Chap. 12 Photochemistry

Photochemical processes

1. Light absorption: \( S_0 \rightarrow S_1, S_0 \rightarrow S_2 \) \( k \approx 10^{15} \)
2. Vibrational Relaxation: \( k \approx 10^{12}/s \), from high \( \nu \) to low \( \nu \)
3. Internal Conversion: to lower electronic state of same multiplicity \( (k > 10^{10}/s) \)
4. Radiationless Decay: \( S_1 \rightarrow S_0 \), no emission, \( k < 10^6/s \)
5. Intersystem Crossing: \( k \approx 10^6 \sim 10^{10}/s \), depends on molecules. (carbonyl fast; alkene slow)
6. Fluorescence: \( S_1 \rightarrow S_0 \), with emission. \( k \approx 10^6 \sim 10^9 \).
7. Phosphorescence: \( T_1 \rightarrow S_0 \) with emission. \( k \approx 10^{-2} \sim 10^4 \)
8. Triplet – Triplet Absorption
9. Singlet – Singlet Absorption
10. Singlet – Triplet Absorption
**Photophysical Processes**

- $S_0$ (ground state) of $\text{H}_2\text{C}=\text{O}$:
  
  $\begin{align*}
  &\left[(1S_\text{O})^2(1S_\text{C})^2(2S_\text{O})^2(\sigma_{\text{C-H}})^2 (\sigma'_{\text{C-H}})^2 \\
  &\quad(\sigma_{\text{C-O}})^2](\pi_{\text{C-O}})^2(n_\text{O})^2
  \end{align*}$

- $S_1$ (1st excited state):
  
  $\begin{align*}
  &\left[(1S_\text{O})^2(1S_\text{C})^2(2S_\text{O})^2(\sigma_{\text{C-H}})^2 (\sigma'_{\text{C-H}})^2 \\
  &\quad(\sigma_{\text{C-O}})^2](\pi_{\text{C-O}})^2(n_\text{O})(\pi^*_{\text{C-O}})
  \end{align*}$

- $S_2$ (2nd excited state):
  
  $\begin{align*}
  &\left[(1S_\text{O})^2(1S_\text{C})^2(2S_\text{O})^2(\sigma_{\text{C-H}})^2 (\sigma'_{\text{C-H}})^2 \\
  &\quad(\sigma_{\text{C-O}})^2](\pi_{\text{C-O}})(n_\text{O})^2(\pi^*_{\text{C-O}})
  \end{align*}$

![Diagram of molecular orbitals and transitions](image)
**UV Absorption and Emission**

- Factors determining radiative transition:
  
  1. Symmetry of electronic state (ini. final state)
  
  2. Multiplicity of the spin
     - Spin-orbit interaction (allows different spin transition mixing due to the mixing of magnetic moment of e\(^{-}\) and the magnetic moment of the nucleus)
     - Heavy atom effect: higher rate of intersystem crossing
     - Greater mixing if S and T are closer in energy, example carbonyl cpds.
  
  3. Frank-Condon term, determined by overlap of nuclear coordinate of init. and final state
**Frank-Condon Principle**

• At the instant of excitation, only electrons are reorganized, the heavier nuclei retain the ground state geometry.

• The excited state has similar molecular geometry as ground state.

(1): Vib. energy diff. of $S_0$
(2): (0,0) transition
(3): Vib energy diff. of $S_1$
**Fluorescence**

- The excited state geometry quite different from ground state geometry => large Stokes shift

(anti-Stokes shift: the fluorescence is at shorter wavelength)
Measurement of Absorption

- Beer-Lambert Law: \[ \log \frac{I_o}{I_t} = \varepsilon c d \]
  - \( I_0 \): incident light
  - \( I_t \): transmitted light
  - \( \varepsilon \): extinction coefficient
  - \( c \): concentration
  - \( d \): light path length

- Quantum yield of emission:
  \[ \Phi_f = \frac{\# \ of \ photon \ emitted \ from \ S_1}{\# \ of \ photon \ absorbed} \]
**Phosphorescence**

- Much reduced due to diffusional quenching with ground state species or O$_2$
- Observed in fixed matrix, such as liquid N2 temperature or surrounded by a host

In aqueous solution with α-CD

**Concentration-Dependent Fluorescence**

- Excimer formation
  - Excimer: A complex formed between an excited molecule with a ground state molecule of same compound

In heptane

A$^*$A $\rightarrow$ AA$^*$
**Geometric Requirement of Excimer Formation**

• The molecular plane can stack together with interplanar distance less than 3.5 Å.

\[
\begin{align*}
\text{n=0} & \quad \text{no overlap of ring} \\
\text{n=1} & \quad \text{excimer formation} \\
\text{n=2} & \quad \text{strain of chain}
\end{align*}
\]

Excimer formation

Partial overlap of ring plane
- Exciplex: complex formed between an excited molecule with a ground state molecule of dissimilar molecule
- $A^*B \leftrightarrow AB^*$ can give exciplex emission or quench emission

![Exciplex diagram]

aromatics / amine
aromatics/conjugate olefin

![Quenching diagram]

Fluorescence quencher

Geometric requirement less stringent
**Energy Transfer and Electron Transfer**

- **Pathways** \( D^* + A \rightarrow D + A^* \)
  
  1) **Radiative energy transfer**
     - \( D^* \rightarrow D + h\nu \)
     - \( A + h\nu \rightarrow A^* \)

     The rate depends on
     1. The quantum yield of emission by \( D^* \) (\( \Phi_D \))
     2. The concentration of (the # of) \( A \) in light path
     3. The light absorbing ability of \( A \) (extinction coefficient)
     4. The overlap of emission spectrum of \( D^* \) and absorption of \( A \) (spectral overlap integral)

  2) **Förster energy transfer**
     - Long range (\( D^* \)-\( A \) distance up to 100 Å)
     - No radiation involved
     - The dipole-dipole interaction of \( D^* \) and \( A \)

     ![Diagram](image)

     • An interaction at a distance via electromagnetic field, induce a dipole oscillation in \( A \) by \( D^* \).

     • Efficient transfer requires a good overlap of emission of \( D^* \) with absorption of \( A \).
3) Collisional energy transfer (Dexter energy transfer): exchange of electron between the donor and acceptor

The exchange of electron via overlap of electron clouds require physical contact between the interacting partners.
- Spectral overlap integral also required
- This process allows triplet state to be generated
  \[ D^* \downarrow + A_0 \uparrow \rightarrow D_0 \uparrow + A^* \downarrow \]
- A short-ranged interaction

**Electron Transfer**

The photo excited state is a better donor (lower oxid. potential) as well as a better acceptor (lower reductive potential) relative to ground state
Acidity and Basicity in Excited States

- $A-H \rightarrow A^- + H^+$
- $[A-H]^* \rightarrow [A^-]^* + H^+$

\[ \text{Intensity} \]

\[ \text{Wavelength (nm)} \]
- \( \Delta H^*+h\nu' = \Delta H+h\nu''' \)

- \( \Delta H^*- \Delta H = +h\nu'' - h\nu' \approx \Delta G^*- \Delta G \)
  - (if \( \Delta S^* \approx \Delta S \) for ionization)
  - \( \Delta G = 2.303RTpK \)
  - \( pK^*-pK = \frac{\Delta G^*-\Delta G}{2.303RT} \approx \frac{h\nu'' - h\nu'}{2.303RT} \)

**Table 12.3** Acidity constants of ground and excited states. (Except as noted, data are from reference 80.)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Reaction</th>
<th>( pK(S_0) )</th>
<th>( pK(S_1) )</th>
<th>( pK(T_1) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Naphthalene(^a)</td>
<td>protonation</td>
<td>-4.0</td>
<td>11.7</td>
<td>-2.5</td>
</tr>
<tr>
<td>2-Naphthol</td>
<td>deprotonation</td>
<td>9.5 ((1))</td>
<td>3.1</td>
<td>7.7 to 8.1</td>
</tr>
<tr>
<td>2-Naphthoic acid</td>
<td>deprotonation</td>
<td>4.2 ((2))</td>
<td>8.2(^b)</td>
<td>4.0(^c)</td>
</tr>
<tr>
<td>2-Naphthylamine</td>
<td>protonation</td>
<td>4.1 ((3))</td>
<td>-2.0</td>
<td>3.1 to 3.3</td>
</tr>
</tbody>
</table>


\(^c\)Reference 81.

(1): more acidic

(2): less acidic

(3): more acidic
When photochem. excited, electron from HOMO $\rightarrow$ LUMO, and change the e$^-$ density
Bond angle, Dipole moments of Excited state

![Chemical structures and images](image)

**Table 12.4** Physical properties of formaldehyde excited states. (Data from references 89, 90, and 91.)

<table>
<thead>
<tr>
<th>Property/State</th>
<th>$S_0$</th>
<th>$S_1$</th>
<th>$T_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Geometry</td>
<td>planar</td>
<td>pyramidal</td>
<td>pyramidal</td>
</tr>
<tr>
<td>Δ (nonplanarity)</td>
<td>0°</td>
<td>20°</td>
<td>35°</td>
</tr>
<tr>
<td>C=O length</td>
<td>1.22 Å</td>
<td>1.32 Å</td>
<td>1.31 Å</td>
</tr>
<tr>
<td>$ν$ C=O stretch</td>
<td>1746 cm$^{-1}$</td>
<td>1182 cm$^{-1}$</td>
<td>1251 cm$^{-1}$</td>
</tr>
<tr>
<td>&lt;HCH</td>
<td>120°</td>
<td>122°</td>
<td></td>
</tr>
<tr>
<td>Dipole moment</td>
<td>2.3 D</td>
<td>1.5 D</td>
<td>1.3 D</td>
</tr>
</tbody>
</table>

**LUMO**  

**HOMO**

$\pi^*$  
$n$  
$\pi$

$S_0$ $\mu = 2.3$ D  
$E = 0$ kcal/mol$^{-1}$  

$S_1$ $\mu = 1.5$ D  
$E \approx 84$ kcal/mol$^{-1}$

$T_1$ $\mu = 1.3$ D  
$E \approx 76$ kcal/mol$^{-1}$
\( S_0 \rightarrow S_1 \) (\( n - \pi^* \)) excited state less polar than the ground state
- hypsochromic (blue) shift with polar solvent

\( S_0 \rightarrow S_2 \) (\( \pi - \pi^* \)) excited state more polar than the ground state
- bathochromic (red) shift with polar solvent
Photochemical Reactions of Carbonyl Compounds

\[
\text{Sat'd Ketone} \xrightarrow{\text{hv}} \begin{array}{c}
\begin{array}{c}
\text{n} \\ \rightarrow \pi^* \\
\end{array}
\end{array}
\Rightarrow \begin{array}{c}
\text{diradical} \\
\text{character}
\end{array}
\]

Norrish Type I Cleavage (α - cleavage)

\[
\begin{array}{c}
\text{R} \\ \text{R}
\end{array}
\xrightarrow{\text{hv}} \begin{array}{c}
\begin{array}{c}
\text{O} \\ \text{R} \\ \text{R}
\end{array}
\end{array}
\Rightarrow \begin{array}{c}
\begin{array}{c}
\text{O} \\ \text{R} \\ \text{R}
\end{array}
\end{array}
\Rightarrow \begin{array}{c}
\begin{array}{c}
\text{CO} \\
\text{R}
\end{array}
\end{array}
\]

\[
\begin{array}{c}
\text{R}
\end{array}
\xrightarrow{\text{hv}} \begin{array}{c}
\text{R}
\end{array}
\Rightarrow \begin{array}{c}
\text{R}
\end{array} + \begin{array}{c}
\text{CO}
\end{array}
\]
\[
\text{CH}_3(\text{CH}_2)_2\text{CH}=\text{CH}_2 + \text{CO} \rightarrow \text{disproportionation}
\]
\[
\text{H}_2\text{C} = \text{CH}_2 + \text{H}_3\text{CCH} = \text{CH}_2 + \text{CO} \rightarrow \text{fragmentation}
\]

\[
\text{H}_2\text{C} = \text{CCH} (\text{CH}_2)_3\text{CHO}
\]

\[\text{S}_1 \rightarrow \text{T}_1 \text{ at vibrationally excited state of } \text{T}_1\]

\[
\begin{align*}
\text{more energetic} & \quad \text{lose CO readily} \\
\text{gas phase} & \\
\text{solution}
\end{align*}
\]

\[
\text{Ketene}
\]

\[
\text{Less energetic; no CO loss}
\]

\[
\begin{align*}
\text{acid} & \\
\text{ROH} & \\
\text{H}_2\text{O}
\end{align*}
\]
**Hydrogen Abstraction Reaction**

\[
\text{hv} \quad \text{O} \quad \text{hv} \quad \text{H-A} \quad \text{O} \quad + \quad \text{A} \quad \cdot
\]

**Photoreduction of benzophenone in iPA**

**Norrish Type II Cleavage (β-Cleavage)**

\[
\text{hv} \quad \alpha \quad \beta \quad \gamma \quad + \quad \text{CH}_2\text{CH}_2
\]

6-membered ring (T.S.)
If the S.M. is retrieved, the $\gamma$ carbon may lose stereochem. (if chiral), so not exactly the same original S.M.

$\alpha - \beta$ unsaturated ketone

Absorb at longer wave length

Photo-driven

De-conjugated absorb at shorter wave length
Oxetene Formation (Paterno-Buchi Reaction)

\[ \text{hv} \]

Photochemical Reactions of Alkene and Dienes

- Isomerization

\[ \pi \rightarrow \pi^* \quad \lambda_{\text{max}} < 200\text{nm} \]

1. Trans compound has longer absorption wavelength

2. Both cis and trans give the same excited state species

\[ \Rightarrow \text{twisted geometry with 90}^\circ \text{rotation of p-orbital relative to each other} \]
A photostationary state will be reached from either side (cis→
photostationary state; trans→ photostationary state)

$$\frac{[C]_{pss}}{[T]_{pss}} = \frac{\varepsilon_t}{\varepsilon_c} \bullet \frac{k_c}{k_t}$$

$k_c =$ formation constant of cis from the excited twisted state

$k_t =$ formation constant of trans from the excited twisted state
For n=4,5,6
For cyclopentene, the cis-trans isomerization doesn’t occur.

The photochemically allowed reaction by symmetry rule may be only one of many reaction pathways.