ABBIOTIC TRANSFORMATIONS

Without biological CATALYSIS Chemical breakdown less likely: Activation Energy is a barrier

\[ \text{Ex} \quad O_2 + \text{Hexane} \rightarrow \Delta G^\pm \rightarrow \Delta G \rightarrow \text{CO}_2, \text{H}_2\text{O} \]

\[ \text{HEXANE} \quad \Delta G \quad \text{CO}_2 + \text{H}_2\text{O} \quad \text{OUT UNFAVORABLE} \quad \Delta G^\pm \]

\[ \uparrow \quad \text{VERY FAVORABLE} \]

But two common ABIOTIC pathways overcome this...

1. PHOTOLYSIS
   - Light photons provide the needed \( \Delta G^\pm \) (act. energy)

2. HYDROLYSIS:
   - Enormous concentration of WATER (55.4 mol/L) overcomes the low probability of getting enough \( \Delta G^\pm \) (Low prob. x Very high "opportunity")
**Planck's Law**

\[ E = h \nu \]

\[ h = 6.6 \times 10^{-34} \text{ J s} \]

Short \( \lambda \) → High Freq (\( \nu \)) → High Energy

E.g. Blue light has \( \sim 2x \) the energy per photon as red.

**Frequency:**

\[ \nu = \frac{c}{\lambda} \cdot \frac{3 \times 10^8 \text{ m/s}}{\lambda (\mu \text{m})} \]

**Energy of each photon:**

\[ E = h \nu \]

So red light may not work but blue light does.
STEPS IN PHOTOLYSIS

1. Run requires certain AC $\Delta$  
   - Only some photons ($\lambda > \lambda_{min}$)  
   Can drive that run ($h\lambda_{min} = AC$)  
   So those wavelengths of light  
   MUST BE PRESENT

2. Molecule must be able to  
   absorb that type of photon  
   "Chromophore" must exist  
   If not, then no photochemistry  
   possible there

\[ dI_\lambda = -\alpha_\lambda I_\lambda \]  
\[ \text{The amount of change in light intensity is } \frac{\text{change in proportion of intensity}}{\text{change in wavelength}} \]

Imagine you invest in a stock fund that is losing at a negative interest rate of 5% per year:
\[ \text{d}S = -0.05 \text{S} \]

For general medium:
\[ dI_\lambda = -\left(\rho k_\lambda ds\right) I_\lambda \]

Integrate over S:
\[ \frac{I_{\lambda_2}}{I_{\lambda_1}} = \exp\left(-\int_{\lambda_1}^{\lambda_2} k_\lambda ds\right) \]

- Allows for variable density $k_\lambda$ over S (S)

\[ \frac{I_\lambda}{I_{\lambda_1}} = e^{-K_S} \]

for a uniform medium  
(or "effectively" uniform)
PRACTICAL APPLICATIONS OF BEER'S LAW:

\[
\frac{I_c}{I_o} = e^{-\alpha_A m}
\]

- \( I_c \) = Cloudless \( I_o \) at surface of earth
- \( I_c \) = Cloudless \( I_o \) at surface
- \( \alpha_A \) = Molecular scattering coefficient of pure air \((\alpha_A/N_A)/Ar/0_2\)

\[
N = \frac{\alpha_c}{\alpha_A} = \text{"Turbidity Factor"}
\]
- \( N = 2.0 \) = Clear uninhabited
- \( N = 5 \) = Smoggy air

\( m \) = Relative thickness of air mass

\( m = \csc \alpha \) (Solar angle)

\[
\frac{I_{S2}'}{I_s} = (1 - \beta) e^{-Kz}
\]

\( I_o \) = Depth of water (m)

\( \beta \) = Percentage of incident light

\( \alpha \) = Solar angle
ABSORPTION OF LIGHT BY WATER: Logarithmic Presentation.

The exponential equation given by Beer's Law can be linearized by taking the natural log of both sides, or, by plotting light intensity on semi-log scaling.

\[ \ln \left( \frac{I_0}{I} \right) = \varepsilon c d \]

\[ \ln(0.01) = \varepsilon c d \]

\[ \ln(0.1) = \varepsilon c d \]

\[ \ln(1.0) = \varepsilon c d \]

\[ \ln(10) = \varepsilon c d \]

\[ \ln(100) = \varepsilon c d \]

\[ \text{Absorbed energy must go into breaking down molecule} \]

\[ \text{But that not only place energy can go...} \]

1. Excited molecule dissipates energy as vibrations (heat)

2. Excited state drops back to ground state & emits a new photon (known as fluorescence)
• Can also "lock" in to a new excited state that only slowly drops down (releasing photon) **phosphorescence**

**OR** **MAY REALLY GET A RXN**

• **DIRECT PHOTODEGRADATION**
  Photon \(\rightarrow\) Excited Mol. \(\rightarrow\) Lysis

• **INDIRECT PHOTODEGRADATION**
  Photon \(\rightarrow\) Excited Mol. \(\rightarrow\) Posses energy
  Mol \#2 \(\rightarrow\) Excited Mol \#2
  Mol \#1 \(\rightarrow\) Drops back to ground state
  \(\rightarrow\) Lysis

**Photon Conc.**
(light intensity)

\[
\text{1 Einstein} \quad \text{= 1 mole of photons}
\]

\[
\text{Molar Absorption} \quad \times \quad \text{Conc.}
\]

\[
\text{Fraction of Einstein's} \quad \text{actually absorbed by molecules}
\]

\[
\text{Heat Flow, Photolysis, Retro Actual Degradation That Lead to Lysis}
\]

**Parameters:**
  - \(k\), molar absorptivity, Quantum Yield

**Variables:**
  - Light intensity, Conc. of Chromophore (conc. of "Co-Compound")
The spherical shape of the earth is very important:

At higher latitudes, light is spread over greater area; hence, less intense.

\[
I_0 = W_0 \sin \alpha = W_0 \cos \phi
\]

for noon at the equinox

\[
\alpha = \sin \alpha = \sin \delta \sin \phi + \cos \delta \cos \phi \cos \psi
\]

\[
\delta = \text{DECLINATION}
\]

\[
\phi = \text{LOCAL LATITUDE}
\]

\[
\psi = \text{HOUR ANGLE}
\]