Organic Mechanisms: Radicals
Chapter 4

Photochemistry

“The Chemistry of Excited States”
Photochemistry is the study of what happens when molecules absorb quanta of light (energy).

Reactions or changes are generally not spontaneous, so we need to input energy to overcome the activation energy barrier.

Often we think more commonly of **heating** a reaction to make it proceed (thermal initiation), but it also possible for **photochemical initiation**.

**Photochemical** initiation involves the absorption of a quantum of light by a suitable **chromophore** (section of a molecule that absorbs the light), and this leads to **electronic** excitation.

So we are going from ground states $\rightarrow$ electronically excited states.

These excited states cannot remain excited for long, and need a way to get rid of the extra energy – either by physical or chemical means (photochemical reactions).
Energies

100 kcal/mol \(= 4.34\) eV \(= 286\) nm \(= 35000\) /cm (near UV)
\[\text{nano} = 10^{-9}\]

286 kcal/mol \(= 12.4\) eV \(= 100\) nm \(= 100000\) /cm (far UV)

Typical Bond Energies

<table>
<thead>
<tr>
<th>Bond</th>
<th>Energy (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-H</td>
<td>110</td>
</tr>
<tr>
<td>C-C</td>
<td>80</td>
</tr>
<tr>
<td>C=C</td>
<td>150</td>
</tr>
<tr>
<td>C=O</td>
<td>170</td>
</tr>
</tbody>
</table>

UV light provides sufficient energy to move electrons out of bonding orbitals (electronic excitation).
States and their energies

Energy levels, rotational and vibrational
A Jablonski diagram, named after the Polish physicist Aleksander Jabłoński, is a diagram that illustrates the electronic states of a molecule and the transitions between them.

The states are arranged vertically by energy and grouped horizontally by spin multiplicity.

Radiative transitions are indicated by straight arrows and nonradiative transitions by squiggly arrows.

The vibrational ground states of each electronic state are indicated with thick lines, the higher rotational states with thinner lines.
Excited states and their fates:

$S_0$ is Singlet, ground state electronic energy level

$S_1$ is Singlet $1^{st}$ excited state

$S_n$ is the Singlet $n^{th}$ excited state

$T_1$ is the Triplet $1^{st}$ excited state

All these states have rotational and vibrational levels also.
$S_0$ is Singlet, ground state electronic energy level

$S_1$ is Singlet 1st excited state

$S_n$ is the Singlet $n^{th}$ excited state

$T_1$ is the Triplet 1st excited state

All these states have rotational and vibrational levels also.
Two Basic Rules:

1) Franck-Condon Principle
The absorption of light (excitation) is very rapid ($10^{-15}$ s duration / “instantaneous”), much faster than the rate for atomic vibration ($10^{-12}$ to $10^{-10}$ s duration), which means that:

*the initial excited state will have the same geometry as the ground state.*

“At the instant of excitation, only the electrons are reorganized; the heavier nuclei retain their ground state geometry”

The initial geometry of the excited state is seldom energy minimal – consequently “something” is going to happen (vibrational cascade, fluorescence, reaction, ...etc.) after absorption.

2) Inversion is forbidden by quantum mechanical selection rules, which requires conservation of spin during excitation transitions. (*Conservation of angular momentum*).

*Electrons do not undergo spin inversion at the instant of excitation.*

Singlet to triplet transitions are called **Inter System Crossing (ISC)** and are formally symmetry forbidden.
Bear in mind that

“some things are more forbidden than others”

There can be some grey area in the area of “allowedness”.

Sometimes it is not “all or nothing”.

Often we talk about events being statistically likely or statistically unlikely / improbable (but not impossible).

Intersystem crossings CAN occur if the energy gap between S and T states is small (their wavefunctions have some overlap).

This means there is more of an opportunity for the process to occur. But it is still going to be a slow process.

This is more common in ketones and aromatics, but less common in alkenes and dienes.
The geometry of the excited state – AFTER vibrational relaxation - is usually different from the ground state.

Simple example of ethene:

Plot of Dihedral angle between the p orbitals (Φ) vs. Energy.

For ethene, in the **ground state**, lowest energy has Φ = 0 and 180°, maximum at 90°.

Then lets think about the **excitation** process...
In alkenes, the electron excitation is $\pi$ to $\pi^*$. If the $hv$ boosts one electron from $\pi$ to $\pi^*$, there are two possible outcomes: it forms a *singlet* excited state (so long as we obey conservation of spin – which we have to!) or it forms a *triplet* state (changed spin of the electron during transition – *forbidden*).

We call the ground state $S_0$ and the 1st excited singlet state is $S_1$. 
However, think about what the $\pi$ bonding picture looks like now – there is no overall $\pi$ bonding.

So now the lowest energy conformation of the “excited ethene” has the CH$_2$ units perpendicular to minimize eclipsing interactions ($\Phi = 90^\circ$) – and an energy maximum when the p orbitals are coplanar ($\Phi = 0$ and $180^\circ$).

This is a good example of:

*The geometry of the excited state – after vibrational relaxation - is usually different from the ground state.*

However there is something else to be aware of... HUND’S RULE.
Hund's rule of Maximum Multiplicity is a principle (1925) of atomic chemistry which states that a greater total spin state usually makes the resulting atom more stable, most commonly manifested in a lower energy state, because it forces the unpaired electrons to reside in different spatial orbitals.

It has been shown that the actual reason behind the increased stability is a decrease in the screening of electron-nuclear attractions. Total spin state is calculated as the total number of unpaired electrons + 1.

As a result of Hund's rule, constraints are placed on the way atomic orbitals are filled using the Aufbau principle. Before any two electrons occupy an orbital in a subshell, other orbitals in the same subshell must first each contain one electron.

Also, the electrons filling a subshell will have parallel spin before the shell starts filling up with the opposite spin electrons (after the first orbital gains a second electron). As a result, when filling up atomic orbitals, the maximum number of unpaired electrons (and hence maximum total spin state) is assured.

So in summary..... $T_1$ is lower in energy than $S_1$
Also recall that we are not allowed to directly go from $S_0$ to $T_1$.

Notice (so far)

Only $S$ to $S$

$S_1$ higher than $T_1$
Photosensitization

This is an important alternative to direct excitation of molecules, most commonly used as a way to create TRIPLET states that are challenging to obtain directly.

For example, Naphthalene has $S_1$ 108 kcal/mol above $S_0$, and $T_1$ 62 kcal/mol above $S_0$.

Notice here $S_1$ and $T_1$ are very different in energy, so very forbidden Intersystem crossing.

Also recall that we cannot go S to T on direction excitation.

So how do we get naphthalene into its $T_1$ excited state?
We can add in a compound (sensitizer), which we can easily irradiate and (1) excite into $S_1$, which then (2) conveniently can ISC down to a $T_1$ state.

This $T_1$ excited state will *conveniently* have the right amount of extra energy, which it (3) can unload to the naphthalene boosting it from $S_0$ to $T_1$.

If this causes the sensitizers to go $T_1$ to $S_0$, then overall *(naphthalene AND sensitizers)* we have **conserved spin**.
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Types of Excitation

When an electron is excited, it usually goes into the lowest available vacant orbital.

For typical organic molecules, there are 4 possible types of electron excitation:

1) $\sigma \rightarrow \sigma^*$
Common for alkanes or things that do not have lone pairs or $\pi$ bonds.

2) $n \rightarrow \sigma^*$
Common for amines, alcohols, ethers or things that have lone pairs but not $\pi$ bonds.

3) $\pi \rightarrow \pi^*$
Common for alkenes, aldehydes, carboxylic acids, esters, or things that have $\pi$ bonds.

4) $n \rightarrow \pi^*$
Common for aldehydes, ketones, esters, things that have lone pairs and $\pi$ bonds.
1) $\sigma \rightarrow \sigma^*$

2) $n \rightarrow \sigma^*$

3) $\pi \rightarrow \pi^*$

4) $n \rightarrow \pi^*$

These are listed in DECREASING energy. (Typically)

The last two are by far the most important in organic photochemistry.

Almost all organic photochemistry is:

$$\pi \rightarrow \pi^*$$

or

$$n \rightarrow \pi^*$$

Most common examples are Alkenes undergoing $\pi \rightarrow \pi^*$, and carbonyl compounds undergoing $\pi \rightarrow \pi^*$ or $n \rightarrow \pi^*$
The UV spectrum for ethene:

This absorption of UV irradiation is causing a $\pi \rightarrow \pi^*$ transition.
Recall that $\text{Abs} = \varepsilon cl$  
$\varepsilon$ (absorption coefficient) can be viewed as “allowedness”
For acetone we see both $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ excitations.

Notice
a) the different energies required (longer $\lambda$ is lower energy)

b) the different $\varepsilon$. The $n \rightarrow \pi^*$ excitation is symmetry forbidden – much lower $\varepsilon$.

So $n \rightarrow \pi^*$ takes less energy, but is forbidden / less likely.
Summary and simplification of allowedness

Selection rules tell us that when the TRANSITION MOMENT INTEGRAL IS ZERO then a process is forbidden.

If it is not equal to zero, it is allowed.

For electrons to move from one orbital to another, then their wavefunctions must overlap.

The more the wavefunctions overlap, the more allowed the process is.

So we can explain why $\pi \rightarrow \pi^*$ is very allowed (large $\epsilon$), and $n \rightarrow \pi^*$ less allowed (smaller $\epsilon$).
\[ \pi \rightarrow \pi^* \] is very allowed (large \( \epsilon \)), and \( n \rightarrow \pi^* \) less allowed (smaller \( \epsilon \)).

For electrons to move from one orbital to another, then their wavefunctions must overlap.

The more the wavefunctions overlap, the more allowed the process is.

The \( \pi \) and \( \pi^* \) are in the same plane, and same areas in space, therefore overlapping wavefunctions.

The lone pairs are perpendicular to the \( \pi \) system, and have little overlap with \( \pi^* \) and so smaller \( \epsilon \).
When a molecule gets excited, there are two possible fundamentally different fates:

**PHYSICAL Processes**

**CHEMICAL Processes. (Photo-chemistry)**
Physical Processes

When a molecule gets photochemically excited, it will not remain in its excited state for long. (unstable)

Most excitations are from the $S_0$ to $S_1$ states.

Remember (S to T are forbidden)

Promotions to $S_2$ or higher S states can and do occur, but these states usually will quickly (around $10^{-12}$ secs) drop to $S_1$ via vibrational cascade and internal conversion. (Including collisions with neighboring molecules).

Therefore in most normal cases, the lowest vibrational level of $S_1$ is the only important excited Singlet state to consider.

There are 5 available physical pathways open to this excited molecule:
There are 5 available **physical** pathways open to this excited molecule:
1) A molecule in the $S_1$ state can cascade down through the vibrational levels of the $S_0$ state, and thus return to the ground state. It achieves this by giving up its energy in small increments to the environment.

This process is called **INTERNAL CONVERSION (IC)**

This is usually a slow process, and is not a preferred pathway.

This is an example of **radiationless transition**, or **nonradiative decay**.
2) A molecule in the $S_1$ state can drop to some low vibrational level of the $S_0$ state by giving off the energy in the form of light. (radiative transition)

This is a **relatively** slow process ($10^{-9}$ secs).

This is called **FLUORESCENCE**.
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This is called FLUORESCENCE.

This process is also not that preferred as it can be slow, and other things can happen before fluorescence has the time to occur.

It is more common in small (diatomic) or rigid (aromatic) molecules.

Since the decay is to some low vibrational level of the $S_0$ state, the hv emitted is of lower energy than that which was put in.

I.e. Fluorescence gives out a longer $\lambda$ than was used to excite.

S $\rightarrow$ S transition is called fluorescence (allowed – faster $10^{-9}$ s)

T $\rightarrow$ S transition is called phosphorescence (less allowed – slower $10^{-3}$ s)
3) It is possible for some (but not necessarily all) molecules in the $S_1$ state to undergo an INTERSYSTEM CROSSING (ISC) to the lowest energy triplet state $T_1$. 

![Diagram of energy levels and transitions involving $S_0$, $S_1$, $S_2$, and $T_1$ states with arrows indicating transitions labeled as $hv$, $hv_f$, $hv_p$, $vc$, and $IC$.]
3) It is possible for some (but not necessarily all) molecules in the $S_1$ state to undergo an INTERSYSTEM CROSSING (ISC) to the lowest energy triplet state $T_1$.

Formally $S$ to $T$ transitions are forbidden (conservation of angular momentum!), but some are more forbidden than others!

ISC is less forbidden when the $S$ and $T$ states are of similar energy (their wavefunctions have some overlap).

More common in carbonyl and/or aromatic systems. Less so in alkene, diene type compounds.

ISC occurs without loss of energy.

Since the excited singlet state is higher in energy than the corresponding triplet state (Hund’s Rule), there will be excess energy that has to be given up.

The most common pathway is to ISC to a $T_1$ state in a high vibrational level, and then have $T_1$ to cascade down to its lowest $T_1$ level.

This cascade can be fast ($10^{-12}$ s).
4) A molecule in the $T_1$ state may return to the $S_0$ state by either emitting:

- **heat** (actually ISC to $S_0$ in a higher vibrational state and then vibrational cascade).

- or

- **light** (this radiative process is called **PHOSPHORESCENCE**).

Since both these involve an ISC, they are relatively slow ($10^{-3}$ to $10^1$ sec) – because of their forbidden-ness.

$T_1$ states therefore tend to have longer lifetimes than $S_1$ states.
5) If nothing else initially happens to the excited molecule, then a molecule in its $S_1$ or $T_1$ state can transfer its excess energy to another molecule.

E.g. Just as in photosensitization described earlier.
Photochemistry

For Carbonyl Compounds, there are 3 common types of photochemical reaction:

1) \(\alpha\) Cleavage (Norrish type I reaction)

2) Hydrogen Abstraction (can be followed by Norrish type II cleavage)

3) Cycloaddition
1) \( \alpha \) Cleavage (Norrish type I reaction)

Carbonyl compounds when irradiated can undergo cleavage of the Carbonyl C - \( \alpha \) bond.

In the \textit{gas phase} the radicals are generated and detected (longer lifetime).
1) $\alpha$ Cleavage (Norrish type I reaction)
In solution the radicals undergo further reactions to give **products**.

\[ \begin{align*}
\text{Product 1} & \quad \text{Product 2} \\
\end{align*} \]

\[ \begin{align*}
\text{Product 3} & \quad \text{Product 4} \\
\end{align*} \]
Writing photochemical mechanisms with arrows

Here we have a bit of a problem, because you **cannot** write an accurate **Lewis structure** to represent an **excited state**.

![Diagram showing photochemical mechanism](image)

Even though it is **convenient** to write the **diradical** form (π bond broken) it is **not accurate**, since it is really one of the lone pair electrons promoted to the π*, if [n, π*] is occurring.
So when we write this type of mechanism, the **cleavage** is a **two step** process.

The radicals can undergo further reactions to give **products**.
Again, you can get further reactions after the cleavage.
2) Hydrogen Abstraction
The radicals can abstract a **Hydrogen atom** from a donor, and the resulting radicals can then undergo further reactions.

E.g. the Photopinacolization Reaction
Intramolecular Hydrogen Abstraction followed by cleavage

= Norrish type II cleavage.

The radicals can abstract a Hydrogen atom from a donor. The resulting radicals can then undergo further reactions.
3) Cycloaddition

Most people are familiar with:
the allowed concerted thermal (4+2) cycloaddition (Diels Alder), and

the thermally forbidden concerted (2+2) cycloaddition, and

the photochemically allowed (2+2) cycloaddition.

Carbonyls will undergo cycloadditions with alkenes under photochemical excitation (of the carbonyl).
The mechanism explains product formation, and also justifies the product ratio.
An intramolecular example:
Here ends *simple* photochemistry.

*We could have also talked about...*

- unsaturated carbonyls

- alkenes and dienes

- aromatics...