \text{I} \rightarrow \text{enol} \rightarrow \text{P} \)) is produced from I. All products can be understood in terms of “plausible” radical reactions of I, as illustrated in reaction 8.6 and Table 8.4.
Thus, the product structures, P, may be said to "imply" a diradical I as a predecessor structure. The diradical, in turn, "implies" an electronically excited precursor structure, *R, capable of abstracting a hydrogen from the side chain. The paradigm teaches that the *R(n,π*) state of the aryl alkyl ketone is a plausible predecessor to I. The analysis is reminiscent or retrosynthetic analysis in organic chemistry, i.e.,

\[ P \overset{\Rightarrow}{\rightarrow} I \quad I \overset{\Rightarrow}{\rightarrow} R^* \]

Importantly, the enol and diradical indicated in Eq. 8.5 were detected by time resolved spectroscopic methods (Section 8.x) long after their existence was inferred via product-reactant relationships. The direct spectroscopic detection of the diradical I formed in reaction 8.4 also provided the tools to study their kinetic behavior; in general the reactions of diradical at the monoradicals centers are similar (and occur with similar kinetics) to those of the analogous monoradicals. For example, diradicals produced from Type II reactions (Scheme 8.x) undergo electron transfer reactions characteristic of the ketyl radical site and hydrogen abstractions typical of alkyl radicals. Thus we can predict diradical behavior from our knowledge of monoradical reactions; only when the spin configuration plays a key role is this rule violated (see Section nn.xx) Tito, we need to check this out and have a section which discusses this point.

8.5 Rules for Proceeding from Rate Laws to Photochemical Reaction Mechanisms

The theoretical rate law for any proposed elementary chemical step is the product of the rate constant for that step times the concentrations of the reactants involved in the proposed step. The empirical rate law is an algebraic expression which relates measured concentrations to the experimental rate of reaction. In many multistep reactions one particular step becomes the "bottleneck" or slow step for product formation; we refer to this elementary step as the rate-determining step.

In photochemical kinetics we interpret "rate-determining step" to mean that step which determines the overall rate of product formation from a given electronically excited state. When the overall rate expression reflects exclusively the kinetics of a single elementary step,
the rate expression can only contain integer exponents, and the concentrations of reactants that appear in this expression are a direct indicator of the molecular formula of the transition state.

As an exemplar of the use of kinetic information to provide information on photochemical mechanisms we consider the photoreduction of acetone to pinacol by isopropanol, Eq. 8.7:\textsuperscript{12}

\[
(CH_3)_2CO + (CH_3)_2CHOH \xrightleftharpoons{hv} \text{H}_3C\text{CH}_3 \text{CH}_3\text{C} \text{H}_3\text{H}_3 \text{C} \text{H}_3
\]  

From absorption and emission data (Chapter 4) it is readily established that the $S_1$ and $T_1$ states of acetone are both $n,\pi^*$ states. From the discussion of the plausible set of primary processes of $n,\pi^*$ states we can deduce that the key primary photochemical step in the reaction 8.7 involves abstraction of a hydrogen atom from the tertiary carbon of isopropanol (Eq. 8.8) by the $n,\pi^*$ state of acetone (a priori, either $S_1$ or $T_1$ is a plausible candidate for $R$ for reaction). This is followed by the formation of a pair of ketyl radicals, which then undergo radical-radical combination to yield the product (Eq. 8.9):

\[
(CH_3)_2CO (S_1 \text{ or } T_1) + (CH_3)_2CHOH \xrightarrow{hv} 2 (CH_3)_2COH
\]  

How can we decide on the basis of empirical rate law data whether this assumed mechanism is provisionally acceptable? How can we decide if $R$ is $S_1$ or $T_1$ (or both)? Experimentally, both the fluorescence and the phosphorescence of acetone are measurable. The intensity and lifetime of each emission can be related to the concentrations of the $S_1$ and $T_1$ excited states. It is found experimentally, by monitoring the triplet decay kinetics as a function of isopropanol concentration, that the measured rate of product formation is expressed by Eq. 8.10.
From our rule for rate laws, we can conclude that (a) acetone triplets and isopropanol are involved in the photochemical rate-determining step for reaction, and (b) S\(_1\) of acetone is not involved in the photochemical rate-determining step, i.e., since the concentration of S\(_1\) does not appear in the empirical rate law S\(_1\) cannot be directly involved in the product-determining step. Thus, we can associate the measured rate constant, k, with the theoretical rate-constant for the reaction:

\[
(CH_3)_2CO (T) + (CH_3)_2CHOH \xrightarrow{h} 2 (CH_3)_2COH
\]  

(8.11)

This simple analysis is consistent with the direct study of the reaction by monitoring the decay of triplet acetone in the presence of various isopropanol concentrations, as well as by the detection of the ketyl radical by both transient absorption and ESR techniques.\(^{12-15}\) Having stated earlier that all reaction mechanisms are provisional, we note that reaction 8.11 is one of the best characterized processes in photochemistry because the structures of *R and I have been firmly established by one or more direct spectroscopic methods. Thus, the photochemical reaction of acetone with isopropanol is an exemplar for the *R \(\rightarrow\) I primary process of hydrogen abstraction from the T\(_1\)(n,\(\pi^*\)) states of ketones (which are discussed in detail in Chapter 9). Reaction 8.11 takes place with a rate constant of 1.0 \(\times\) 10\(^6\) M\(^{-1}\) s\(^{-1}\) in 2-propanol at room temperature.\(^{16}\) An alternate approach to confirm the participation of the triplet state may involve the addition of a triplet-specific quencher. For example, in Chapter 7 it was noted that conjugated dienes (which possess triplet energies much lower but singlet energies much higher than most ketones) are known to selectively quench many carbonyl triplets at close to the diffusion controlled limit, but to quench carbonyls singlets more slowly. Addition of a diene such as \textit{cis}-1,3-pentadiene results in a decrease of the rate of product formation with concurrent cis-trans diene isomerization. The observation further supports triplet involvement. We will develop further this type of quenching experiments and the quantitative relationships that govern the effect of added quenchers later in this chapter.
The conclusion that the triplet state of acetone, rather than its higher energy singlet state, is the reactive species may seem counter-intuitive, since both are n, π* states. Furthermore, the singlet state possesses a higher energy, so the *R → I step is more exothermic for the singlet the final product of hydrogen abstraction, I, is the same in both cases. Why should the singlet be less reactive? One could imagine the singlet reaction “preempting” triplet chemistry (since the singlet precedes the triplet), but not the reverse. The explanation is in fact quite simple: the singlet is reactive, but it does not react efficiently. We can understand this initially counter-intuitive situation of *R being reactive but inefficient by considering not only the rate constant for the hydrogen abstraction reaction of the singlet, but also the rate constants for competing reactions which deactivate the singlet.

The rate constant for hydrogen abstraction from the singlet can be measured directly without interference of the triplet by measuring the quenching of fluorescence by hydrogen donor. From such analysis the rate constants for hydrogen abstraction from the singlet state of acetone, 1k_H, are in fact more reactive than the rate constants for the corresponding triplet, 3k_H. For example, the reactivity ratio, 1k_H/3k_H is ~9 for isopropanol and ~3 for 1,4-cyclohexadiene (an excellent hydrogen donor for both singlets and triplets). The reaction proceeds almost exclusively from the triplet state simply because the triplet is around one thousand times longer than the singlet state. During its short lifetime (~2 ns) the singlet state (that reacts with isopropanol with a rate constant of 9.1 x 10^6 M^-1 s^-1) does not have much of a chance of reacting, thus paving the way for the longer lived triplet state to take over. In fact, even in pure isopropanol, which is ca 10 M as a neat liquid, only about 20% of the singlets react with isopropanol, showing that in this kinetic competition, intersystem crossing is the clear winner.

Another useful rule is related to the principle that chemical species of similar energy and structure possess similar chemical properties. Using this principle, we may make the following statement concerning the structure of transition states, known as the Hammond postulate:

\[ \text{If a transition state and an intermediate possess comparable energies and occur consecutively along a reaction coordinate, the chemical composition, the chemical} \]
constitution (structures) and chemical properties of the transition state will be similar to those of the intermediate.

Extending this idea to photochemical reactions, if $E_a$ is small (a few kcal/mol) for reaction from an excited state, then we may postulate that the transition state "looks like" the initial excited state in most important chemical aspects. This in turn leads to the corollary that the excited-state configuration is a guide to excited-state reactivity; i.e., if the transition state "looks like" the initial excited state, the orbital interactions should relate to the initial excited-state electronic configuration.

Note that reactions 8.4 and 8.11 are essentially identical hydrogen transfer processes except that they occur in intra- and intermolecular fashion, respectively. Similar reactivity is expected and found for the $n,\pi^*$ excited state of carbonyl compounds and alkoxy radicals when the $n$-orbital is the major MO involved in the radical reactions being compared (e.g., $(\text{CH}_3)_3\text{CO}^\bullet$, see tables 8.4 and 8.5). This striking analogy results from the similarity of the electronic configuration, a half filled $n$-orbital at the oxygen atom in the alkoxy radical and an $n,\pi^*$ state.17

8.6 Rules for Proceeding from Efficiency Laws to Information on Photochemical Reaction Mechanisms

As we have seen, $^*R$ always has the possibility of more than one possible deactivation pathway available for a photophysical or a photochemical process. The efficiency of any particular pathway from $^*R$ depends on the rates of these pathways and therefore indirectly contains kinetic and therefore mechanistic information. The efficiency of a photochemical reaction can be expressed in two ways:

1. The quantum yield ($\Phi$) or efficiency of formation or destruction of a number of given species ($R, ^*R, I, P$) can be based on the number of photons (Einsteins) absorbed by the system in the $R + h\nu \rightarrow ^*R$ process.

2. The state efficiency ($\phi$) of formation or destruction of a given species ($R, ^*R, I, P$) can be determined from the number of molecules produced from a given state ($^*R, I, P$).
It is important to distinguish these efficiency terms. We shall call $\Phi$ (the efficiency based on photons absorbed) the (absolute) quantum yield, and $\phi$ (the efficiency from a given state) the state efficiency.

The efficiency of a process based on the quantum yield, $\Phi$, is given by Eq. 8.12. Recall that an Einstein is equal to a mole of photons.

Quantum yield:

$$\Phi = \frac{\text{moles of a given species formed or destroyed}}{\text{moles of photons absorbed by the system}} \tag{8.12}$$

The state efficiency, $\phi$, is given by Eq. 8.13.

State efficiency:

$$\phi = \frac{\text{moles of a given species formed or destroyed}}{\text{moles of a given state formed by absorption of an Einstein}} \tag{8.13}$$

In a practical sense, the absolute quantum yield $\Phi$ is the more interesting and fundamental quantity because it relates the effectiveness with which the absorbed photons in the $R + h\nu \rightarrow *R$ process can form I or P. Although the magnitude of $\Phi$ may vary from 0 to very large values ($>10^4$), in the absence of chain reactions (or trivial stoichiometric factors) the maximum value of $\Phi = 1$. From the theoretical standpoint, in order to understand the factors determining $\Phi$, an "overall" quantity of a reaction, we must understand the factors determining $\phi$, a quantity which relates to individual steps from excited states ($*R$) or intermediates (I) along the reaction pathway. By definition, the value of $\phi$ cannot exceed 1.

All quantum yields may be considered as the product of three probabilities as shown in Eq. 8.14: (1) $\phi_{*R}$, the probability that light absorption will produce the reactive state $*R$; $\phi_I$ the probability that $*R$ will undergo a particular reaction on the pathway to I; and $\phi_P$ the probability that any metastable intermediate (I) which exists between $*R$ and P will lead to P. Thus, we can use Scheme 8.6, as a modified version of Scheme 1.1:

$$R \xrightarrow{\text{hv}} *R \xrightarrow{\phi_I} I \xrightarrow{\phi_P} P$$

Reactants \hspace{5cm} Products
Scheme 8.6: Efficiencies of the various steps in a photochemical transformation. Each value of $\phi_i$ is defined as in equation 8.14.

The absolute quantum yield for the formation of $P$ from $R$, $\Phi_R$, will be given by the product of the relevant efficiencies, i.e.:

$$\Phi_R = \phi_{sR} \times \phi_I \times \phi_P$$ \hspace{1cm} (8.14)

In direct excitation experiments ($R + h\nu \rightarrow \ast R$) in solution, $\phi_{sR}$ is generally unity if $\ast R = S_1$ since Kasha’s rule is typically obeyed (see Chapter 4).

When $\ast R = T_1$, then $\phi_I$ is identical to $\Phi_{ST}$ (intersystem crossing quantum yield) and is given by Eq. 8.15.

$$\Phi_{ST} = \frac{k_{ST}}{k_{ST} + k_d + k_q(Q)} = k_{ST} \times \tau_s$$ \hspace{1cm} (8.15)

In Eq. 8.15, $k_{ST}$ is the rate constant for singlet-triplet intersystem crossing, $k_d$ the rate constant for all photophysical and photochemical unimolecular processes in which the excited singlet participates (including fluorescence), and $k_q$ the rate constant for singlet state quenching by quencher $Q$; the last term in the denominator takes into account all intermolecular modes of excited singlet decay.

In determining photochemical reactivities, the state efficiency $\phi_{sR}$ is often crucial. This efficiency is given by Eq. 8.16

$$\phi_R = \frac{k_D}{k_D + k_d} = k_D \tau_A^*$$ \hspace{1cm} (nn.16)

where $k_D$ is the rate constant for reaction of $\ast R$ to form I or $P$ and $k_d$ represents the rate of major decay of $\ast R$. We are now in a position to formulate some general rules for the relationship between quantum yields and state efficiencies.

Rule 1. The quantum yield for reaction from a given state equals the state efficiency for reaction, times the quantum yield for formation of the reacting state (Eq. 8.17):

$$\phi_{(\text{given state})} = \phi_{sR} \times \Phi_{(\text{formation of state})}$$ \hspace{1cm} (8.17)
From Eq. 8.17, we can understand how a high state efficiency, $\Phi_R$, for reaction can be consistent with a low quantum yield, $\Phi_s$, for reaction from the state. This is the situation if the state of interest is inefficiently produced after the absorption of the photon. The apparent low reactivity of the singlet state of acetone towards 2-propanol provides a good example of this situation. Even with a quantum yield of formation ($\Phi_s$) of 1 (the singlet $^1R$ is the primary “product” of light absorption), only about 20% efficiency is achieved (Eq. 8.18)

$$\Phi_s = \phi_s \frac{k_s[substrate]}{\tau_s^{-1} + k_s[substrate]} = \frac{9.1 \times 10^6 \times 13.1}{(2 \times 10^{-3})^{-1} + 9.1 \times 10^6 \times 13.1} = 0.193$$

In Eq. 8.18, $\Phi_s$ refers to the quantum yield of product formation from the singlet state, and 13.1 is the molarity of pure 2-propanol.

The following rules relate the magnitude of the quantum yield to mechanistic conclusions:

**Rule 2.** If $\Phi > 1$ (for reasons not trivially associated with reaction stoichiometry), then a chain reaction must be involved in the mechanism. This rule derives from the generalization that one photon excites only one molecule.

**Rule 3.** If $\Phi < 1$, then the provisional mechanism must account for the reaction inefficiency by some specific cyclic pathway which degrades the energy of the absorbed photon and returns the system back to its original ground state without net reaction. Such cyclic processes may be of a chemical or photochemical nature.

### 8.7 Experimental Methods for Determining Rate Constants of Photoreaction

In this section we will discuss the common experimental methods for determining $k$, the reaction rate constant, of a primary photochemical reaction ($^1R \rightarrow I$).

The term “instantaneous” applied to a reaction rate once meant “less than a second”, or a time comparable with that required for reagent mixing. It is now possible to study reactions which are well on their way to completion in $10^{-12}$ s (a picosecond) or less. The mechanical problem of “mixing” liquid reagents and the time limitation required before measurement could be made is overcome by methods based on the rapid “pulsed” perturbation of a system
from its equilibrium and then following the rate of return of the system to equilibrium. In other words, in order to examine the dynamics of transients such as *R and I, it is necessary to identify a pulsed source that can produce the intermediate on a time scale which is fast compared with the time scale in which the species reacts or decays.

In photochemistry the perturbation is conveniently applied by subjecting the system to a very short pulse of light from a pulsed laser source, such as a pulsed laser. Absorption of the energy pulse from the laser causes a number of molecules to suddenly find themselves in electronically excited states *R during the very short lifetime of the pulse. Various fast spectroscopic detection methods (UV-VIS, UV-VIS emission, IR, EPR) are then employed monitor the concentration of *R and I with time and to characterize the structure of *R and I. The development of highly reliable lasers coupled with very fast methods of detection during the last three decades has greatly facilitated this task. Indeed, lasers capable of providing pulses of the order of $10^{-15}$ s (a femtosecond) are currently available. A femtosecond is the time scale of the fastest vibrations of organic molecules!

A second method of studying very fast reactions is based on kinetic competition between two reaction pathways, under conditions in which the rate of one of the pathways is known or calculable and can therefore be employed as a “clock”. From knowledge of the rate of one pathway and the ratio of partitioning between the pathways, the rates of the other pathway can be evaluated. The Stern-Volmer equation frequently aids in the application of this concept and is discussed later in this chapter.

**Pulsed Excitation to produce *R**

In the simplest possible photochemical system, a molecule may be excited by a very short pulse of light to yield an excited state which decays exclusively to yield the ground state of the reactant. Under these conditions Scheme 8.1 simplifies to Scheme 8.7.

\[
R \xrightarrow{hv} [R^*] \xrightarrow{TR} R
\]

**Scheme 8.7:** A simple photoprocess in which the only pathway for *R is its return to R.
The return of *R to R may involve either a photophysical process or a photochemical process that produces a short lived intermediate, I, that yields R as the exclusive product. Interestingly, this simple principle is widely employed in sun-blocks and polymer photostabilizers, where “cyclic” photochemistry (R + h\nu \rightarrow *R \rightarrow I \rightarrow R) effectively converts light into heat, thereby reducing the efficiency and damage which might be caused by the absorption of light. Figure 8.3 shows a plot of the concentrations of R and *R following pulsed excitation. In Figure 8.3 the decay of *R has been assumed to occur in a first order reaction, according to the rate law of Eq. 8.19:

\[
[R^*] = [R^*] e^{-t/\tau_R} = [R^*] e^{-k_R t}
\]  

(8.19)

In Eq. 8.19 \(\tau_R\) is the experimental lifetime for *R and \((R^*)_0\) and \((R^*)_0 e^{-k_R t}\) are the concentrations of *R at time = 0 and time = t, respectively.
Figure nn.3: Pulsed excitation at $t = 10$ excites 40% of the $R$ molecules. Reading to an excited state ($^{*}R$) that decays with $\tau_R = 20$. Excited decay is accompanied by the concurrent regeneration of $R$. (Provide a real experimental example from a ketone primary process)

Pulsed excitation to trigger photochemical reactions was invented in the 1950s. The first pulsed sources were “flash lamps” which produced millisecond pulses of a wide range of wavelengths and latter flash lamps produced microsecond pulses$^{20,21}$. In 1966$^{22}$ demonstrated the use of a pulsed laser as an excitation source and achieved time resolutions of $\sim 100$ ns. Nanosecond experiments are routine nowadays, and experimental set-ups or the picosecond$^{23}$ ($10^{-12}$s) and femtosecond ($10^{-15}$s) time scales are available in many laboratories. Norrish and Porter were awarded Nobel Prizes for the invention of microsecond flash lamp pulsed methods and Zewail was awarded for developing pulsed laser methods to produce femtosecond pulsed laser methods.

Figure 8.3 shows a hypothetical “concentration” of $R$ and $^{*}R$ as a function of time; in practice, many properties can be measured, such that they bear simple relationship (ideally a direct proportionality) with the concentration of a transient such as $^{*}R$ or $I$. The structures of $^{*}R$ and $I$ can be monitored after the pulsed excitation by a variety of detection methods which can be related directly to the concentration of $^{*}R$ and $I$, i.e., UV, VIS or IR absorbance, electrical conductivity, luminescence intensity and NMR or ESR signal intensity.

Two photon techniques for exciting upper electronic states.

In general for photochemical reactions in solution, the paradigm says to apply Kasha’s rule and assume that $^{*}R$ conforms only to $^{*}R(S_1)$ or $^{*}R(T_1)$. As with all rules there will be exceptions to Kasha’s rule. Since rules are based on an approximation of the global paradigm, exceptions are expected and allowed as long as they can be rationalized by appeal to the deeper global paradigm. The basis of Kasha’s rule is the hypothesis that internal conversion and vibrational deactivation to $^{*}R(S_1)$ or to $^{*}R(T_1)$ after intersystem crossing is faster than any other photochemical or photophysical process from upper states that may be excited after the Franck-Condon $R + h\nu \rightarrow ^{*}R$ process. Clearly the global paradigms allows for exceptions when a photophysical or photochemical process competes with ordinary vibrational relaxation.
(typical time scale $10^{12}$-$10^{13}$ s\(^{-1}\)) or when vibrational relaxation is unusually slow for some rationalizable reason. For example, photoionization may not be energetically plausible for long wavelength excitation but at short wavelengths or in polar solvents such a process becomes plausible. The processes of photoionization could be considered as being indistinguishable in some cases from the $R + h\nu \rightarrow \cdot R$. In other words, the process $R + h\nu \rightarrow \cdot R$ could become $R + h\nu \rightarrow I$, where $I = R^+ + e^-$. It would not be surprising to find violations of Kasha’s rule when they are due to the onset of photoionization.

Upper triplets ($T_n$ where $n > 1$) can be produced via direct excitation into $S_n$ followed by intersystem crossing. However, except in cases where $T_2$ is below $S_1$, this approach is not successful. An alternative method for producing these higher triplet states involves direct excitation via a $T_1 + h\nu \rightarrow T_n$ absorption. This “two photon” approach lends itself to study with pulsed laser sources, since achieving high transient concentrations of $\cdot R$ (singlets or triplets) is relatively easy under these conditions. In this method a population of the lowest triplet state produced initially is converted to the higher triplet state by employing a second light source.\(^{24}\) Sufficient concentrations of molecules in $T_1$ state are accumulated by employing either low temperature matrices or high intensity light sources. In some cases, where the absorption of $T_1$ overlaps extensively with that for the ground state, a single laser pulse can achieve both effects (i.e., $S_0 \rightarrow T_1$ and $T_1 \rightarrow T_n$). Occasionally, two-photon excitation can be achieved with conventional (lamp) sources,\(^{25}\) as in the first example below, that takes advantage of the long triplet lifetime.

**Low Temperature Matrix Techniques**

The technique of low temperature matrix isolation involves the photolysis of $R$ in an inert matrix at temperature of the order of 77K (boiling liquid nitrogen) or lower. An elegant illustration of the low temperature matrix technique is provided by the photochemistry of pleiadene precursor (Scheme 8.8)\(^{26}\) Compound A rearranges to pleiadene (B) only after population of an upper triplet state by biphotonic excitation of $T_1$ in rigid glasses at 77 K. It is important to note that solution irradiation, both at room and low temperatures, leads to no reaction, and that triplet sensitization in solution is similarly ineffective. The reaction was achieved only in matrices at 77 K using both UV and visible radiation sources simultaneously in a biphotonic process, or with a single UV source in a monophotonic process,
at wavelengths much shorter than that required to populate $S_1$. In the two-photon excitation experiments, the product yield has been maximized by tuning the visible source to wavelengths appropriate for known naphthalene $T_1 \rightarrow T_n$ absorption maxima (~400-415 nm), the basic chromophore present in Scheme 8.8. The proposed mechanism for the above two light source experiments involves UV absorption followed by relaxation to a long-lived $T_1$ state (3.3 s for 53 at 77 K), triplet-triplet absorption of the visible photon to populate a higher triplet state $T_n$, from which steps leading to the chemical reaction occur.

![Scheme 8.8](image)

**Scheme 8.8**

*Two Laser (Two Color) Flash Photolysis:* While the matrix isolation spectroscopy is experimentally relatively straightforward, the technique only is useful for unimolecular processes. Bimolecular processes are extremely unusual at low temperatures in a matrix, since diffusion is severely restricted under these conditions. To observe bimolecular reactions the upper excited state chemistry needs to be conducted at room temperature in isotropic solution media where diffusion is relatively rapid and stands a chance of competing with deactivation of $^*R$. The high intensity light sources required to produce high concentrations of $^*R$ are achieved through the use of two lasers.

In the two laser (two color) technique, two lasers of different wavelengths, firing sequentially, are employed to produce the upper excited states of molecules. The first laser
produces the lowest excited state (*R) of the molecule and the second laser selectively excites these excited molecules into an upper level of *R. By this approach a variable delay time can be introduced between the two photons to allow the lower excited state concentration to build up. By using a tunable laser the wavelength of the second photon can be adjusted to correspond to the absorption maximum of the lower excited state. Since excited singlets (S1) are typically too short-lived in comparison with common conventional nanosecond laser pulses to allow for efficient upper singlet production, the two laser set up is best suited for populating upper triplets than upper singlets.

An exemplar of the above technique is found in the cleavage reactions of several carbonyl and aromatic systems which do not cleave in solution when irradiated with conventional light sources. For example, benzil (Scheme 8.9) does not cleave when populated to the T1 (π,π*) state by either direct excitation or triplet sensitization. However, generation of a higher triplet through excitation of T1 results in α-cleavage.

![Scheme 8.9](image)

Bromoaromatics (Scheme 8.10) are generally relatively relatively stable to UV radiation in solution. However when bromonaphthalene, bromoanthracene and bromophenanthrene are subjected to the two laser experiments, they undergo loss of the bromine radical (which is detected as a complex with the solvent benzene). Scheme 8.10 illustrates the mechanism for 2-bromonaphthalene. The proposed general mechanism for two photon excitation of upper triplets is shown in Figure 8.4. In such studies, the exact energetic location of the reactive state
in the triplet manifold (T₂, T₃, T₄, etc.) is most often unknown. Further, the quantum yield of cleavage tends to be low (∼0.05) due to the competition with the high rate of internal conversion as expected from Kasha’s rule.

![Scheme 8.10](image-url)

Scheme 8.10.
Figure 8.4: Energy diagram illustrating the general mechanism for two-photon sequential excitation leading to upper levels of the triplet state ($T_2 \ldots T_n$).

Laser Jet Experiments

The two laser (two-color) technique described above provides excellent spectroscopic information on the transients produced during the formation of products from upper excited states. However, isolation of the products of a photoreaction by this approach is tedious. For product isolation, a “laser jet” apparatus is often used. In this laser jet technique a high velocity microjet of a solution of material to be irradiated is injected into the focal region of an argon ion laser beam. The typical microjet flow rates can be controlled and the sample recycled as many times as necessary to bring the reaction to completion. Consequently, isolation of significant quantities of products is possible. Usually, a high intensity CW argon ion laser is used to excite molecules. In this method, sufficient concentration of molecules in their $S_1$ or $T_1$ states are trapped within a “microbubble” so that they can absorb a second
photon. Reactions employing the laser jet technique generally occur from the upper excited states. Structural and electronic details of the state from which the reactions occur are often lacking.

Scheme 8.11 illustrates an example for which products have been produced by the laser jet method. The ketone x shown in Scheme 8.11 is stable to low intensity light (fluorescent tubes in the UV region). However, when irradiated with an Argon ion laser under laser jet conditions, it yields the product shown in Scheme 8.11 believed to be derived via T₂.³¹

Scheme 8.11

Laser jet experiments take advantage of the high power of modern CW lasers; a similar technique, suited for pulsed lasers, has also been developed: the laser-jet drop technique synchronizes the drops falling from a needle with the pulse from a laser, thus concentrating the power in a small drop (just a few microliters) and achieving a similar result as the laser-jet method.³²

Stern-Volmer Analysis of Photochemical Kinetics; Lifetime-Concentration Measurements

A Stern-Volmer analysis of photochemical kinetics postulates a reaction mechanism which involves a competition between an inherent unimolecular decay of *R and a bimolecular quenching by Q as shown in Eqs 8.20 and 21.
Unimolecular decay of $R^*$

$$\begin{align*}
R^* & \xrightarrow{k_t} \text{product} \\
\text{(8.20)}
\end{align*}$$

Quenching of $R^*$ by $Q$

$$\begin{align*}
R^* + Q & \xrightarrow{k_q} \text{quenching of } R^* \\
\text{(8.21)}
\end{align*}$$

The simplest situation is one in which these are the only two processes that occur. The lifetimes of $R^*$ in the absence and presence of $Q$ are given by Eqs. 8.22 and 8.23.

**Lifetime of $R^*$, no quencher**

$$\frac{1}{\tau_1} = k_1 \tag{8.22}$$

**Lifetime of $R^*$, quencher present**

$$\frac{1}{\tau_2} = k_1 + k_q[Q] = \frac{1}{\tau_1} + k_q[Q] \tag{8.23}$$

In Eqs. 8.22 and 8.23, $k_{\text{expt}} = \tau$ is the experimental rate constant for decay of $R^*$ determined by first order kinetic analysis, i.e., by treating the transient decay as a monoexponential function; $\tau_1$ and $\tau_2$ refer to the values of the lifetime of $R^*$ in the absence and presence of quencher, respectively.

As an exemplar, consider the quenching of $R(T_1)$ of xanthone in the presence and absence of 9 mM pyridine, used as a quencher. The experimental lifetimes of xanthone in the presence and absence of pyridine are measurable, as illustrated in Figure 8.5.
Figure 8.5: Decay of triplet xanthone monitored at 600 nm following 355 nm laser excitation in acetonitrile. The faster decay process is in the presence of 9 mM pyridine. Quenching is due to charge-transfer interactions such as those discussed in Chapter 7.

The value of $k_q$ can be obtained by plotting $k_{\text{expt}}$ as a function of $[Q]$. The slope of such plot is equal to $k_q$ in units of $M^{-1} \text{s}^{-1}$, i.e., the units of a second order rate constant. Figure 8.6 shows representative plots for the quenching of xanthone and azaxanthone triplets by pyridine in acetonitrile. The rate constants derived from it are $7.23 \times 10^6$ and $7.75 \times 10^7 \text{M}^{-1} \text{s}^{-1}$, for xanthone and azaxanthone, respectively.33
Figure 8.6 Quenching of the triplet states of xanthone and azaxanthone by pyridine in benzene, following 337 nm laser excitation.

The examples of Figures 8.5 and 8.6 are based on transient absorbance data determined in laser flash photolysis measurements. In fact, any experimental parameter that is linearly proportional with the excited state concentration will serve the same purpose. Other common ones are the emission intensities due to phosphorescence or fluorescence captured as a function of time, i.e., fluorescence or phosphorescence lifetimes. We will see in the next section that steady state emission intensities can also be used to acquire kinetic information about excited states.

Comment: seek examples closer to the exemplar systems. Show the T-T spectra as inserts.

Stern-Volmer Quenching: Efficiency versus Concentration Measurements

If an excited state, *R, undergoes a unimolecular reaction in competition with other unimolecular excited state processes, such as emission, both the emission efficiency and the reaction efficiency can be measured. Often the excited state lifetime of can also be measured by monitoring either the decay of the emission of the absorption of *R. From the expressions
for reaction efficiency under steady-state excitation (Eqs. 8.24 and 8.25), we note that measurement of $\phi_e$, $\phi_r$, and $\tau_\Lambda$ allow evaluation of $k_e$ and $k_1$.

$$R^* \xrightarrow{k_e} R + \text{light} \quad \phi_e = \frac{k_e}{k_e + k_1} = k_e \tau_R$$ (8.24)

$$R^* \xrightarrow{k_1} \text{products} \quad \phi_R = \frac{k_e}{k_e + k_1} = k_e \tau_R$$ (8.25)

If $\tau_R = 1/(k_e + k_1)$ cannot be measured directly, indirect methods of determining $k_1$ are possible. For example, since the value of $k_e$ may be approximated, from the theoretical relationship (Eq. 4.x) between a radiative rate constant and the absorption spectrum, $\tau_R$ may be estimated from a measured value of $\Phi_e$ and a calculated (theoretical) value of $k_e$. From the measured value of $\Phi_e$ and estimated value of $\tau_R$, $k_1$ can be determined; thus, effectively using a variation of the “clock” method already mentioned.

A second indirect method of evaluating $k_1$ employs specific bimolecular quenching by a quencher whose rate constant is known or can be readily approximated. Either $\phi_e$ or $\phi_r$ may be determined as a function of quencher concentration. Assuming a simple competition between emission, reaction, and quenching, Eqs. 8.26 and 8.27 hold for emission and reaction in the presence of quencher $Q$:

$$\phi_e = \frac{k_e}{k_1 + k_e + k_q[Q]} \quad \text{rate of emission of } R \quad \text{total rate of deactivation of } R$$ (8.26)

$$\phi_R = \frac{k_1}{k_1 + k_e + k_q[Q]} \quad \text{rate of reaction of } R \quad \text{total rate of deactivation of } R$$ (8.27)

If we define the quantum yields of emission or reaction in the absence of $Q$ as $\Phi_e^0$ and $\Phi_r^0$ we have Eqs. 8.28 and 8.29:
Thus, a plot of the relative efficiencies of emission in the presence or absence of a quencher (or of reaction in the presence or absence of quencher) versus $[Q]$ is predicted to yield a straight line of slope equal to $k_q \tau_R$ and intercept equal to 1 (see Fig. 8.8 later on for an example).

It is desirable to employ a quencher whose rate constant $k_q$ can be estimated (Section 8.xx). In such cases, a value of $\tau_R$ is available from the experimental values of $k_q \tau_R$ and the estimated $k_q$. From independent measurement of $\phi_R$, a value of $k_1$ is available. A common situation where $k_q$ can be readily estimated is the case where quenching involves exothermic energy transfer, where $k_q$ frequently approaches the diffusion control rate; in this case $k_q$ is largely determined by the viscosity of the solvent (see Chapter 7). Figure 8.7 shows a representative example of the use of the Stern Volmer equations as described above.

**Figure 8.7 quenching plot based on luminescence here (Sandros??)**

Figure 8.7 is not on the page with all the figures

If the photochemical reaction of $^*R$ is bimolecular, the same general situation holds, except that $k_1$ is replaced throughout by $k_2[M]$, where $k_2$ is the bimolecular rate constant for reaction of $A^*$ and $[M]$ is the concentration of substrate $M$ reacting with $A^*$.

In this analysis for low conversion to products, we assume that $[M]$ does not change significantly during the measurement; accordingly, this concentration is treated as a constant.

**Stern-Volmer Analysis Based on Data from Gated Detection**

A special situation arises when a detection system reports signals that, while appearing as a “continuous” (or CW) measure, they have in fact been acquired at a fixed time following excitation by a pulsed source. This situation is common nowadays when many commercial
spectrofluorimeters employ pulse light sources for excitation. This measurement approach enhances the capabilities of the instrument, for example, by allowing the selective detection of phosphorescence in the presence of strong fluorescence, by delaying the detection until the short-lived fluorescence emission has extinguished. Figure 8.8 illustrates an example of this type of “gated” detection.

![Diagram of gated detection]

**Figure 8.8**: Schematic representation of a luminescence decay monitored using gated detection. The instrument “reads” the emission after a time $t_d$ following excitation, averaging the signal for a short time.

For the purposes of our analysis we will assume that the duration of the excitation pulse and of the detection gate are short compared to the lifetime of the excited state, $^*R$. Addition of a quencher $Q$ will shorten the lifetime of the excited state $^*R$ in the same way as shown in equations 8.20 and 8.21, while equation 8.17 (check equations) will govern the change in concentration of $^*R$ with time and of the signal from $^*R$, for example, the emission intensity, $\Phi_e$.

If the detection takes place immediately after the excitation pulse, the emission intensities with and without quencher would be the same, since at that point all the excited molecules $^*R$ generated will still be present. By analogy, in Figure 8.8 the amplitude of the
signal with and without quencher is the same. The emission intensity at time t in the absence and presence of Q will be given by:

\[ I_t^o = I_{t0}^o \exp(-k_d t_d) \quad (8.30) \]

\[ I_t^Q = I_{t0}^Q \exp((-k_d + k_q[Q]) t_d) \quad (8.31) \]

where the superscripts “o” and “Q” refer to the absence and presence of Q and the subscripts “o” and “t” refer to time zero and t, respectively. The ratio of emission intensities is then given by

\[ \frac{I_t^o}{I_t^Q} = \exp(\tau_d k_q[Q]) \quad (8.32) \]

or

\[ \ln \left( \frac{I_t^o}{I_t^Q} \right) = \tau_d k_q[Q] \quad (8.33) \]

Interestingly, this “gated” Stern Volmer equation takes an exponential form and does not incorporate the lifetime of the excited state. Therefore, with an instrument that incorporates this capability it is possible to determine rate constants, such as \( k_q \), without a prior, independent knowledge of excited state lifetimes.

8.8 Experimental Examples of the Measurements of Photochemical Rate Constants

As typical examples of the use of Stern-Volmer analysis to determine rate constants, we shall discuss (a) a unimolecular photoreaction for which the excited state does not emit
measurably, and (b) a bimolecular photoreaction for which emission of the reactive excited state is measurable.

An example of case (a) is the exemplar Type II intramolecular hydrogen abstraction reaction of phenyl alkyl ketones (Eq. 8.4 and 8.5). As described earlier in this Chapter, the mechanism of this reaction involves intramolecular hydrogen abstraction by the T₁ (n,π*) state of the ketone. The T₁ state may be specifically quenched as the result of electronic energy transfer by 1,3-dienes with a rate constant close to that for diffusion controlled reactions. The details of the mechanism of the quenching mechanism are not of direct interest in a Stern-Volmer analysis as long as the quenching products do not interfere with the analysis (e.g., by competing with the reactive state for light absorption, by being quenchers themselves, etc.).

The quantum yield for a Type II reaction may be measured in terms of the efficiency of disappearance of reactant or appearance of products. Let Φ₀ be the quantum yield of Type II reaction measured in the absence of 1,3-diene, and Φ_q be the quantum yield measured in the presence of 1,3-diene. A typical plot of Φ₀/Φ_q versus [1,3-diene] is shown in Figure 8.10.

![Figure 8.10](image)

Experimental plot of Φ₀/Φ_q versus [1,3-pentadiene] for the Type II reaction of triplet butyrophenone (Eq. 8.3, R₁ = R₂ = H). The data follows Eq. 8.28 within experimental error. The intercept is 1.0 and the slope is 700 M⁻¹. Data taken from Kocietar, I. E. H., PhD Dissertation, Michigan State University, 1970. See also Reference 6b.

**Figure 8.10 (above).** This was Fig. 8.2 in MMP.

If only one excited state is quenched by the diene, then the intercept of the plot will be 1.0 and the slope of the plot will be linear and equal to kₚτₚ, according to Eq. 8.29.
Experimentally, the slope of a plot of $\Phi_0/\Phi_q$ versus [1,3-diene] is linear and the intercept is 1.0 (Figure 8.10), thereby supporting the assumed mechanism. The value of $k_qt_R$ for the specific case of butyrophenone (Eq. 8.4, $R_1 = R_2 = H$) in acetonitrile is 700 M$^{-1}$. The maximum value of $k_q$ for quenching of a $T_1(n,\pi^*)$ state is that for the rate constant for diffusion in acetonitrile. Thus, if $k_q = 10^{10}$ M$^{-1}$ s$^{-1}$ (a maximum value for acetonitrile), then $\tau = 700/k_q = 7 \times 10^{-8}$ s (minimum value). The minimum value for the rate constant $k_1$ is equal to $1/\tau$. Therefore:

$$k_1^{\text{min}} = 1/\tau = 1.4 \times 10^7 \text{ s}^{-1} \quad (8.34)$$

The confidence that can be placed in the value of $k_1$ depends on the confidence that can be assigned to the selection of a value of $k_q$. In this case the confidence level is high because for $T_1(n,\pi^*)$ states such as acetophenone, acetone, or benzophenone the value of $k_q$ for a 1,3-diene as quencher may be measured by direct quenching of the phosphorescence and/or the transient absorption due to the triplet state. Such determinations support the assumptions made here. Hug et al.$^{34}$ have reported a detailed compilation of $k_q$ values for triplet states under a variety of conditions which should provide an extensive data base to which Stern-Volmer studies of the type described above can be related.

Note that while equation 8.28 and 8.29 and Figure 8.10 have been expressed in terms of quantum yields ($\Phi$), in fact it is not necessary to measure actual quantum yields. A convenient property of the Stern-Volmer equation is that the ratio of any property that is proportional to the quantum yield can be employed. This may include emission intensities in arbitrary units, chromatographic peak areas, NMR signal integrals, or the amplitude of a transient absorption signal.

We may wonder at this point if traditional indirect techniques such as Stern-Volmer analysis are necessary, when excited states can be observed directly, as illustrated in Figure 8.5 and exemplified for the case of triplet xanthone in Figure 8.6. However, in the case of butyrophenone discussed above, the direct measurement is difficult to interpret because both the triplet state and the diradical (see reactions 8.4 and 8.5) both absorb in the same spectral region and emission from the triplet state (phosphorescence) is too weak for adequate kinetic analysis. However, time resolved techniques, such as laser flash photolysis can still be employed, by using an approach which is very similar to the Stern-Volmer method just discussed. For
example, the triplet state of butyrophenone (\(^*\text{R}\)) – but not the diradical (I)- can also be quenched by naphthalene or its substituted derivatives. The quenching process leads to energy transfer (discussed in detail in the next chapter), as illustrated in reaction 8.35. Naphthalenes (1-methylnaphthalene is usually preferred for these studies because it is a liquid) have a strong triplet-triplet absorption around 420 nm and can be easily monitored with laser flash photolysis techniques. Furthermore, naphthalenes possess a triplet energy that is lower than that of most ketones, so that energy transfer from ketone triplets is expected to occur at near the diffusion controlled limit. Thus, at sufficiently high concentrations of naphthalene, energy transfer competes with the Norrish Type II process of reactions 8.4 and 8.5 and the long lived triplet of naphthalene is produced, which, for practical purposes is “stable” in the time scale of the experiment.

\[
\text{Butyrophenone triplet} + \text{1-Methylnaphthalene ground state} \rightarrow \text{Butyrophenone ground state} + \text{1-Methylnaphthalene triplet} \quad (\sim 420 \text{ nm absorption})
\]

The signal due to triplet 1-methylnaphthalene (MeN*) can be easily monitored, as shown in the inset in Figure 8.11. The formation of MeN* obeys pseudo-first order kinetics and the concentration of MeN* produced after energy transfer is complete is given by:

\[
[MeN^*]_\infty = \frac{k_q[MeN]}{\tau_0 + k_q[MeN]}[BTP^*]
\]

Where \(\tau^0\) is the lifetime of the butyrophenone triplet (BTP*) in the absence of 1-methylnaphthalene; the first term on the right side accounts for the efficiency of energy transfer. The growth of the MeN* concentration follows the expression:

\[
[MeN^*] = [MeN^*]_\infty \left(1 - e^{-t/\tau_0}\right)
\]
where \( t \) is time and \( \tau \) the triplet butyrophenone lifetime in the presence of any given concentration of quencher. While excited state concentrations can be determined by laser flash photolysis, the parameter derived directly from the experiment is \( \Delta OD \), the absorbance difference between the transient species (e.g., \( \text{MeN}^* \)) and its precursor. Equation 8.37 readily converts to equation 8.38 which is employed for the kinetic fits of traces such as that in the inset of Figure 8.11.

\[
\Delta OD_t = \Delta OD_\infty \left( 1 - e^{-t/\tau} \right) \quad \text{(8.38)}
\]

A plot of \( \tau^{-1} \) against the concentration of quencher (\( \text{MeN} \)) follows equation 8.39,

\[
\tau^{-1} = \tau_o^{-1} + kq[Q] \quad \text{(8.39)}
\]

Thus, the slope of such a plot would give \( k_q \), and the intercept the reciprocal of the triplet lifetime in the absence of quencher (\( \tau_0 \)). Unfortunately, in the case of butyrophenone a combination of overlap of triplet and diradical signal with that from triplet 1-methylnaphthalene, and the fast processes involved (see the trace in Figure nn.11) makes this approach inconvenient, which suggests that to take advantage of another quenching resource.

The following figure will be replaced
Figure 8.11: Quenching plot showing the rate constant ($k_{\text{growth}}$) for the formation of the 420 nm signal due to triplet 1-methylnaphthalene following 355 nm laser excitation of butyrophenone in xxx containing various amount of quencher. 1-Methylnaphthalene is transparent at 355 nm and can only be excited by energy transfer. The inset shows a representative laser flash photolysis trace in the presence of xx mM 1-methylnaphthalene, monitored at 420 nm.

The same experiment as in Figure 8.11 also yields a value for the absorbance due to the 1-methylnaphthalene triplet ($\Delta OD_{\infty}$) for each concentration of quencher employed. If we plot the reciprocal of equation 8.36, we obtain:

$$\frac{1}{[MeN^*]_0} = \left(1 + \frac{1}{k_q \tau_0 [MeN]} \right) \frac{1}{[BTP^*]_0}$$

(8.40)

In terms of $\Delta OD_{\infty}$, Eq. 8.40 readily converts to Eq. 8.41.

$$\frac{1}{\Delta OD_{\infty}} = a + \frac{a}{k_r \tau_0 [MeN]}$$

(8.41)
In Eq. 8.41, \( a \) is a constant which is a function of \([\text{BTP}^*]_0\) and the extinction coefficient of triplet 1-methylnaphthalene. Fortunately, it is not necessary to evaluate these parameters separately, since the ratio of intercept-to-slope (shown in Figure 8.12) gives \( k_q \tau_0 \), the same parameter as that obtained in the Stern-Volmer analysis of equation nn.31. Figure 8.12 yields \( k_q \tau_0 = 3300 \text{ M}^{-1} \). Since the value of \( k_q \) for this type of energy transfer reaction is known to be around \( 10^{10} \text{ M}^{-1} \text{ s}^{-1} \), we can estimate the lifetime of the triplet state of butyrophenone as ca. 330 ns.

Figure nn.12: Stern-Volmer-type plot according to equation 8.41 for the quenching of butyrophenone triplets by 1-methylnaphthalene in acetonitrile. The insert shows the growth of the naphthalene triplet monitored at 420 nm following 355 nm laser excitation of a sample containing 0.085 M quencher. The initial fast growth, essentially an absorption jump is due to some absorption by the butyrophenone triplet at this wavelength. Given the fast intersystem crossing that characterizes aromatic ketones, the triplet state is formed essentially instantaneously in this time scale.
As a second example, consider the reaction of $S_1(n,\pi^*)$ of acetone and 1,2-dicyanoethylene (DCE). In this case the easily measured fluorescence of acetone is used to monitor the $S_1(n,\pi^*)$ state. The fluorescence of acetone is quenched by DCE and an oxetanone (1) is formed as a product:

$$
\text{O}\overset{\cdot}{=}\text{CN} + \overset{\cdot}{\text{CN}} \text{CN} \rightarrow \overset{\cdot}{\text{CN}}\overset{\cdot}{\text{CN}}
$$

A plot of $\Phi_F^0/\Phi_F$ vs. [DCE] is linear (see Figure nn.13) with intercept equal to 1.0 and slope equal to 7 M$^{-1}$. Thus, the value of $k_q\tau$ is equal to 7 M$^{-1}$. The lifetime of the acetone singlet state is readily measured from the decay of its fluorescence and equals $2 \times 10^{-9}$ s. Thus, $k_q$ is given by: $k_q = 7/(2 \times 10^{-9}) = 3.5 \times 10^9$ M$^{-1}$ s$^{-1}$.
Figure 8.13: Experimental plot of $\Phi_0/\Phi$ versus [trans-1,2-dicyanoethylene] for the cycloaddition of acetone singlets to the ethylene (Eq. nn.42). The data follow Eq. nn.29 within the experimental error. The intercept is 1.0 and the slope is $7 \text{ M}^{-1} = k_q\tau$.

**Measurement of Absolute Efficiencies in Determining Kinetic Parameters**

In a Stern-Volmer analysis in which relative efficiency is measured, information concerning absolute efficiencies is lost. Although the maximum rate constant for quenching or unimolecular reaction is established by this type of analysis, the absolute rate for the process of interest is not established unless the absolute efficiency is known. For example, the limiting absolute quantum yield $\Phi$ for addition of acetone to DCE is about 0.10. This means that even if every $S_1(n,\pi^*)$ state is quenched by DCE, only 10% of the quenched singlets proceed to product. This conclusion, in turn, requires a bimolecular quenching pathway of $S_1$ by the alkene which does not lead to oxetane.

Experimentally, a plot of $\Phi$ versus quencher concentration will yield a limiting value of $\Phi$, as expected from Eq. 8.43.

$$\Phi = a \frac{k_2[B]}{k_D + k_q[B]}$$

In Eq. 8.43, $a$ = efficiency of formation of $^*R$, $k_2$ is the rate constant for bimolecular reaction leading to the oxetane of reaction nn.42, $k_q$ is the rate constant for all imolecular quenching (i.e., reaction and other bimolecular deactivation of $^*R$, and $k_D$ is the rate constant for inherent rate of unimolecular deactivation of $^*R$. A plot of $\Phi$ versus [B] yields a curve which flattens out to a limiting value when $k_q[B] >> k_i$. The value of $\Phi$ for the plateau is related to $a$, $k_2$, and $k_q$ by:

$$\Phi = a \frac{k_2[B]}{k_q[B] >> k_D} = ak_2/k_q$$

Note that the value of $k_q$ would equal $k_2$ if all quenching events lead to products. Thus, measurement of evaluation of $\Phi$, $a$, and $k_q$ are necessary to evaluate $k_2$. In the case of acetone
and DCE, since the reactive state is \( S_1(n, \pi^*) \), we may assume that \( a = 1.0 \) (Kasha’s Rule).

From the Stern-Volmer quenching analysis we found that \( k_q = 3.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1} \). Since \( \Phi \) in the limit equals 0.1, we calculate \( k_2 = 3.5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1} \).

A second method may be used to handle the quantum yield data. There is “kinetic information” in the curved plot of \( \Phi \) versus \([B]\). To extract this information it is convenient to invert the expression for \( \Phi \) as shown in Eq. 8.45.

\[
\frac{1}{\Phi} = \frac{k_q[B] + k_d}{a k_2[B]} = \frac{1}{a} \left( \frac{k_q}{k_2} + \frac{k_d}{k_2[B]} \right)
\]  

Now a plot of \( 1/\Phi \) versus \( 1/[B] \) (see Figure 8.8) is predicted by Eq. 8.45 to yield a straight line with slope equal to \( s = k_q/ak_2 \) and intercept of \( I = k_q/ak_2 \).

\[
\frac{1}{s} = \left( \frac{k_q}{a k_2} \right) \left( \frac{a k_2}{k_d} \right) = \frac{k_q}{k_d} = k_q \tau
\]

Figure 8.14: Experimental plot of nn.45 addition of acetone singlet to DCE (Eq. 8.42).
Note the similarity between equation 8.46 and the analysis of Eq. 8.36 used for the data in Figure 8.7.

In the case of reaction from $S_1$, this product, $k_{q_1}$, is the same product we derive from a Stern-Volmer analysis employing relative fluorescence efficiencies (Eq. nn.28). Thus, in the case of oxetane formation between acetone and DCE, we predict that the mechanism of fluorescence quenching is the same as that for oxetane formation. The value of intercept/slope from a plot of $1/\text{ versus } 1/[\text{DCE}]$ will equal $\sim 7 \text{ M}^{-1}$.

**Kinetics of Reactions Involving More than One Excited State**

In some photoreactions both $S_1$ and $T_1$ undergo the same chemical transformation. In such cases consideration of differential quenching of the two states is necessary if kinetic information is to be extracted. For example, both $S_1$ and $T_1$ of alkanones (e.g., 2-hexanone) undergo Type II reactions (in contrast with aromatic ketones where only the triplet shows significant reactivity).

![Diagram of alkanone reaction](nn.47)

Experimentally, 1,3-dienes are found to quench $T_1(n,\pi^*)$ states of alkanones with rate constants approaching those for diffusion $k_q \sim 10^9$-$10^{10} \text{ M}^{-1} \text{ s}^{-1}$), but the values of rate constants for quenching of $S_1(n,\pi^*)$ states of alkanones are much smaller ($k_qS \sim 10^7 \text{ M}^{-1} \text{ s}^{-1}$) since the singlet energy of naphthalene is much higher than the singlet energy of an alkanone. Thus, given a concentration of diene, the relative rates of quenching of $S_1$ and of $T_1$ are:
The efficiency of quenching of $S_1$ relative to $T_1$ is given by Eq. 8.49.

\[
\frac{\phi_{qS}}{\phi_{qT}} = \frac{k^S_q \tau_q}{k^T_q \tau_T} \tag{8.49}
\]

Since $\tau_T$ is generally larger in value than $\tau_s$, $\Phi_{qT}^T >> \Phi_{qS}^S$, i.e., $S_1$ is less efficiently quenched than $T_1$. The situation is similar to that we already encountered in the reaction of acetone with isopropanol (Eq. 8.11) where the triplet reaction over singlet reaction because of the short singlet lifetime.

The kinetic expressions for systems in which more than one state reacts are quite complicated and will not be derived here (Reference to Wagner, other reviews). However, the form of the experimental Stern-Volmer plot may be derived intuitively (Fig. 8.15, left).

Suppose differential quenching of the triplet portion of the Type II reaction of an alkanone may be achieved with a 1,3-diene as quencher. To the first approximation we can assume that at high concentrations of diene all the triplets will be selectively quenched and that none of the singlets will be quenched. In this limiting case, the value of $\Phi_q / \Phi_q$ will reach a limiting value corresponding to the reaction of the singlets and will not vary with $[Q]$ at sufficiently high concentration of Q. On the other hand, at low $[Q]$, both $S_1$ and $T_1$ will react, but only $T_1$ will be quenched. Thus, we expect that the form of the experimental plot of $\Phi_q / \Phi_q$ versus $[Q]$ will be a curve for low $[Q]$ which then plateaus at high $[Q]$. Equation 8.50 shows an example where this type of behavior is observed.

\[
\text{reaction occurs from both } S_1 \text{ and } T_1
\]
Figure nn.15: Experimental example of selective quenching – a situation in which both S₁ and T₁ undergo the same reaction. The Norrish Type II reaction of 2-n-propylcyclohexanone (see Eq. 8.50) is quenched by 1,3-pentadiene. The left plot is a simple Stern-Volmer plot according to equation 8.26, while the plot on the right side uses values that have been corrected according to equation 8.51.

We can estimate the contribution of the singlet state to $\Phi_q$ by determining the plateau value in Figure nn.15. The value obtained is $\sim 1.40$ (which is easier to determine from a double reciprocal plot). With this information in hand, we can now correct the $\Phi_q / \Phi_0$ values to eliminate the singlet component, according to the following expression:

$$\frac{\Phi_q}{\Phi_0} - \frac{1}{\text{plateau value}} = \frac{\Phi_T}{\Phi_0^T}$$ (8.51)

The values thus obtained can be used to obtain $\Phi_q / \Phi_0^T$ exclusively for the triplet reaction. The reciprocal of these values are the plotted (Figure nn.15, right) in the standard Stern-Volmer way to lead to $k_q^T = 11 \text{ M}^{-1}$. If we assume the value of $k_T \tau \sim 10^{10} \text{ M}^{-1} \text{ s}^{-1}$, then $\tau_T = 1.1 \times 10^{-9} \text{ s}$ or 1.1 ns.

Wagner has provided a number of rules for the quantitative interpretation of the curvature in Stern-Volmer plots. The complex equations which can be derived for cases
involving more than one excited state can be interpreted in terms of the rules in Table 8.6. The criteria of Table 8.6 are thus an integral component of the paradigm of organic photochemistry.

**Table 8.6:** Possible forms of Stern-Volmer quenching plots.\(^{36}\)

<table>
<thead>
<tr>
<th>Plot Type</th>
<th>Cause</th>
</tr>
</thead>
</table>
| A) Linear | 1) Only one excited state reacts;  
2) Two rapidly equilibrating excited states with either or both quenched.  
3) Two non-interconverting states coincidentally quenched with the same value of \(k_q\);  
4) The first of two consecutively formed states is quenched, with either one reacting; |
| B) Downward Curvature | 1) Reaches a zero slope. Two reactive excited states, but only one is quenched;  
2) Reaches a positive asymptotic slope. (a) Two non-interconverting excited states quenched with different \(k_q\) values, or b) Two interconverting excited states with the shorter lived or both reacting; the quencher disrupts the interconversion equilibrium. Final slope corresponds to initial shorter state. |
| C) Upward Curvature | 1) Two consecutive excited states are quenched, but only the second one is reactive;  
2) Two non-interconverting excited states are both reactive and quenched with different \(k_q\) values;  
3) Two interconverting excited states, with only the lower one reactive and with the quencher disrupting the interconversion equilibrium  
4) Same as B2  
5) A sensitized reaction with both sensitizers and substrate states quenched. |
The Probe Method for Detecting “Invisible” Transients.

Can laser techniques be employed to determine the rate constant for a reaction where all the reagents and all the products are “invisible” to the detection technique used? The answer is “yes”, and the “probe technique or probe method” for tracking “invisible” transients has found wide application in studies of a wide range of excited states and reaction intermediates.

We will illustrate the probe technique with the example of photogenerated tert-butoxyl radicals, for which it was originally introduced. For example, if we want to study the reaction of tert-butoxyl with 1,7-octadiene, as in reactions 8.52 and 8.53, we may find that for practical purposes all the participants are transparent in the region above 350 nm where absorbance monitoring is possible when using 337 nm laser excitation. This was the wavelength available for those experiments, and at the concentrations of peroxide required, the solution is not transparent at shorter wavelengths. The probe method requires the identification of a substrate that, upon reaction, will yield a readily detectable signal in the spectral region accessible. Diphenylmethanol is a convenient choice, since it is a good hydrogen donor and by reaction with tert-butoxyl (reaction 8.54) yields the ketyl radical from benzophenone, one of the best characterized reaction intermediates, with a characteristic and strong absorbance at 535 nm. Thus, it is straightforward to monitor the formation of this radical, as is shown in the insert in Figure 8.16. In the presence of both, the probe (PH) and the substrate (SH), the growth can be fit with an exponential expression that yields \( k_{expt} \) (Eq. 8.55), which is, in turn, can be related to the rate constants of interest according to Eq. 8.56.
where \( A \) and \( A_t \) are the absorbances due to the probe radical in the plateau region and at time \( t \), respectively, \( SH \) is the substrate (1.7-octadiene) and \( PH \) is the probe, diphenylmethanol in this case. The rate constant \( k_0 \) includes all modes of decay of tert-butoxyl in the absence of both \( SH \) and \( PH \). Thus, by keeping the concentration of \( PH \) constant and varying that of \( SH \), it is possible to determine \( k_{SH} \) from a plot of \( k_{expt} \) against \([SH]\) as shown in Figure 16.

\[
\text{Figure 8.16: Evaluation of } k_{RH} \text{ using equation nn.xx for 1,7-octadiene (D), cumene (and for diphenylmethanol 0.17 and 0.099 M), and toluene (and for diphenylmethanol 0.167 and 0.888 M). Data recorded following 337 nm laser excitation in benzene:tert-butyl peroxide at room temperature.}^5 \text{ The insert shows the formation of ketyl radical in the presence of 0.069 M diphenylmethanol and no substrate.}
\]

Note that in Figure 8.16 the data have been plotted as \( k_{expt} - (k_0 + k_{PH}[PH]) \) in order to show that the slope is independent of the probe concentration. The term \( k_0 + k_{PH}[PH] \) is readily obtained, since it represents the experimental value of \( k_{expt} \) in the absence of \( SH \). Many of the values in Table 8.5 were obtained using the probe methodology.
Is something lost in the process of determining rate constants with this indirect “probe” technique? While the kinetic information is generally quite accurate, it is clear that this method provides no information on the mechanism for reaction. For example, the reaction shown in Eq. 8.53 has been written as an abstraction of an allylic hydrogen. The experiment only tells us that tert-butoxyl reacts with 1,7-octadiene with a rate constant of \(2.3 \times 10^6 \text{ M}^{-1} \text{s}^{-1}\), but the form or site of reaction must be established independently, perhaps from product studies, or because the paradigm of free radical reactivity tells us that allylic hydrogens are generally more reactive than other positions, or other reactions such as addition to the double bonds.

**Experimental Measurement of the Efficiency of Radiationless Processes. The Photoacoustic Method.**

Many radiationless processes, such as internal conversion, intersystem crossing, or reversible photoreactions, are, because of their very nature, not associated with accompanying emission processes and/or permanent chemical change. The efficiency of such radiationless processes has traditionally been determined from the deficiency of the balance the over quantum yield of other detectable processes. Radiationless processes of different origins have in common the fact that they result in the release of energy to the medium in the form of heat. This release of heat results in two different types of phenomena generally discussed as photoacoustic and photothermal effects.\(^\text{37}\)

Let us assume that a pulsed light source (such as a laser) leads to a rapid local deposition of energy in a small portion of a solution. Some of this energy will be converted into heat (the remainder being used to induce chemical change and/or emission of light). This rapid local release of heat within the sample results in the generation of a pressure or acoustic wave which travels within the solution at the speed of sound and can be detected by a suitable pressure-sensitive detector (a microphone!) coupled to the sample. The amplitude of this photoacoustic signal is proportional to the heat released within the time response of the detector. The technique which measure the heat released are termed photoacoustic spectroscopy and have been used for a variety of purposes including the determination of intersystem crossing yields and efficiencies of internal conversion. Further, by devising
relationships between enthalpies of reaction and energy deposited in the system it has also been possible to determine bond dissociation energies by photoacoustic spectroscopy.

Laser-induced photoacoustic (also called optoacoustic) calorimetry relies on a simple calorimetric balance as expressed by Eq. 8.57:

\[
\text{laser energy} = \text{energy emitted as light} + \text{energy used for chemical change} + \text{energy released as heat}
\]

Numerous systems have been examined using photoacoustic spectroscopy, which can yield information on both the thermochemical and volume changes involved in photochemical processes, as well as information on the reaction kinetics. The latter can sometimes be independently verified using conventional laser flash photolysis techniques. For example, the photochemistry of the donor-acceptor system of Figure 8.17 has been studied using this the photoacoustic technique. The amplitude and phase of the attenuated photoacoustic wave contain information on both the thermochemistry and volume changes, that in this case relate to intramolecular exciplex formation (see Chapter 4.x). Figure 8.17 also shows the proposed structures of the ground and excited states. Thus, excitation leads to a negative change in the molar volume, \(\Delta V\), a result of both molecular contraction and solvent reorganization.
Figure 8.17: Photoacoustic wave obtained following 308 nm laser excitation of the donor-acceptor in n-pentane, and below the proposed conformation for the ground state (left) and the exciplex (right). The “reference”, ortho-hydroxybenzophenone is a molecule that converts light into heat rapidly and quantitatively. The fact that the amplitude for the reference is larger than from the sample means that less heat is released in the latter; this energy has been “stored” by the photoinduced chemical transformation. [Wegewijs, 1996 #133].

In addition to acoustic phenomena, local heat deposition also induces a temperature change which causes changes in the density and refractive index of the solution. The solution in this region behaves as a divergent lens, and any light passing through the solution will be defocused leading to a decrease in the beam brightness. This effect is referred to as thermal blooming or thermal lensing. The signals obtained in this manner can be calibrated to obtain information of the heat released by a reaction.39

8.9. Reactive Intermediates: Experimental Detection and Characterization

As we have noted, the use of experimental methods for characterizing the transient and *R and I (which we will term as reaction intermediates for the purpose of this discussion) are
of fundamental importance in establishing photochemical reaction mechanisms. Three general
types of experimental methods are commonly employed for identification and characterization
of non-isolable or transient intermediates that cannot be isolated by “conventional” techniques:
(a) spectroscopic methods, which employ the absorption or emission of light by \(*R\) and the
absorption of light by \(I\); (b) chemical methods, which employ some characteristic chemical
reaction with known structural factors that are related to mechanism (such as regiochemistry
and stereochemistry of \(P\)); and (c) kinetic methods, which employ some characteristic behavior
of concentration of a \(*R\) or \(I\) as a function of time.

The most important types of spectroscopic techniques available for the detection of
organic reaction intermediates are:

1. **Electronic spectroscopy**, involving the absorption or emission of UV or visible light as
   the result of electronic transitions.

2. **Vibrational spectroscopy**, involving the absorption of infrared light as the result of
   vibrational transitions.

3. **Magnetic resonance spectroscopy**, involving the absorption of microwave radiation as
   the result of electronic spin transitions (ESR) or the absorption of radio frequency
   radiation as the result of nuclear spin transitions (NMR).

Table 8.7 provides an outline of the methods frequently employed in the study of
reaction intermediates \(*R\) and \(I\).

**Table 8.7: Methods for the Study of Reaction Intermediates**

<table>
<thead>
<tr>
<th>Method</th>
<th>Basis</th>
<th>Characteristics and uses</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kinetic absorption spectroscopy</td>
<td>Optical absorption of intermediate</td>
<td>Can be used for almost any intermediate which possesses a reasonable extinction coefficient at a detectable wavelength. Time resolution is as short as femtoseconds. Nanosecond and picosecond laser flash photolysis is the most widely used of this group of techniques.</td>
</tr>
<tr>
<td>Emission</td>
<td>Radiative</td>
<td>Excited states with significant radiative yields (usually fluorescence)</td>
</tr>
<tr>
<td>Method</td>
<td>Description</td>
<td></td>
</tr>
<tr>
<td>------------------------</td>
<td>-----------------------------------------------------------------------------</td>
<td></td>
</tr>
<tr>
<td>Spectroscopy (processes)</td>
<td>or phosphorescence). From femtoseconds and up.</td>
<td></td>
</tr>
<tr>
<td>ESR (also called EPR)</td>
<td>Electron spin Useful for paramagnetic intermediates. Radicals in solution and matrices. Triplet states (excited triplets, carbenes, diradicals) usually in matrices at cryogenic temperatures. Nanoseconds and longer.</td>
<td></td>
</tr>
<tr>
<td>CIEDEP</td>
<td>Electron spin polarization As above for ESR, but providing a signature for the processes leading to the intermediate, with time resolution in the vicinity of 100 ns to 100 μs.</td>
<td></td>
</tr>
<tr>
<td>CIDNP</td>
<td>Nuclear spin polarization Polarization effects of NMR of products contains information on the precursors (see Chapter zz)</td>
<td></td>
</tr>
<tr>
<td>Matrix isolation</td>
<td>Long lifetime of intermediates Traditionally used at cryogenic temperatures, although isolation in supra-molecular systems can also be employed. Most useful for intermediates without an intrinsic lifetime; i.e. better for radicals than for triplet states. Excellent for diagnostic purposes, limited for reactive processes</td>
<td></td>
</tr>
<tr>
<td>Thermal methods</td>
<td>Calorimetric balance Includes photoacoustic calorimetry and thermal lensing. Allows for thermochemical studies on reaction intermediates, as well as kinetic studies (usually 10 ns and up). Normally requires knowledge of quantum yields and simple and well understood chemical processes.</td>
<td></td>
</tr>
<tr>
<td>Conductivity</td>
<td>Ion concentration changes Same principles as normal conductivity. Useful for photoionizations, electron transfer and heterolytic cleavages. Submicrosecond time resolution.</td>
<td></td>
</tr>
<tr>
<td>Light scattering</td>
<td>Light scattering Useful for large molecules or molecular aggregates, particularly polymers.</td>
<td></td>
</tr>
<tr>
<td>Chemical trapping</td>
<td>Formation of a signature product Wide applicability, but in many cases time resolution can be lost. Not only for stable products, but also metastable intermediates that can be characterized by other methods, such as ESR (spin trapping) or laser flash photolysis (probe methods).</td>
<td></td>
</tr>
<tr>
<td>Product studies</td>
<td>Analytical techniques Same as throughout organic chemistry. Product type, stereochemistry and regiochemistry provide useful information.</td>
<td></td>
</tr>
</tbody>
</table>
In general, all methods of direct spectroscopic characterization of reactive intermediates require that the method of study have a time resolution shorter, or at least comparable to the lifetime of the reactive intermediate. This can be achieved in two general ways:

1. By making the technique sufficiently fast that it can access the time scale in which the intermediate naturally lives.
2. By isolating the intermediate under conditions where its lifetime is long enough for the technique of choice (such as in matrix isolation in Table 8.7).

Both methods have advantages and shortcomings. Isolation usually provides a better diagnostic and spectroscopic tool, but information on reactivity is lost. Method 1 closely looks at the intermediate under its reactive conditions, but some of the spectroscopic details may be lost, since time resolution usually has a price in spectral quality. Method 2 allows very detailed examination of the spectroscopy of a reactive intermediate under conditions its reactivity is “quenched”.

**Examples of the application of spectroscopic methods for determining the details of the Type I reactions of ketones.**

- Find UV of benzoyl, IR of benzoyl, EPR of benzoyl, CIDNP of products of benzoyl
- TREPR of T₁ (Matrix isolation)
- Other piece. Product detection by probe methods? Addition to ethylenes.

**Experimental Tests for Reactive Intermediates**

Reactive intermediates, *R and I*, represent a shallow minimum in the potential energy surface that describes the system under investigation. In order to qualify as a “reactive intermediate”, we shall require that such a species possess a molecular structure sufficiently stable such that its existence is subject to experimental confirmation by spectroscopic methods or chemical trapping, but that the species is too reactive to be isolated and “put in a bottle”.

This means that the structures of “true” reactive intermediates must imply an experimental test that “confirms” the structure, i.e., a potentially measurable experimental quantity which relates to the structures must exist that is consistent with paradigms that related measured experimental quantities to molecular structure. For convenience we shall classify the
observation employed for detection and characterization of reactive intermediates in terms of (a) chemical measurements or (b) physical measurements (Table 8.7).

**Experimental Tests for the Involvement of Electronically Excited Excited States: Qualitative Aspects**

Although the most definitive experimental test for the occurrence of an electronically excited state, \( ^*R \), is the observation of its emission spectrum, many excited states emit too weakly for experimental detection. For example, with rare exceptions, only the \( S_1 \) and \( T_1 \) states of organic molecules emit measurably. This means that \( S_2, S_3 \), etc., and \( T_2, T_3 \), etc., in general, cannot be detected by conventional emission spectroscopy. How does one decide if “upper excited states” are involved in photoreactions?

If a photoreaction is wavelength-independent, i.e., it occurs with the same efficiency and/or rate and yields the same products irrespective of their \( S_1, S_2, S_3 \), etc., is excited, then we conclude that a common structure is responsible for the result. Since only \( S_1 \) is energetically allowed as a common structure, we conclude that reaction does not occur from \( S_2, S_3 \), etc., and that Kasha’s Rule is obeyed. Can we conclude that reaction occurs from \( S_1 \) based solely on these results? The answer is no. The lack of a wavelength-dependence would only eliminate upper singlet levels as candidates for reaction. It would be possible for \( S_1 \) or some triplet derived from it to be the reactive state and still observe a wavelength independence of reaction.

Suppose an overall reaction, \( R + h\nu \rightarrow P \), has been found to be wavelength-independent. For simplicity, let us assume that only one triplet (\( T_1 \)) lies lower in energy than \( S_1 \), and that \( S_1 \) and \( T_1 \) exhibit different photoreactivities. How does one decide experimentally whether reaction occurs from \( S_1 \) or \( T_1 \) (or both)? Since \( T_1 \) is formed from \( S_1 \), quenching of \( S_1 \) will not prove much, since quenching of \( S_1 \) stops reaction from both \( S_1 \) and from \( T_1 \). However, two general procedures have been developed to decide whether \( S_1 \) or \( T_1 \) is the reactive state in a photoreaction:

1. Selective quenching of \( T_1 \).
2. Selective photosensitization of formation of \( T_1 \) via an energy-transfer process.

The mechanism of energy transfer and selective triplet quenching has been discussed in Chapter 7. Selective quenching of \( T_1 \) is a commonly employed technique, already discussed in
connection with the system of reaction 8.48 and Figure 8.15. In the case of ketones, 1,3-dienes and naphthalenes can frequently be used as selective carbonyl triplet quenchers.

The idea of triplet sensitization is to test if a given triplet reaction can be induced while completely bypassing the singlet manifold of that compound. Thus, for efficient and selective sensitization by energy transfer, the sensitizer should have the following characteristics:

1. Triplet energy higher than that of the molecule to be sensitized.
2. An absorption in a region where the energy acceptor under study is transparent, so that selective excitation of the sensitizer can be readily achieved.
3. Either a very short singlet lifetime, or a sufficiently large S-T energy gap to place the sensitizer S1 level significantly above the S1 level of the sensitized molecule to ensure negligible sensitization of the singlet state of the energy acceptor.

Although these procedures are commonly employed in mechanistic studies, they are only qualitative. The conclusions become convincing if they can be made quantitative. For example, the failure to observe a reaction undergo “triplet photosensitizing conditions” may result from failure to efficiently cause production of T1 by triplet energy transfer. This failure may be due simply to improper experimental conditions, i.e., the concentrations and sensitizer-acceptor pair must be selected to optimize energy transfer. Similarly, the failure to observe quenching of reaction in the presence of a “selective triplet quencher” may result from too low a concentration of quencher or too short a lifetime of T1. Knowledge of rate constants for energy transfer and triplet lifetimes removes these ambiguities. It is good practice to attempt to observe directly both sensitization of triplet reactant phosphorescence and quenching of triplet reactant phosphorescence.

A couple of interesting, even if somewhat special, exemplars are worth mentioning. Triplet states are widely employed to sensitize the formation of singlet oxygen. The fact that oxygen has a triplet ground state makes its promotion to the singlet oxygen by a triplet sensitizer a spin allowed to process. Further, singlet oxygen can also be used as a diagnostic tool to establish triplet participation in a reaction. These processes are discussed in detail in Chapter zz.
The other interesting sensitization and quenching example involves a simple technique to selectively study carbonyl singlet reactions proposed by Wagner.\textsuperscript{40} In this method, 1-methylnaphthalene (a liquid at room temperature) is used as the solvent and singlet sensitizer. Photoexcitation of the naphthalene, as shown in Figure 8.18 leads to $S_1$. Naphthalenes have sufficiently long singlet lifetimes (largely a reflection of the large S-T gap and slow florescence lifetime, see Chapter \textit{zz}) to allow for singlet energy transfer to moderately large concentrations of aliphatic ketones (step “a”); the singlet ketone (step “e”) can yield products in competition with intersystem crossing (step “b”). Once $T_1$ has been formed, it is quenched in less than 0.1 ns (remember that 1-methylnaphthalene is the solvent), step “c”. Finally triplet 1-methylnaphthalene decays to $S_0$ ground state in step “d”. The method works largely because $\pi,\pi^*$ states (1-methylnaphthalene) have much larger S-T gaps than $n,\pi^*$ states (e.g., aliphatic ketones) and the singlet lifetime of 1-methylnaphthalene is relatively long for a $S_1$ state. Interestingly, this interplay of energy transfer processes makes nabumetone (an anti-inflammatory drug containing naphthalene and ketone moieties) quite photostable.\textsuperscript{41}
Figure 8.18: Singlet sensitization and triple quenching of ketones by 1-methylnaphthalene. Positions of the energy bars are not to scale, simply in the incorrect order. The numbers next to the state bars are approximate excited state energies in kcal/mol.

Experimental Tests for the Involvement of Electronically Excited States: Quantitative Aspects

Although triplet photosensitization and quenching provide useful qualitative tools for deciding whether a given excited state ($S_1$, $T_1$, etc.) is involved along a reaction pathway, mechanistic tests are more convincing when they can be applied quantitatively. The basic idea behind a quantitative application of sensitization and quenching is the notion that if all of the appropriate rates are known, the probabilities of various reaction pathways can be calculated.
For example, the notion of a “selective” triplet quencher is made quantitatively by the measurement of $k_q^s$ for quenching $S_1$ and $T_1$. The reason that 1,3-dienes have been commonly employed as specific triplet quenchers of ketones is the large differential between $k_q^s$ and $k_q^T$, the rate constants for quenching of $S_1$ and $T_1$ of alkanones, respectively. In the case of acetone with 1,3-pentadiene as quencher, the value of $k_q^s$ is $\sim 10^8$ M$^{-1}$ s$^{-1}$, whereas $k_q^T$ is $\sim 5 \times 10^9$ M$^{-1}$ s$^{-1}$. This factor of $\sim 50$ means that at a given concentration of 1,3-pentadiene and excited states, acetone triplets are quenched 50 times faster than acetone singlets. However, the actual rate of quenching of $S_1$ and $T_1$ depends on the steady-state concentrations of $S_1$ and $T_1$:

$$\text{rate of quenching of } S_1 = k_q^s [S_1][Q] \quad (8.58)$$

$$\text{rate of quenching of } T_1 = k_q^T [T_1][Q] \quad (8.59)$$

The efficiencies for singlet and triplet quenching by $Q$ are given in Eqs. 8.60 and 8.61, respectively.

$$\phi_q^S = \frac{k_q^S [Q]}{\tau_s^{-1} + k_q^S [Q]} = \frac{k_q^S \tau_s [Q]}{1 + k_q^S \tau_s [Q]} \quad (8.60)$$

$$\phi_q^T = \frac{k_q^T [Q]}{\tau_s^{-1} + k_q^T [Q]} = \frac{k_q^T \tau_s [Q]}{1 + k_q^T \tau_s [Q]} \quad (8.61)$$

Remember that these efficiencies only reflect those events that occur once a given electronic states has been reached. This is important for the triplet, since only those singlet states that survive quenching by $Q$ can proceed to the triplet state. The survival efficiency for the singlet is given by:

$$\phi_{sv}^S = \frac{\tau_s^{-1}}{\tau_s^{-1} + k_q^S [Q]} = \frac{1}{1 + k_q^S \tau_s [Q]} \quad (8.62)$$
If we assume that the singlet state has no other pathways other than intersystem
crossing or quenching by Q (e.g., we neglect fluorescence), then we can calculate the relative
efficiencies of singlet and triplet quenching as being given by Eq. 8.63.

\[
\frac{\text{singlet quenching}}{\text{triplet quenching}} = \frac{k_q^S \tau_s [Q]}{1 + k_q^S \tau_s [Q]} + \frac{k_q^T \tau_T [Q]}{1 + k_q^T \tau_T [Q]}
\]

(8.63)

For acetone at room temperature (in acetonitrile, a typical “inert” solvent for reactions
of n,\(\pi^*\) states)) \(\tau_s \sim 2 \times 10^9\) s and \(\tau_T \sim 50 \times 10^{-6}\) s. Thus, for a 0.1 M concentration of 1,3-diene,
we have:

\[
\frac{\text{singlet quenching}}{\text{triplet quenching}} = \frac{(10^9) \times [2 \times 10^4]}{(5 \times 10^9) \times [50 \times 10^{-6}]} \times \left(1 + (5 \times 10^9) \times (50 \times 10^{-6}) \times 0.1\right)
\]

(8.64)

\[
\approx \frac{1}{50}
\]

Note that the ratio of Eqs. 8.63 and 8.64 increase with increasing [Q]. This may be
somewhat misleading by suggesting that lesser quencher is better. One must keep in mind (see
Eq. 8.61) that one also requires \(\phi_q^T\) to be high. With 0.1 M 1,3-diene, over 99.99\% of the
triplets will decay via quenching.

From the above analysis a long triplet lifetime can be seen to be useful in selective
triplet quenching. Even if \(k_q^S \sim k_q^T\), the effective ratio of quenching of \(S_1\) relative to \(T_1\) goes as
\(\tau_s/\tau_T\), so if \(S_1\) is short-lived, and \(T_1\) is long-lived, selective triplet quenching can still be
achieved.

Without quantitative information about quenching constants, many tests for the
involvement of \(S_1\) and \(T_1\) become ambiguous. We have seen that if \(S_1\) is quenched, then no
information is revealed about whether S₁ or T₁ is involved along the reaction pathway because T₁ is generally derived from S₁. Thus, if a quencher is observed to be effective, it must be established that S₁ is not quenched. Experimentally, knowledge of $k_q$, $\tau_s$, and [Q] allow the adjustment of concentrations so that S₁ will not be quenched (see Eq. 8.63). However, the best method to determine whether S₁ is quencher comes from florescence quenching. Here the answer is clear cut if fluorescence can be measured by either steady state or time resolved methods: if the fluorescence is quenched then S₁ is quenched.

Is it possible that quenchers may inhibit a reaction without deactivating S₁ or T₁? This can occur when a reactive intermediate, I, produced from S₁ or T₁ is intercepted by the quencher, i.e., $I + Q \rightarrow \text{Not } P$. Since the lifetime of such a reactive intermediate will generally be different from that of S₁ and T₁, the occurrence of such a situation may be revealed from a Stern-Volmer analysis which indicates a $k_q\tau$ value inconsistent with that expected for quenching of S₁ or T₁ as measured by fluorescence, phosphorescence, or transient absorbance quenching.

For example, the radicals produced in hydrogen transfer to ketones (Eq. 8.8) could undergo hydrogen transfer and/or addition reactions with the conjugated dienes frequently employed as selective triplet quenchers. Such a reaction would mask the actual outcome of excited state reactions. Reaction 8.65 shows a plausible example:

\[
\begin{array}{c}
\text{H}_2\text{C} \cdot \text{OH} + \begin{array}{c} \text{H}_3\text{C} \end{array} \rightarrow \begin{array}{c} \text{H}_3\text{C} \text{CO} \end{array} + \begin{array}{c} \text{H}_3\text{C} \cdot \end{array}
\end{array}
\]

(8.65)

Molecular oxygen has traditionally been employed as a quencher of photochemical reaction, and sometimes quenching by oxygen has been used to infer a triplet state reaction (already mentioned in this section). Oxygen will, in fact, intercept singlet and triplet excited states, as well as a wide range of reaction intermediates including free radicals, diradicals, and carbenes (see chapter zz). Without other pieces of mechanistic information, and a quantitative analysis of the type presented above for 1,3-pentadiene, oxygen quenching cannot be employed to infer the involvement of a triplet state, although quenching is consistent with triplet involvement.
A most valuable piece of information concerning oxygen quenching can be derived from emission spectroscopy in the near infrared region of the spectrum. Triplet states frequently interact with oxygen via energy transfer to yield “singlet oxygen” (\(^1\text{O}_2\)), a high energy form of O\(_2\) which emits weakly at 1.37 (see also Chapter zz), i.e.:

\[
\text{T}_1 + ^3\text{O}_2 \rightarrow \text{S}_0 + ^1\text{O}_2
\]

Show spectrum here?

Thus, near-infrared emission resulting from oxygen quenching of a reaction is strong evidence for the involvement of a triplet state. Singlet oxygen is a very important intermediate in photochemistry and in biology, and its spectroscopic and chemical properties will be presented in detail in Chapter zz.

An upper limit to the magnitude of the bimolecular quenching constant \(k_q\) is usually set by the rate of diffusion (\(k_{\text{diff}}\)) of the excited state and quencher into a solvent cage (discussed in more detail in Chapter zz). It is informative to examine the relationship of the rate of bimolecular quenching of the decay rate (\(k_D\)), or lifetime (\(\tau_D\)) of an excited state *R. Let \(k_q\) be the bimolecular rate constant for bimolecular quenching of *R by a quencher, Q. Figure 8.19 shows how the quencher concentration \([Q]\), \(k_q\), \(\tau_D\), and \(k_D\) are related.

![Graph showing the relationship between quencher concentration and bimolecular quenching constant](image_url)
Figure 8.19: Relationship between concentrations, lifetimes, and quenching rate constants.
The left plot gives the quencher concentration required to achieve 50% quenching for different excited state lifetimes, as a function of the quenching rate constant. The same is shown on the right, for 99% quenching. Note that the line for $\tau = 10^{12}$ s is not included in the right plot because the concentrations required always exceed 100 M!

Taking $k_q = 10^{10}$ M$^{-1}$ s$^{-1}$ as typical of diffusion-controlled quenching, it is clear from Figure 8.19 that if $[Q] < 10^{-3}$ M then virtually no quenching will occur if $\tau_D < 10^{-8}$ s ($k_D > 10^{8}$ s$^{-1}$). However, if $\tau_D > 10^{-3}$ S ($k_D < 10^{3}$ s$^{-1}$), at $[Q] = 10^{-5}$ M more than 99% of the D* molecules will be quenched. Note that for lifetimes of one nanosecond ($10^{-9}$ s) or less, it is virtually impossible to achieve efficient quenching unless the quenching process approaches diffusion control. Note that most pure substances do not exceed 10 M even as a neat liquid.

In general, since $k_p$ is greater than $10^6$ s$^{-1}$ (Table 22), most fluorescent molecules are not quenched efficiently by any quencher whose concentration is $< 10^{-3}$ M, since $k_q$ rarely exceeds $10^{10}$ M$^{-1}$ s$^{-1}$. However, since $k_p$ is rarely larger than $10^2$ s$^{-1}$, most phosphorescent molecules will be strongly quenched at concentrations $> 10^{-4}$ M if Q is a diffusional quencher. Finally, if $[Q] > 0.1$ M, both fluorescence and phosphorescence will generally be quenched if $k \sim 10^{10}$ M$^{-1}$ s$^{-1}$.

The Use of Kinetic Methods to Detect and to Identify Intermediates

The experimental observation of a Stern-Volmer quenching of a photochemical reaction is, in itself, evidence for an intermediate, *R or I, i.e., something is being intercepted by the quencher. The Stern-Volmer constant $k_q^s$ (the slope of the Stern-Volmer quenching plot) is a reaction constant characteristic of that intermediate for a given solvent, temperature, and quencher. Thus, the value of $k_q^s$ may serve to characterize the intermediate being quenched. Because $k_q$ is limited by the rate of diffusion, we can calculate the minimum lifetime of the species being quenched if we calculate $t$ under the assumption $k_q = k_{diff}$.

A relevant exemplar of the application of the above principles is found in a “classic” argument for the involvement of $T_1(n,\pi^*)$ of benzophenone as the chemically reactive agent in the photoreduction of benzophenone by benzhydrol:
This argument is informative because it is convincing and has been completely confirmed, yet was proposed before emission spectroscopy and flash spectroscopy were widely available for direct detection of excited states. The components of “chemical mechanism” assumed for the reaction is shown in Scheme 8.12.

Scheme nn.12: Mechanism for the photoreduction of benzophenone by benzhydrol and relevant kinetic expressions.

The question is whether \( S_1(n,\pi^*) \) is involved in the abstraction step. We have seen that if a photoreaction involves the competition between a bimolecular reaction and a unimolecular decay of \( B^* \), then an efficiency-rate law of the form of Eq. 8.68 should exist:

\[
\frac{1}{\Phi} = \frac{1}{a} + \frac{k_d}{ak_r[BH_2]} \quad (8.68)
\]
where \( a \) = the efficiency of formation of BP*. A plot of \( 1/\Phi \) (where \( \Phi \) = the quantum efficiency for disappearance of benzophenone or the formation of benzopinacol) vs. \( 1/[BH_2] \) is predicted to yield a straight line of slope \( = k_d/a \), and an intercept of \( 1/a \). Such a plot is shown in Figure 8.20.

**Figure 8.20:** Schematic representation of the plot of Eq. 8.69 for the photoreduction of benzophenone to benzopinacol by \((C_6H_5)CDOH\) and \((C_6H_5)CHOH\), Scheme nn.12.

First, the linearity of the plot confirms the assumed mechanism as a very probable one and allows us to identify the value of slope with the ratio \( k_d/a \) and the intercept with \( 1/a \). The value of the intercept for both reducing agents is equal to 1.0. Therefore the value of the slope equals \( k_d/k_r \). The measured value of 0.05 means that \( k_d = 0.05k_r \).

If known concentrations of such a bimolecular quencher, Q, are added to benzene solutions of benzhydrol and benzophenone, the following rate law is predicted:

\[
\frac{1}{\Phi} = \frac{1}{a} + \frac{k_d}{ak_r[BH_2]} + \frac{k_q[Q]}{ak_r[BH_2]^2}
\]  

(8.69)
Since \( k_d/k_F \) and \( a \) are known from treatment of data for \([Q] = 0\), a plot of \(1/\Phi\) versus \([Q]\), a fixed initial concentration of \([BH_2]\) will yield a slope equal to \( k_q/k_F[BH_2] \) since as we already have seen, \( a = 1 \). Figure nn.20 shows such a plot for \(Q = 1,3\)-pentadiene, for which \( k_q/k_F = 500 \). The same ratio should be derivable from variation of \([BH_2]\) at constant \([Q]\), as in fact it is.

From the experimental ratios of \( k_d/k_F \) and \( k_q/k_F \) an upper limit for the value of \( k_d \), the inherent decay rate of \( BP^* \), can be evaluated. The maximum value of \( k_q \) is \( k_{\text{diff}} = 5 \times 10^9 \text{ M}^{-1}\text{s}^{-1} \), i.e., the rate constant for diffusion in benzene. Thus \( k_F(\text{max}) = 5 \times 10^9/500 = 1 \times 10^7 \text{ M}^{-1}\text{s}^{-1} \) we now determine the maximum possible value of \( k_d \) from Eq. 8.70.

\[
k_d(\text{max}) = 0.05k_F(\text{max}) = 5 \times 10^5 \text{ s}^{-1}
\]  

\(8.70\)

**Figure 8.21:** Example of the quenching of a bimolecular reaction. The concentration of reactant, \( \text{Ph}_2\text{CHOH(BH}_2\text{)} \) is held fixed, and the concentration of quencher, \((1,3\)-pentadiene\)) is varied. It is important to note that Eq. 8.69 is valid only if \([BH_2]\) does not change significantly during the reaction, and that \([Q]\) also remains constant.

Only very weak fluorescence \((\Phi_F < 10^{-4})\) is observed from benzophenone. Based on its absorption spectrum, the inherent radiative lifetime of \(S_1(n,\pi^*)\) of benzophenone is theoretically (Eq. 5.11) expected to be of the order of \(10^5\)-\(10^6 \text{ s}^{-1}\). Thus, the rate constant for
The deactivation of $S_1(n,\pi^*)$ must be greater than $10^9-10^{10}$ s$^{-1}$ in order to account for the very weak fluorescence efficiency. However, Eq. 8.70 requires that the reactive state is deactivated at a maximum rate of $5 \times 10^5$ s$^{-1}$.

$$k_d(\text{max}) = 0.05k_r(\text{max}) = 5 \times 10^5 \text{ s}^{-1} \quad (8.70)$$

Under the premise that BP* must be $S_1(n,\pi^*)$ or $T_1(n,\pi^*)$, $S_1(n,\pi^*)$ is excluded as a plausible reactive intermediate. This conclusion has since been completely vindicated by measurements of quenching of $T_1(n,\pi^*)$ monitored by triplet-triplet absorption and phosphorescence.

The experiments described above provide a range of simple experiments, largely based on product yields, that from a mechanistic, as well as historical point of view help us understand how the building blocks of the mature and robust paradigms of photochemistry were established. However, there are today a wide range of experimental methods that could allow us to establish the mechanism in a more direct way. In the system of Scheme 8.12 those experiments have confirmed the mechanism presented above and have simply refined the kinetic parameters derived from product or competitive studies.

Benzophenone shows a characteristic triplet-triplet absorption (Fig. 8.23, top), readily detectable with time resolved techniques, such as laser flash photolysis. Similarly, the ketyl radical from benzhydrol (BH• in Scheme nn.12) has a characteristic spectrum (Fig. 8.23 bottom), even if it overlaps significantly with that of the triplet state. Figure 8.22 (left) shows transient decay trees recorded at 530 nm, where both species (BP* and BH•) absorb, although the triplet is more intense. The spectra from both species are illustrated in Figure 8.22, where they have been normalized to correspond to their accepted extinction coefficients.

Examination of Figure 8.22 leads to the following observations:

1. In the absence of benzhydrol the traces decay to the original ‘baseline’ level, suggesting that no permanent chemical change has occurred.

2. While the benzophenone triplet returns to the ‘baseline’ level, the decay process is somewhat more complex than the simple exponential that would be anticipated from Eq.19 (not shown).
(3) Addition of benzhydrol reduces the triplet lifetime, as judged by the faster decays (traces B and C). In addition, a residual or long lived absorption is observed under these conditions.

(4) Examination of the residual absorption mentioned above reveals that in much longer time scales it decays by a bimolecular reaction (i.e., can be fitted with second order kinetics).

(5) A plot of the reciprocal benzophenone triplet lifetime as a function of benzhydrol concentration is linear (see Figure 8.21, right).

(6) Addition of 1,3-pentadiene (not shown), also reduces the triplet lifetime, but in this case no residual absorption is observed.

(7) The transient spectra (see Figure 8.22) in the absence and presence of benzhydrol are consistent with BP* and BH•; the later has independently been characterized in radiolysis experiments.

**Insert Figure nn.22 (p. 34.6)**

**Figure 8.22:** *Left:* Transient decay trees recorded following 355 nm laser excitation of benzophenone in deaerated acetonitrile. The traces were recorded at 530 nm at room temperature and the concentrations of benzhydrol are A = 0, B = 0.15 M and C = 0.30 M. *Right:* Effect of benzhydrol on the lifetime of triplet benzophenone. The slope of the plot gives the second order rate constant, i.e., k_r in Scheme 8.12. The value obtained was $xx \times 10^6$ M$^{-1}$ s$^{-1}$. 
The observations above are consistent with our conclusions based on quenching and product studies. That the decay of triplet benzophenone occurs without chemical change (point 1) is normal in an inert solvent; a minor deviation from first order kinetics (point 2) is common in laser work and reflects processes such as triplet-triplet annihilation and self-quenching (see Chapter zz), bimolecular processes, which tends to participate at the high transient concentrations generated under laser excitation. Points 3, 5 and 7 all support the chemistry and mechanism of Scheme 8.12. Point 4 is consistent with the involvement of free radicals that decay by second order kinetics, as proposed in Scheme 8.12. Finally, addition of a 1,3-diene (point 6), simply confirms that the triplet state is involved with Figure nn.22.

While the combination of experiments described above is more than sufficient to adequately characterize the system, it would be possible to make a series of predictions which could be verified experimentally, e.g.:

(a) Quenching by oxygen should lead to singlet oxygen characteristic emission (see Chapter zz).
(b) Quenching by oxygen should also involve interaction with BH•, which is known to yield hydrogen peroxide.

(c) The process involving quenching by 1,3-pentediene should lead to its cis-trans isomerization (see Chapter zz), which would be readily observable if a pure isomer was employed as quencher.

(d) The phosphorescence from benzophenone, while weak under the solution conditions of these experiments, should be quenched by benzhydrol.

(e) The ketyl radical BH is known to be highly fluorescent. Its emission should be observable under appropriate experimental conditions.

8.11 Experimental Tests for the Involvement of Radicals and Diradicals

Since radicals, diradicals (diradicals), and radical pairs are extremely common intermediates in organic photoreactions, all of the experimental methods (Table nn.4) for detecting and characterizing intermediates may be employed to detect radicaloid species as transients in photochemical reactions. In this section we shall discuss product structure criteria and transient absorption studies, while powerful methods involving magnetic resonance are presented separately in Chapter zz.

NJT was planning to add here. May be by reference to other chapters.

Reactions involving diradical intermediates

We have already come across many photoreactions which involve free radicals. Scheme 8.12 dealing with the photoreduction of benzophenone is one such example. Diradicals (also called diradicals) and radical pairs also play a key role in many photochemical reactions. We may ask: are the properties of diradicals and radical-pairs intrinsically different from those of free radicals? When are two radical centers more than just the mere sum of the properties of each center? Based on the paradigm of conservation of spin angular momentum, we can reasonably assume that singlet diradicals (^1BR) can only be expected to yield singlet products, while triplet diradicals (^3BR) can only yield triplet products (Scheme 8.13). We can also expect that they will interconvert, although whether or not spin equilibrium will be established will depend largely on the specific chemical system and conditions.
What is the difference between a diradical and a radical-pair? In the case of a radical-pair, the radical sites can separate to large distances (in principle they can achieve infinite separation) without any need to create or break new bonds. On the other hand, the separation of the radical sites of a diradical can only separate to distances that are limited by the molecular structure between the radical sites.

Let us take as an example 1,4 diradicals which are commonly implicated in intramolecular hydrogen abstraction (Norrish Type II) reactions and cycloadditions of ketone triplet \( \pi,\pi^* \) states. Of the various unimolecular processes which are probable, the singlet diradical \( ^1\text{BR} \) can generally undergo several general processes expected from radical-radical processes, discussed earlier, which lead directly to molecular products: (a) coupling, (b) disproportionation, and (c) fragmentation of the 2,3 bond (Eq. 8.5). In addition, \( ^1\text{BR} \) can proceed to other diradicals via (d) internal rearrangements, and (e) undergoing electron transfer to produce zwitterions. In competition with these chemical reactions of \( ^1\text{BR} \) are the physical processes of (f) conformational changes, and (g) intersystem crossing. Finally, \( ^1\text{BR} \) and \( ^3\text{BR} \) may undergo bimolecular reactions with molecules in the system which can serve to "trap" the species. These trapping processes can be hydrogen abstraction and/or addition to unsaturated systems.

Experimentally, it has been observed that the 1,4-diradical derived from \( \gamma \)-methylvalerophenone has an absorption spectrum very similar to that for the ketyl radical from acetophenone,\(^{42}\) showing that the ketyl moiety is the dominant chromophore; the diradical spectrum is shown in Chapter xx (Figure xx.22), and Scheme 14 highlights the common chromophore between \( \gamma \)-methylvalerophenone and acetophenone.
Scheme 8.14: Comparing diradical and radical chromophores that lead to virtually identical spectra for both species.\textsuperscript{42}

The 1,4-diradical derived from $\gamma$-methylvalerophenone undergoes a wide range of typical monoradical reactions, as illustrated in Scheme 8.15. In addition, the pKa and optical absorption of Norrish Type II diradicals matches well those of typical ketyl monoradicals (e.g. derived from acetophenone).\textsuperscript{43} Overall, these results indicate that one can assume that diradicals undergo the same reactions as monoradicals; further, kinetic studies suggest that also the rate constants are comparable.

\begin{align*}
\text{Hydrogen abstraction} \\
\text{Initiation of polymerization} \\
\text{Addition to reactive double bonds}
\end{align*}
Scheme 8.15: Representative radical-like reactions of Norrish Type II diradicals.

An interesting type of interaction is that of $^3\text{BR}$ with paramagnetic substrates, such as oxygen, dialkynitroxides or some metal ions, such as Cu$^{2+}$. In all these cases the reagent can provide a mechanism for assisted intersystem crossing. Quenching by nitroxides can lead to products from $^3\text{BR}$ in ratios different from those obtained by "spontaneous" intersystem crossing.

The unusual characteristics mentioned above reflect a general characteristic of many diradicals derived from triplet excited states: they are ‘born’ in the triplet spin configuration and retain that configuration for most of their lifetime. As soon as they undergo intersystem crossing, they essentially ‘collapse’ to products which “capture” the structure of the conformation that the diradical possesses at the instant of intersystem crossing. In other words, the intersystem crossing of Scheme 8.13 is irreversible in the case of Norrish Type II diradicals. Thus, in the reactions of Scheme 8.14 there is no manifestation of the spin configuration of the diradical. Reactions of singlet diradicals are believed to be extremely fast, so that they can in fact be faster than bond rotations. Thus, the products of singlet diradical collapse can ‘remember’ the conformation in which triplet-to-singlet intersystem crossing took place. Conceptually, we can easily understand this by noting from Scheme nn.16 that only the cisoid conformer can undergo cyclization, while both can fragment. Thus, if an intersystem crossing catalyst (e.g. a nitroxide) induces intersystem crossing from a different conformation from which it occurs spontaneously, this can be reflected in the products.

Scheme 8.16: The Norrish Type II diradical from $\gamma$-methylvalerophenone can undergo cyclization from only one rotational conformer.
Thus, for example (Scheme 8.17), the persistent radicals TEMPO and di-tert-butyl nitroxide 'quench' Norrish Type II diradicals with rate constants of \(~ 6 \times 10^9 \text{ M}^{-1}\text{s}^{-1}\). While the reaction of these nitroxides with carbon centered monoradicals leads to C-O bond formation, the analogous reaction does not occur to any significant extent with Norrish Type II diradicals, Scheme nn.9. Since reactions with monoradicals are relatively slow (\(~10^8 \text{ M}^{-1}\text{s}^{-1}\) ) it is not surprising that the faster assisted intersystem crossing dominates. In other words, we can think of it as a simple kinetic competition between the two processes of Scheme 8.17. Nitroxides are paramagnetic and make catalytic intersystem crossing spin allowed. This will be discussed further in Chapter zz.

\[ \text{Ph} \quad \text{OH} \quad \text{R} \quad \text{R} \quad \text{N} \quad \text{O} \quad \text{TEMPO} \quad \text{Ph} \quad \text{OH} \quad \text{R} \quad \text{R} \quad \text{N} \quad \text{O} \quad \text{•} \quad \text{not formed} \]

**Scheme 8.17:** Competition between the formation of Norrish Type II products and chemical trapping by nitroxide; the latter does not contribute, even if it is a common (and rapid) reaction in the case of carbon centered monoradicals.\(^9,10\)

Oxygen provides another example of chemical behavior distinct from that expected from monoradicals. Oxygen quenches type II diradicals with rate constants of \(~ XX \times 10^9 \text{ M}^{-1}\text{s}^{-1}\); these values are quite comparable for those observed in the case of monoradicals, where peroxyl radical formation occurs. In this case, assisted intersystem crossing and chemical trapping (see Scheme 8.18) are both kinetically plausible. We will see in Chapter zz that the fact that molecular oxygen is a ground state triplet also makes both processes allowed with a 1:3 probability ratio of chemical trapping to assisted intersystem crossing.\(^44\)
Scheme 8.18: Competition between chemical trapping and assisted intersystem crossing in the quenching of Norrish Type II diradicals by oxygen.

The systems of Schemes 8.17 and 8.18 show new pathways characteristic of diradicals, not available in the case of monoradicals. (Point out that the 1,4 cleavage and the ISC issue make diradicals different. Use example of changing lifetimes with MIF and MIE effects.) While the outcome of the competition between monoradical and diradical-specific pathways will depend on each specific type of diradical and quencher, we should clearly include in our paradigm for diradical behavior the fact the novel pathways can be anticipated when the quencher/scavenger is paramagnetic.

We noted in Scheme 8.13 that 3BR could also proceed directly to triplet products. Yet, this is a very uncommon behavior when it involves the formation of closed shell molecular products. For example, reaction 8.71 provides an example of an energetically unfavorable process.

In general, these reactions are not observed. Similarly, in the Norrish Type II case the excited states of all products (e.g., enol or cyclobutenol) are not energetically accessible. In contrast, diradicals frequently undergo unimolecular decompositions from the triplet state when they can yield another diradical. A common case is that involving the Norrish Type I reaction of cyclic alkanones as illustrated in Scheme 8.19.
Scheme 8.19: The Norrish Type I reaction of 2,6-diphenylcyclohexane involves the fragmentation of a triplet diradical to another triplet diradical following rapid decarbonylation.

What the two diradical in Scheme 19 have in common is that the average S-T splitting is expected to be small (of the order of small calories per mol) compared to typical excited state energies in the 20-100 kcal/mol range. We can generalize this by stating that triplet diradicals may undergo unimolecular processes when the products do not require the formation of the excited state of an otherwise closed-shell molecule. For practical purposes this is a convenient re-statement of the law of energy conservation, but also a useful guideline in the case of diradical chemistry.

Re-examination of the examples just presented lets us construct a series of rules that we can use as our paradigm for diradical-mediated photoreactions. They are given in Table 8.8.

**Table 8.8:** Concepts in the paradigm for diradical-mediated photochemical reactions

<table>
<thead>
<tr>
<th>RULES</th>
<th>Diradical paradigm concepts</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rule # 1</td>
<td>$^1$BR will only yield singlet products</td>
</tr>
<tr>
<td>Rule # 2</td>
<td>$^3$BR will only yield triplet products. These reactions are uncommon, unless another diradical is produced (see the example of Scheme 8.19)</td>
</tr>
<tr>
<td>Rule # 3</td>
<td>Diradicals undergo monoradical-like reactions with essentially the same</td>
</tr>
</tbody>
</table>
rate constants as typical monoradicals. Whether or not these processes dominate will largely depend on the dynamics of diradical-specific reactions (see rule # 4)

| Rule # 4 | \(^3\)BR will undergo diradical-specific reactions when they interact with paramagnetic species, such as oxygen, nitroxides and certain transition metal ions |
| Rule # 5 | Intersystem crossing (\(^3\)BR ↔ \(^1\)BR) plays an important role in diradical reactions. Equilibration is rarely achieved. For triplet diradicals intersystem crossing is frequently irreversible and determines their lifetime |
| Rule # 6 | The decay of \(^1\)BR to molecular products can be fast enough to compete with bond rotations. As a result the partition among different diradical products may depend on the conformation at which intersystem crossing occurs |
| Rule # 7 | The lifetime of \(^3\)BR will depend on the factors that control spin-spin interactions, such as distance, S-T energy gap, and spin-orbit coupling interactions (these effects will be covered in detail later in this chapter) |
| Rule # 8 | Structures in which odd electrons are of the same spin are more stable the further apart are the location of the unpaired electrons |

An example of rule #7 is the case of Paterno-Buchi 1,4-diradicals, which contain an oxygen atom in the backbone; their lifetimes are much shorter than Norrish Type II diradicals with an all-carbon frame, see Scheme 8.12. The effect has been attributed to an increase in spin-orbit coupling due to oxygen. (Add other examples and range of diradical lifetimes)
Norrish Type II biradical  

\[
\begin{align*}
\text{OH} \\
\cdot \\
\cdot \\
\end{align*}
\]

Paterno-Buchi biradical  

\[
\begin{align*}
\cdot \\
\cdot \\
\cdot \\
\cdot \\
\cdot \\
\end{align*}
\]

lifetime of Norrish biradical > lifetime of Paterno Buchi Biradical

Examples:

\[
\begin{align*}
\text{OH} \\
\cdot \\
\cdot \\
\cdot \\
\cdot \\
\cdot \\
\cdot \\
\cdot \\
\cdot \\
\cdot \\
\cdot \\
\cdot \\
\cdot \\
\cdot \\
\cdot \\
\cdot \\
\cdot \\
\cdot \\
\end{align*}
\]

\( \tau \sim 100 \text{ ns} \)

Scheme nn.20: Inclusion of an oxygen atom in the triplet diradical backbone reduces its lifetime.

An example of rule #8 is the cyclization of a bis-allylic triplet to a cyclized cyclopropyl carbinyl diradical, reaction 8.72.

Detecting Radicals, Radical Pairs, and Diradicals

Magnetic resonance is a powerful experimental tool for the detection and characterization of radicaloid structures. The technique of magnetic resonance is a form of spectroscopy which measures from the absorption or emission of light due to change in
electronic or nuclear magnetic spin states. Monoradicals may be directly detected and characterized by the form of magnetic resonance known as (ESR) Electron Spin Resonance. This form of spin spectroscopy is applicable to the liquid, solid, and gaseous phases. In the solid phase ESR may be employed to characterize the electronic configuration of triplet states.

Techniques based on spin resonance will be discussed in detail in Chapter zz.

Several other techniques, particularly those based on kinetic absorption spectroscopy (such as laser flash photolysis with ultraviolet, visible or infrared detection), have been widely used in studies of radical species. Some examples have been provided above.

Discuss magnetic effects on radical pairs and diradicals. Z not affected. Use α-cleavage exemplar. Use CIDNP and CIDEP to indicate tests for the involvement of *R → I(D) step.

8.12 Chemical Spectroscopy: The Use of Photochemical Reactions to Measure Excited-State Energetics and Dynamics

The term chemical spectroscopy has been coined to define a principle which involves the use of photochemical reactions to measure properties of electronically excited molecules which are normally determined directly by spectroscopic means. For example, must employ an alternative to ordinary spectroscopy such as chemical spectroscopy, if a molecule does not show measurable phosphorescence or singlet-triplet absorption under the reaction conditions being studied.

For example, chemical spectroscopy has been successfully employed in the estimation of triplet energies and in the measurement of intersystem crossing efficiencies. Great care must be taken in the selection of systems and in the interpretation of results of experiments because the method is based on the assumption of a very simple scheme, an assumption which may not apply under the conditions of a particular experiment.

The concepts behind the principle of chemical spectroscopy as they apply to the triplet state are given by the following scheme for determining intersystem crossing quantum yields.
The *substrate* molecule of interest is assumed to possess standard decay pathways from \( S_1 \) and \( T_1 \). Addition of an energy acceptor molecule, \( A_0 \), introduces a step that quenches \( T_1 \) of the substrate and produces the acceptor triplet \( A_T \), which then either undergoes a characteristic reaction or produces a characteristic *signature*. This analysis assumes:

1. That \( S_1 \) is not quenched by \( A_0 \).
2. That \( T_1 \) produces \( A_T \) quantitatively for each quenching of \( T_1 \).
3. The reaction or signature of \( A_T \) is independent of the reaction conditions.

If these conditions are met, then \( \Phi_{ST} \) is measured by completely quenching \( T_1 \) and measuring the quantum yield of reaction from \( A_T \) based on absorption to produce a product (\( \Phi_R \)). If the efficiency of reaction from \( A_T \) is \( \phi_A \), then we have Eq. 8.73.

\[
\Phi_R = \Phi_{ST} \phi_A \quad \text{or} \quad \Phi_{ST} = \frac{\Phi_R}{\phi_A} \quad 8.73
\]

From Eq. 8.73, we note that the efficiency of sensitized reaction of \( A \), under conditions of complete quenching of \( T_1 \), is the product of the quantum yield of formation of \( T_1 \) (\( \Phi_{ST} \)) and the inherent reaction efficiency of \( A_T \). Since both \( \Phi_R \) and \( \phi_A \) are measurable, \( \Phi_{ST} \) may be evaluated from photochemical data, namely by quantum yield measurements. A Stern-Volmer
analysis of the sensitized reaction of A will yield the ratio \( k_q/k_T \) which is equal to \( k_q \tau_T \). If \( k_q \) is assumed to be the value of diffusion-controlled quenching, \( \tau_T \) can be evaluated if \( k_{\text{diff}} \) is known. This assumption is questionable in the absence of independent evidence that the quenching step is diffusion-controlled. However, it is frequently possible to use a rate constant measured for a similar or the same chromophore under comparable experimental conditions. Representative values are included in Chapter zz.

The scheme discussed above, with its numerous assumptions, does work in carefully selected systems. The energy levels of the acceptor usually can be chosen so that triplet-triplet energy transfer is exothermic and singlet-singlet energy transfer is endothermic (see Chapter 7). This situation requires the same concepts as in Figure 8.18, except that under these conditions the carbonyl compound would be excited directly by the incident light. In this case the concentration of triplet quencher (1-methylnaphthalene) would be relatively small and determined by the lifetime of the excited ketone, such that >99% of the ketone triplets would decay via energy transfer, as shown in Figure 8.24. We have used the term signature before to indicate an experimentally characteristic feature of \( \ast R \) or I that can be used to selectively identify the occurrence of a reactive intermediate in a photochemical reaction sequence. Figure 8.24 provides such an example; triplet 1-methylnaphthalene does not undergo any significant chemistry, however in laser flash photolysis it can be readily identified by its strong, long lived absorption at around 420 nm (the naphthalene triplet signature). (Connect this idea to the probe method)
Figure 8.24: Energy transfer (as in Scheme 8.21) for a system where the acceptor gives a characteristic "signature", readily detectable by laser flash photolysis.

In fluid solutions, the majority of directly measured quenching constants for the reactions involving an acceptor whose triplet energy is lower than that of the donor are generally close to the rate constant for diffusion. However, the scheme is not universally true.

An interesting application of chemical spectroscopy involves the determination of triplet energies. The key idea here is that if a pair of molecules or conformers possess different triplet energies, then

1. Donor triplets will excite acceptor molecules equally effectively as long as energy transfer is a few kcal/mol exothermic (i.e., transfer to each molecule is assumed to approach diffusion-control).
2. Donor triplets will be ineffective in exciting the molecule when energy transfer becomes endothermic.

The same principles are applicable to either the determination of the triplet energy of the donor (by using a range of quenchers) or the triplet energy of the acceptor (by using a range of sensitizers with known triplet energies). An example of fumaric acid is shown in Figure 8.25.\textsuperscript{45} In this case the rate constants for the quenching of a wide range of sensitizers by fumaronitrile were examined in benzene at room temperature. From the energies of the sensitizers that fall below the diffusion limit, a triplet energy of $59 \pm 2 \text{ kcal/mol}$ was estimated for fumaronitrile. The cis isomer (maleonitrile) has approximately the same triplet energy.

![Figure 8.25: Rate constant for the quenching of various sensitizers by fumaronitrile in benzene at room temperature. A triplet energy of $59 \pm 2 \text{ kcal/mol}$ for fumaronitrile has been estimated from this plot.\textsuperscript{45}](image)

**Figure 8.25:** Rate constant for the quenching of various sensitizers by fumaronitrile in benzene at room temperature. A triplet energy of $59 \pm 2 \text{ kcal/mol}$ for fumaronitrile has been estimated from this plot.\textsuperscript{45}

### 8.13 Some Exemplar State-Energy Diagrams

It is useful and important to calibrate one's expectations of the behavior of electronically excited states in terms of exemplar models of $^1\text{R}$. In the case of electronically excited states, the state-energy diagrams of many molecules are derivable from a combination
of absorption and emission data. In this section we present briefly some archetype state-energy diagrams, e.g., for some ketones, alkenes, aromatic compounds, and enones, whose photochemistry will be described in detail in Chapters 9-11. The archetype state-energy diagrams serve as a paradigm which may be the basis for deciding on reaction or mechanistic feasibility. These diagrams are readily constructed if the energies of $S_1$, $T_1$ and the dynamics of deactivation of these states are known.

**Ketones**

The state energies and configurational assignments of some typical organic ketones are given in Table 8.9. In proceeding from acetone to acetophenone to benzophenone to methyl naphthyl ketone, the energy diagrams present some interesting contrasts. The first big contrast is the rate constant of intersystem crossing for acetone relative to benzophenone ($\approx 5 \times 10^8$ s$^{-1}$ and $\approx 10^{11}$ s$^{-1}$, respectively). As a result of these relatively rapid intersystem crossing rate constants and relatively slow fluorescence rates, ketones generally possess a low fluorescence yield. Although both molecules possess lowest $n,\pi^*$ singlet and triplet states, the $S_1 \rightarrow T_1$ crossing in benzophenone is of the $1(n,\pi^*) \rightarrow 3(\pi,\pi^*) \rightarrow 3(n,\pi^*)$ type, whereas acetone is of the $1(n,\pi^*) \rightarrow 3(n,\pi^*)$ type. According to El-Sayed’s rule (Chapter 5) the former is always much faster than the latter. Alkanones tend to possess relatively "pure" $n,\pi^*$, $S_1$, and $T_1$ states. Benzophenones possess "mixed" $n,\pi^*$ and $\pi,\pi^*$ states which may be dominated by either $n,\pi^*$ or $\pi,\pi^*$ characteristics. Naphthyl ketones may possess mixed $n,\pi^* \rightarrow \pi,\pi^*$ singlet states but tend to possess mainly $\pi,\pi^*$ triplet state characteristics. These conclusions are reached from both direct spectroscopic properties of the triplet states and indirect photochemical evidence (chemical spectroscopy from reactivity characteristics) or computational methods.
### Table 8.9 Energetics and Dynamics of Carbonyl Compounds

<table>
<thead>
<tr>
<th>Molecule</th>
<th>(E_1^a)</th>
<th>(E_3^a)</th>
<th>(k_s^b)</th>
<th>(k_{st}^b)</th>
<th>(k_T^b)</th>
<th>(\phi_{st})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetone</td>
<td>84</td>
<td>78</td>
<td>(10^9)</td>
<td>(10^9)</td>
<td>(10^6)</td>
<td>1.0</td>
</tr>
<tr>
<td>2-Pentanone</td>
<td>84</td>
<td>78</td>
<td>(10^9)</td>
<td>(10^7)</td>
<td>0.9</td>
<td></td>
</tr>
<tr>
<td>2-Hexanone</td>
<td>84</td>
<td>78</td>
<td>(10^{10})</td>
<td>(10^9)</td>
<td>(10^8)</td>
<td>0.5</td>
</tr>
<tr>
<td>Cyclobutanone</td>
<td>84</td>
<td>78</td>
<td>(10^{11})</td>
<td>(10^9)</td>
<td>--</td>
<td>0.0</td>
</tr>
<tr>
<td>Cyclopentanone</td>
<td>84</td>
<td>78</td>
<td>(10^9)</td>
<td>(10^8)</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>Cyclohexanone</td>
<td>84</td>
<td>78</td>
<td>(10^9)</td>
<td>(10^7)</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>Acetophenone</td>
<td>80</td>
<td>74</td>
<td>(10^{10})</td>
<td>(10^1)</td>
<td>(10^5)</td>
<td>1.0</td>
</tr>
<tr>
<td>Benzophenone</td>
<td>76</td>
<td>69</td>
<td>(10^{11})</td>
<td>(10^1)</td>
<td>(10^5)</td>
<td>1.0</td>
</tr>
<tr>
<td>2-Acetophenone</td>
<td>77</td>
<td>59</td>
<td>(10^{10})</td>
<td>(10^1)</td>
<td>(10^3)</td>
<td>0.8</td>
</tr>
<tr>
<td>4-Phenylbenzophenone</td>
<td>75</td>
<td>62</td>
<td>(10^{10})</td>
<td>(10^1)</td>
<td>(10^3)</td>
<td>1.0</td>
</tr>
<tr>
<td>Fluorenone</td>
<td>65</td>
<td>53</td>
<td>(10^9)</td>
<td>(10^4)</td>
<td>0.9</td>
<td></td>
</tr>
<tr>
<td>2-Acetylnaphthalene</td>
<td>75</td>
<td>58</td>
<td>(10^9)</td>
<td>(10^4)</td>
<td>0.9</td>
<td></td>
</tr>
<tr>
<td>Biacetyl</td>
<td>62</td>
<td>55</td>
<td>(10^8)</td>
<td>(10^8)</td>
<td>(10^4)</td>
<td>1.0</td>
</tr>
<tr>
<td>Camphorquinone</td>
<td>57</td>
<td>51</td>
<td>(10^8)</td>
<td>(10^8)</td>
<td>(10^5)</td>
<td>1.0</td>
</tr>
</tbody>
</table>

*Energies in kcal/mol*

*Rate constants are in sec\(^{-1}\), \(k_s\) = measured singlet lifetime, \(k_{st}\) = measured rate of \(S_1 \rightarrow T\) intersystem crossing, \(k_T\) = measured triplet lifetimes. Values are order-of-magnitude only and refer to measurements in “inert” solvents under deaerated conditions.*
Alkenes and Polyenes

Direct dynamic information on $k_S$, $k_{ST}$, $k_T$, etc. from measurement of $^*R$ is almost nonexistent for alkenes and polyenes. However, values of singlet and triplet energies are usually available from absorption spectroscopy and chemical spectroscopy (Table 8.10). An important feature of these molecules is the general lack of (or very weak) fluorescence and phosphorescence. Evidently, based mainly on chemical evidence (Chapter 10), $S_1 \rightarrow T_1$ intersystem crossing is generally very inefficient from the $S_1(\pi, \pi^*)$ states of alkenes and polyenes. The singlet and triplet state energies of alkenes and polyenes generally decreases with increasing conjugation.

Table 8.10. Singlet and Triplet Energies for Some Ethylenes and Conjugated Polyenes

<table>
<thead>
<tr>
<th>Molecule</th>
<th>$E_1^a$</th>
<th>$E_3^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_2$ = CH$_2$</td>
<td>120</td>
<td>82</td>
</tr>
<tr>
<td>CH$_2$ = C(CH$_3$)$_2$</td>
<td>95</td>
<td>81</td>
</tr>
<tr>
<td>trans-CH$_3$CH = CHCH$_3$</td>
<td>95</td>
<td>81</td>
</tr>
<tr>
<td>cis-CH$_3$CH = CHCH$_3$</td>
<td>95</td>
<td>78</td>
</tr>
<tr>
<td>(CH$_3$)$_2$C = C(CH$_3$)$_2$</td>
<td>86</td>
<td>76</td>
</tr>
<tr>
<td>cis-CHCl = CHCl</td>
<td>--</td>
<td>76</td>
</tr>
<tr>
<td>Norbornene</td>
<td>--</td>
<td>74</td>
</tr>
<tr>
<td>trans-CHCl = CHCl</td>
<td>--</td>
<td>72</td>
</tr>
<tr>
<td>CH$_2$ = CH - CH= CH$_2$</td>
<td>80</td>
<td>60</td>
</tr>
<tr>
<td>CH$_2$ = CCH$_3$ - CCH$_3$ = CH$_2$</td>
<td>80</td>
<td>60</td>
</tr>
<tr>
<td>1,3-Cyclohexadiene</td>
<td>75</td>
<td>54</td>
</tr>
<tr>
<td>1,3,5-Hexatriene</td>
<td>70</td>
<td>48</td>
</tr>
</tbody>
</table>

$^a$ Energy of $S$ in kcal/mol.

$^b$ Energy of $T$ in kcal/mol.
Aromatic Hydrocarbons

A list of the energies of some commonly encountered aromatic hydrocarbons is given in Table 8.11. Aromatic hydrocarbons often exhibit both fluorescence and phosphorescence at low temperatures, so that their state-energy diagrams can be well established. In the case of anthracenes, an interesting feature occurs in the accidental closeness of T2 and S1. Depending on the substitution pattern of an anthracene, T2 may lie somewhat above or below S1. Thus, either S1 $\rightarrow$ T2 $\rightarrow$ T1 or S1 $\rightarrow$ T1 intersystem crossing mechanisms can operate. Both S1 and T1 energies decrease monotonically with increasing condensation of rings in a linear manner (benzene $\rightarrow$ naphthalene $\rightarrow$ anthracene).

Table 8.11. Energetics and Dynamics of Aromatic Hydrocarbons

<table>
<thead>
<tr>
<th>Molecule</th>
<th>$E_1^b$</th>
<th>$E_3^b$</th>
<th>$k_s^c$</th>
<th>$k_{ST}^c$</th>
<th>$k_T^{cd}$</th>
<th>$\Phi_{ST}^e$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>115</td>
<td>85</td>
<td>$\sim 10^7$</td>
<td>$\sim 10^7$</td>
<td>$\sim 10^6$</td>
<td>$\sim 0.2$</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>90</td>
<td>61</td>
<td>$\sim 10^7$</td>
<td>$\sim 10^7$</td>
<td>$\sim 10^3$</td>
<td>$\sim 0.7$</td>
</tr>
<tr>
<td>1-Fluoronaphthalene</td>
<td>89</td>
<td>60</td>
<td>$\sim 10^7$</td>
<td>$\sim 10^7$</td>
<td>$\sim 10^3$</td>
<td>$\sim 0.7$</td>
</tr>
<tr>
<td>1-Chloronaphthalene</td>
<td>89</td>
<td>59</td>
<td>$\sim 10^8$</td>
<td>$\sim 10^7$</td>
<td>$\sim 10^3$</td>
<td>$\sim 1.0$</td>
</tr>
<tr>
<td>1-Bromonaphthalene</td>
<td>89</td>
<td>59</td>
<td>$\sim 10^9$</td>
<td>$\sim 10^7$</td>
<td>$\sim 10^3$</td>
<td>$\sim 1.0$</td>
</tr>
<tr>
<td>1-Iodonaphthalene</td>
<td>89</td>
<td>59</td>
<td>$\sim 10^{10}$</td>
<td>$\sim 10^7$</td>
<td>$\sim 10^3$</td>
<td>$\sim 0.7$</td>
</tr>
<tr>
<td>Anthracene</td>
<td>76</td>
<td>42</td>
<td>$\sim 2 \times 10^8$</td>
<td>$\sim 10^7$</td>
<td>$\sim 10^3$</td>
<td>$\sim 0.7$</td>
</tr>
<tr>
<td>Pyrene</td>
<td>83</td>
<td>48</td>
<td>$\sim 2 \times 10^7$</td>
<td>$\sim 10^6$</td>
<td>$\sim 10^3$</td>
<td>$\sim 0.3$</td>
</tr>
<tr>
<td>Triphenylene</td>
<td>81</td>
<td>67</td>
<td>$\sim 3 \times 10^7$</td>
<td>$\sim 10^7$</td>
<td>$\sim 10^3$</td>
<td>$\sim 0.9$</td>
</tr>
</tbody>
</table>

- *Energies in kcal/mol and correspond to 0.0 emission.*
- *Rates in sec$^{-1}$ from decay of fluorescence or phosphorescence in fluid solution near room temperature in the absence of oxygen.*
- *This rate constant is only approximate because impurities or other bimolecular quenching usually determines the observed value (except for benzene).*
- *Later system crossing quantum yield.*
Conjugated Enones and Dienones

Enones and dienones are similar to alkenes and polyenes in that they exhibit only weak emission at best. An interesting feature of both enones and dienones is the occurrence of two energetically similar T states, one $n\pi^*$ and the other $\pi\pi^*$. Dynamic information on $S_1$ and $T_1$ of enones and dienones is relatively scarce. However, values of singlet and triplet energies are available. The state energies of some selected enones and dienones are given in Table 8.12. The electronic configuration of $T_1$ of a number of enones has been probed and spectroscopic evidence is available in some cases which allows a configurational assignment.

The important feature to be noticed, from the standpoint of enone and dienone photochemistry, is that the lowest $T_1$ state may be $n\pi^*$ or $\pi\pi^*$ depending on substituents, and that these two configurations will commonly be comparable in energy. As a result, the solvent may have a major influence on which configuration best corresponds to the lowest triplet.

Table 8.12 p. 58.1 here
References


26. GET REF. FROM MURTHY


31. LASER JET REF. FOR SCHEME 11 - get from Murthy


34. Compilation on triplet rates


