Elementary Photophysical Transitions and Photochemical Reactions

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Photochemistry’s Icons
Why I am here.


From Photochemistry of Organic Compounds by Peter Klán and Jakob Wirz, 2009
Photo by Lilli Kasha ca. 1970

1920 - 2013
Intersystem Crossing

Phosphorescence and the Triplet State


\[ E_T = 2.86 \times 10^4/\lambda (\text{nm}) \text{ in kcal/mol} \]

Naphthalene phosphorescence – triplet energies
Internal and External Heavy Atom Effects

$\alpha$-Chloronaphthalene is yellow in EtI, JCP, 1952
Singlet $O_2$ in Chemiluminescence and in Triplet Energy Transfer
Double Proton Transfer in 7-Azaindole Proton Transfer Spectroscopy
The Blue Daylily and Intramolecular $S_1$ Proton Transfer in Flavonoids
The Kasha Guitar
Triplet Sensitization

\[ S_0 \rightarrow S_1 \rightarrow T_1 \rightarrow S_0 \]

- **S\_1**: First excited singlet state
- **T\_1**: Triplet state
- **S\_0**: Ground state
- **hv**: Photon energy
- **Energy transfer**
- **Light filter**
- **Donor**
- **Acceptor**
Triplet Sensitized Stilbene Photoisomerization

The Saltiel Plot

\[ \frac{[c]}{[r]} \]

\( E_T \) (Kcal/mole)

The Photostationary State

\[ \begin{align*}
1\text{t-St} + 3\text{S}^* & \rightarrow 3\text{t}^* + 1\text{S}^* \\
3\text{t}^* & \rightarrow 3\text{p}^* \\
3\text{p}^* & \rightarrow \alpha 1\text{t} + (1-\alpha) 1\text{c} \\
1\text{c-St} + 3\text{S}^* & \rightarrow 3\text{c}^* + 1\text{S}^* \\
\frac{d[1\text{t}]}{dt} & = -k_t[3\text{S}^*][1\text{t}] + \alpha k_d[1\text{p}^*] = 0 \\
\frac{d[1\text{c}]}{dt} & = -k_c[3\text{S}^*][1\text{c}] + (1-\alpha) k_d[1\text{p}^*] = 0 \\
k_t[3\text{S}^*][1\text{t}] & = \alpha k_d[1\text{p}^*] \\
k_c[3\text{S}^*][1\text{c}] & = (1-\alpha) k_d[1\text{p}^*] \\
\frac{[1\text{c}]}{[1\text{t}]}_{PSS} & = \frac{k_t}{k_c} \frac{(1-\alpha)}{\alpha}
\end{align*} \]
Figure 2. Proposed potential energy curves for twisting about the central bond of stilbene in $S_0$ and $T_1$. 
Nonvertical Triplet Energy Transfer

Figure 2. Proposed potential energy curves for twisting about the central bond of stilbene in $S_0$ and $T_1$. 
Average bond energies
C-C        83 kcal/mol
C=C        146 kcal/mol
π bond    ~ 63 kcal/mol
van der Waals strain due to crowding of cis-methyl groups

cis and trans-2-Butene

cis-2-butene

trans-2-butene
cis- and *trans*-2-butenes are stable separable isomers. They have the same connectivity and are stereoisomers. Rotation about a double bond occurs only at very high *T* or following light absorption.

\[ \pi \text{ bond} \sim E_{\text{act}} = 62.4 \text{ kcal/mol} \]
\[ h^\nu \]

\[ S = \frac{1}{2} - \frac{1}{2} = 0 \quad S = \frac{1}{2} - \frac{1}{2} = 0 \quad S = \frac{1}{2} + \frac{1}{2} = 1 \]

\[ M = 1 \quad M = 1 \quad M = 3 \]

**Singlet** \( S_0 \)  **Singlet** \( S_1 \)  **Triplet** \( T_1 \)

\[ M = 2S + 1 \]

**Spin States** \( \alpha\alpha, \beta\beta, \sqrt{1/2}(\alpha\beta + \beta\alpha), \sqrt{1/2}(\alpha\beta - \beta\alpha) \)

\[ T \quad T \quad T \quad S \]
Effect of Conjugation

Absorbance

$A = \log(I_0/I) = \varepsilon c l$

<table>
<thead>
<tr>
<th>n</th>
<th>$\lambda_{\text{max}}, \text{nm}$</th>
<th>$\varepsilon_{\text{max}} \times 10^{-3}, \text{M}^{-1}\text{cm}^{-1}$</th>
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Molecular Orbital Analysis of the Diels-Alder Reaction

The diene is the electron donor and the dienophile is the electron acceptor. The concerted nature of the D-A reaction can be understood by considering the interaction of the HOMO of the diene with the LUMO of the dienophile (Fukui/Kyoto, Woodward/Harvard, Hoffmann/Harvard now Cornell---Nobel prize in Chemistry)
Frontier Orbital Control of Diels-Alder Reaction
Electrocyclic reactions are stereospecific
Rotation in the **same direction** leads to a bonding interaction (+ lobe on + lobe or - lobe on – lobe). The reaction passes through the same TS in both directions.
Rotation in **opposite directions** leads to a bonding interaction (+ lobe on + lobe or - lobe on – lobe).
The reaction passes through the same TS in both directions.
\[ \phi_{ct} = 0.03, \phi_{tc} = 0.016 \]

1,6-Dideuteriohexatrienes

Havinga’s NEER Principle

Egbert Havinga
1909-1988

Photocyclization
Long $\lambda$

Photoisomerization
Short $\lambda$
NPE Conformers

$\text{t-NPE}_A$ \leftrightarrow $\text{c-NPE}_A$

$\text{t-NPE}_B$ \leftrightarrow $\text{c-NPE}_B$
trans-1-(2-Naphthyl)-2-phenylethene and the NEER Principle

\[
\begin{align*}
\text{hv} & \quad - \quad \text{hv} \\
\text{t-NPE}_A & \quad \text{hv} & \quad - \quad \text{hv} \\
\end{align*}
\]
Fluorescence Emission Spectra of t-NPE as a Function of $\lambda_{\text{exc}}$ in Ar Outgassed Benzene at 20 °C
Summary of PCA-SM Mathematical Operations

- Transposed Matrix \( x \) × Spectral Input Matrix = Covariance Matrix
- Number of Components ⇐ Eigenvalues ⇐ Diagonalized Matrix
- Eigenvectors ⇐ Eigenvector Matrix
- Pure Component Spectra
  - Pure Component Coefficients
  - Experimental Spectra
TWO COMPONENTS

\[ S_i = \alpha_i V_\alpha + \beta_i V_\beta \]

\[ \alpha \Sigma V_\alpha + \beta \Sigma V_\beta = 1 \]

\[ \alpha V_\alpha k + \beta V_\beta k \geq 0 \]
Principal Eigenvectors

Global Stern-Volmer Plots

Conformer Spectra

Stern-Volmer equation:
\[ \frac{\phi_0}{\phi} = 1 + K_{SV}[Q] \]

Global Stern-Volmer equation:
\[ \frac{F_0(\beta_0 - \beta_B)}{F(\beta - \beta_B)} = 1 + K_{SV}^A[Q] \]
Stern-Volmer Quenching

**Equation**

\[ 1^A + h\nu_{\text{exc}} \rightarrow 1^A^* \]

\[ 1^A^* \rightarrow 1^A + h\nu_f \]

\[ 1^A^* \rightarrow 3^A^* \]

\[ 1^A^* \rightarrow P \]

\[ 1^A^* + Q \rightarrow 1^A + Q^* \]

**Rate**

\[ I_a \]

\[ k_f[1^A^*] \]

\[ k_{is}[1^A^*] \]

\[ k_p[1^A^*] \]

\[ k_q[Q][1^A^*] \]
The Stern-Volmer Plot

\[
\frac{d[hv_f]}{dt} = k_f[1^* A^*]
\]

\[
\frac{d[1^* A^*]}{dt} = I_a - (k_f + k_{is} + k_p)[1^* A^*] = 0
\]

where \( I_a \) is the rate of light absorption

\[
[1^* A^*] = \frac{I_a}{k_f + k_{is} + k_p}
\]

\[
\frac{d[hv_f]}{dt} = \frac{k_f I_a}{k_f + k_{is} + k_p}
\]

\[
\phi^o_f = \frac{1}{I_a} \frac{d[hv_f]}{dt} = \frac{k_f}{k_f + k_{is} + k_p} = k_f \tau
\]

\[
\phi_f = \frac{k_f}{k_f + k_{is} + k_p + k_q[Q]} = \frac{k_f \tau}{1 + k_q \tau[Q]}
\]

\[
\left( \frac{\phi^o_f}{\phi_f} \right) = 1 + k_q \tau[Q] = 1 + K_{SV}[Q]
\]
The $n, \pi^*$-transition of formaldehyde.
Benzophenone State Diagram

$S_2(\pi,\pi^*)$
100 kcal mol$^{-1}$

$S_1(n,\pi^*)$
74 kcal mol$^{-1}$

$T_2(\pi,\pi^*)$
100%

$T_1(n,\pi^*)$
69 kcal mol$^{-1}$

$S_0$

$10^6$ s$^{-1}$ (calc)

10%

90%

$<10^7$ s$^{-1}$

1.7 s$^{-1}$

1.5 $\times$ 10$^2$ s$^{-1}$
El-Sayed’s Rules for Intersystem Crossing
Figure 1. Benzophenone luminescence spectra (self-absorption-corrected, instrumental-response-uncorrected) at different temperatures (Table 1) from the degassed CCl₄ solution. The inset shows the set of Gaussian functions used to compensate the spectra for thermal broadening.
Figure 3. (a) Ratios of the third to the first eigenvalue (circles) and the third to the second eigenvalue (squares) as a function of the compensating broadening parameter $k$. (b) First and second eigenvectors before the compensation for thermal broadening (dashed lines) and after the compensation.
Figure 5. $\alpha \beta$ normalization line for the benzophenone luminescence system. The standard deviation for the van’t Hoff plot as a function of $\beta$ is also shown. The minimum determines the $\beta_{DF}$ value corresponding to the spectrum of the pure delayed benzophenone fluorescence.
Figure 9. Emission spectra of benzophenone in CCl₄ corrected for nonlinearity in instrumental response and normalized to unit area: phosphorescence (dashed–dotted line), delayed fluorescence (solid line), and prompt fluorescence (dashed line). The first two spectra are obtained by extrapolation of the $\alpha$, $\beta$ coefficients of the pure component spectra to 23.5 °C, and the prompt fluorescence is an average of 40 spectra measured at room temperature (ca. 22.0 °C) for $\lambda_{exc} = 326$ nm.
Multidimensional Isomerization – Conical Intersections – Trapping Twisted Intermediates

\[ \vec{h}_{S_0S_1} = (E_1 - E_0)^{-1} \left| \psi_{S_0}^e \frac{\partial \hat{H}}{\partial R} \psi_{S_1}^e \right| \]


Acknowledgments

PCA-SM
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Shipra Gupta
Sumesh Krishnan
Support
NSF (1965-2020)
Conformer specific photochemistry in $c$- and $t$-NPE
UV Spectrum of cis,trans-1,3-cyclooctadiene

\[ \lambda_{\text{max}} \quad 230 \text{ nm} \]
\[ \varepsilon_{\text{max}} \quad 2630 \]
Figure 2. Temperature dependence of the n, π* absorption spectrum of a 0.0093 M benzophenone solution in CCl₄: experimental spectra (4.7–68.1 °C), solid lines; extrapolated spectra (73.5–88.5 °C), dashed lines (see the Supporting Information).
The Saltiel Plot for Stilbene Triplet Photoisomerization
1,3-Diene Triplets: Conformer Specific Photoisomerization and Photodimerization

Fluorenone sensitized photoisomerization

\[ \begin{align*}
57 \text{ kcal/mol} & \quad \xrightleftharpoons[K]{} \quad 52 \text{ kcal/mol} \\
{s-t,^0t} & \xrightleftharpoons[K']{} \quad {s-c,^0t} \\
59 \text{ kcal/mol} & \quad \xrightleftharpoons{} {} \\
{s-t,^0c} & \quad \xrightleftharpoons{} {} \\
\text{Not present} & \quad \text{Not present}
\end{align*} \]

\[ \begin{align*}
& \xrightarrow{K} \quad 0.31 \text{tt} + 0.50 \text{ct} + 0.19 \text{cc} \\
& \xrightarrow{0.69} \quad 0.70 \text{tt} + 0.30 \text{ct}
\end{align*} \]
1,3-Diene Triplets: Conformer Specific Photoisomerization and Photodimerization

Fluorenone sensitized dimerization
Saltiel Plots

1,3-butadiene dimerization
- dashes
1,3-pentadiene $E,Z$ isomerization
- solid line
Figure 2-1. State diagram (commonly called Jablonski diagram) depicting molecular states and photophysical processes. The vertical position of thick horizontal lines represents the electronic energy minimum. Vibrational energy levels are shown as thin lines. The width of the horizontal lines and their position along the abscissa are chosen merely to avoid congestion in the graphical diagram and have no physical connotation.
Heptane
Water