Slide 1

Basic concepts of photochemistry, interaction between photons and molecules

Slide 2

The subject of photochemistry

- For "life on Earth", the Sun is an essential source of energy
  - **1st law of thermodynamics**: energy in a closed system is constant
  - **2nd law of thermodynamics**: the difference between ordered and disordered energy (work and heat).
    - Heat can never be transformed into work with 100% efficiency.
    - In every spontaneous process, entropy increases, so the useful energy (work) is transformed into disorderly energy (heat).
- The Earth's free energy supply comes from the Sun
  - Photosynthesis
  - Coal, petroleum, natural gas

Slide 3

The subject of photochemistry

- The goal of **photobiology** and **photochemistry**: getting to know the solar energy utilization systems. Understanding the following phenomena:
  - Photosynthesis
  - Photocatalysis
  - Phototaxis
  - Mechanism of vision
  - The mutational genetic effect of light

Slide 4

The subject of photochemistry

- The subject of **photochemistry**:
  - study of the reactions and processes that are triggered by **molecules with excited electron states**.
  - **Formation of excited molecules**: after absorbing energy from Vis or UV light
- The first step in photochemical reactions is the actual interaction between electromagnetic radiation and molecules or ions

Slide 5

The nature of light

- Light – depending on the nature of the interaction – can have **particle- and wave-type properties**
- Electromagnetic radiation refers to the waves of the **electromagnetic field**, propagating (radiating) through space, carrying energy.
- When we consider light as a discrete particle, we call it **photon**.

Crookes radiometer

solar sail

Slide 6

The nature of light

- Characterization:
  - Wavelength, λ
  - Frequency, ν
  - Wave number, $\tilde{\nu}$
  - Energy, E
    - *Planck's constant, h* = $6.626 \cdot 10^{-34}$ J s
    - *Speed of light, c*
    - $c^* = 2.998 \cdot 10^8$ m s^{-1} (in vacuum)
    - or $c = c^*/n$ (where n is the refractive index of the medium)

$$E = h\nu = \frac{hc}{\lambda} = hc\tilde{\nu}$$

- When the light passes from one medium to another, its wavelength and wave number changes, but its frequency and energy does not.

Light absorption, photochemical activation
(7)

- The interaction of a molecule (built-up from electrically charged nuclei and electrons) and a vibrating electromagnetic space produces an excited, highly reactive molecule.
- The **1st law of photochemistry** (**Grotthous–Draper law** or principle of photochemical activation) *states that only light which is absorbed by a system can bring about a photochemical change.*

Light absorption, photochemical activation
(8)

- **Beer–Lambert law**: gives the probability (degree) of light absorption
  - Lambert's law: *The portion of absorbed light entering a given medium is independent of the light intensity and each successive layer absorbs the same proportion of the input light.*
  - Beer's law: *The amount of radiation absorbed is proportional to the amount – or concentration – of particles that absorb radiation.*
  - $-\dfrac{\mathrm{d}I}{I} = \alpha c\,\mathrm{d}x$ Integrated with the following boundary conditions:
    - $I = I_0$ when $x = 0$
    - $I = I$ when $x = \ell$

$$A = \lg\frac{I_0}{I} = \varepsilon c\ell$$

$$I_{\text{absorbed}} = I_0 - I = I_0\left(1-10^{-\varepsilon c\ell}\right)$$

- ε (absorptivity or molar attenuation coefficient) depends on λ.

Light absorption, photochemical activation
(9)

- **Beer–Lambert law**: gives the probability (degree) of light absorption

  - If there are several components with different absorption coefficients in the solution, the measured absorbance is the sum of the light absorptions of each components: $A = \Sigma \varepsilon_i c_i \ell$

  - $-\dfrac{\mathrm{d}I}{I} = \alpha c\,\mathrm{d}x$ Integrated with the following boundary conditions:
    - $I = I_0$ when $x = 0$
    - $I = I$ when $x = \ell$

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$$I_{\text{absorbed}} = I_0 - I = I_0\left(1-10^{-\varepsilon c\ell}\right)$$

Light absorption, photochemical activation
(10)

  - Light-absorbing molecules, ions become excited, their properties are significantly different from both the ground-state and the thermally activated particles.
  - The amount of products produced by photochemical reactions is determined by the amount of light absorbed by the system.
- **Bunsen–Roscoe law** (reciprocity law): *The exposure duration required to elicit a given photobiological or photochemical response varies as the reciprocal of the incident irradiance.*

$$I_{\text{absorbed}} = I_0 - I = I_0\left(1-10^{-\varepsilon c\ell}\right)$$

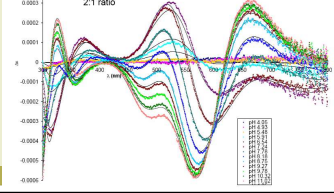## Light absorption, photochemical activation
(11)

- Interaction of linearly polarized light with material: **circular birefraction**
  - **circular birefraction**: there are materials that have a different refractive indexes to the right and to the left circularly polarized light → the polarization plane of the linearly polarized light rotates

Light absorption, photochemical activation
(12)

- Interaction of linearly polarized light with material: **circular dichroism**
  - **circular dichroism**: there are materials that have a different molar absorbance to the right and to the left circularly polarized light → the linearly polarized light becomes elliptically polarized
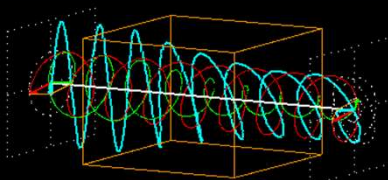
Light absorption, photochemical activation

(13)

- Interaction of linearly polarized light with material: **circular birefraction** and **circular dichroism**
  - circular birefraction: there are materials that have a different refractive index to the right and to the left circularly polarized light → the polarization plane of the linearly polarized light rotates
  - circular dichroism: there are materials that have a different molar absorbance to the right and to the left circularly polarized light → the linearly polarized light becomes elliptically polarized

Light absorption, photochemical activation

(14)

- Interaction of linearly polarized light with material: **circular birefraction** and **circular dichroism**

Comparison of thermal and photochemical activation

(15)

- As a result of <u>thermal energy</u> absorption, the translational, rotational, vibrational and electron states of the particles can also change.
- Based on the **Boltzmann distribution**, the ratio of two particles having the same degree of degeneration, with ΔE energy difference is:

$$\frac{n_2}{n_1} = \exp\left(-\frac{\Delta E}{RT}\right)$$

- When $\Delta E = 250$ kJ mol^{-1}, then
  - at 25 °C: $n_2/n_1 = 2\cdot10^{-44}$
  - At least 6800 °C is required to have 1% of the particles in the excited state.

Comparison of thermal and photochemical activation

(16)

- If the molecules absorb the <u>light of 500 nm</u>, electron state excitation will certainly occur.
- The concentration of excited molecules depends on
  - the light intensity,
  - the rate of their photophysical and photochemical processes.
- The excited state molecules are highly reactive due to the high excitation energy (<u>238 kJ mol^{-1}</u>).
  - The energies of photons responsible for photochemical processes is comparable to the energies of chemical bonds.
  - Often, the excitation energy is comparable to the E_a of the ground-state particle. The excited molecule reacts faster than the ground-state one.

Comparison of thermal and photochemical activation

(17)

- Thermal and photochemical reactions differ significantly:
  - The concentrations of high-energy, photochemically excited particles can be very high.
  - As a result of excitation, the electron state of the molecule changes, a new electron configuration is created.
  - If the photochemical excitation is sufficiently narrow, a monoenergy product is formed. Such can only be produced thermally with very special techniques (*e.g.* molecular beam technique).

Comparison of thermal and photochemical activation

(18)

- Steps of a photochemical process:
  - **Light absorption** (primary process),
  - thermal **(primary) reactions** of the excited electron state molecules formed in light absorption. They can be very diverse.
  - **secondary reactions**: further (thermal) reactions of the products of the primary reactions.
- Light absorption can also be followed by radiation energy loss (so without any chemical reaction – not photochemistry!) It is called **luminescence**. Types:
  - Spin allowed – **fluorescence** (some 10 ns)
  - „forbidden" – **phosphorescence** (much slower: even s or h)

Comparison of thermal and photochemical activation

[19]

- Steps of a photochemical process:

$$NO_2 \xrightarrow{h\nu} *NO_2$$

  ○ **light absorption (primary process)**,

$$*NO_2 \longrightarrow NO + O$$

  ○ **primary reaction**,

$$O + O_2 \longrightarrow O_3$$

  ○ **secondary reaction**. It can only be considered as a photochemical reaction because the reacting particle(s) would not be formed without light.

Comparison of thermal and photochemical activation

[20]

- Reactive molecules, ions, radicals = intermediates
- Reactivity is not the same as instability!
  ○ A reactive **intermediate** (*e.g.* NO, O) can be stable for a long time in an isolated surrounding (vacuum),
  ○ for an **excited particle** (*e.g.* *NO$_2$), the half-life is determined by the probability of an irradiated energy release, independently of the environment.

- In the case of a radical intermediate, a chain reaction often occurs (*e.g.* **photochemical chain reaction between H$_2$ and Cl$_2$**)

Comparison of thermal and photochemical activation

[21]

$$Cl_2 \xrightarrow{h\nu} 2Cl^{\bullet}$$
  ○ **chain initiation**
  primary process

$$Cl^{\bullet} + H_2 \longrightarrow HCl + H^{\bullet}$$
$$H^{\bullet} + Cl_2 \longrightarrow HCl + Cl^{\bullet}$$
  ○ **chain propagation**
  secondary process

$$H^{\bullet} + Cl^{\bullet} \longrightarrow HCl$$
$$2H^{\bullet} \longrightarrow H_2$$
$$2Cl^{\bullet} \longrightarrow Cl_2$$
  ○ **chain termination**
  secondary process

Quantum yield and quantum efficiency

[22]

- **Quantum efficiency**, *QE*: the effectiveness of a step (such as the formation of a photoactive molecule, luminescence…), *i.e.* the probability of its occurrence.
  ○ The **Stark–Einstein law** says that *absorbing light is a one-step process*,
  ○ therefore the sum of the quantum efficiencies of the primary processes of the excited molecule is necessarily 1.
  ○ In a primary photochemical reaction, more than one molecule cannot undergo on changes as a result of the absorption of one photon.

Quantum yield and quantum efficiency

[23]

- **Quantum yield**, *Φ*: shows that as a result of one absorbed photon, how much product is produced from a reactant molecule under the given conditions.
  ○ This includes the effectiveness of primary and secondary processes, *i.e.* characterizes the net photochemical reaction.
  ○ For consecutive reactions, the quantum yield is the product of the quantum efficiencies of the successive steps.
  ○ If *Φ* > 1, then it is certain that secondary reactions will also consume the reactants (*e.g.* chain reactions).

Quantum yield and quantum efficiency

[24]

  ○ If the ratio of the **quantum yield** and the **quantum efficiency** for a primary sub-step in a photochemical reaction is greater than 2, then a chain reaction will surely occur (photo-reaction between H$_2$ and Cl$_2$: *Φ/QE* = 10^6).
  ○ If the ratio is less than or equal to 2, it may be a 2:1 stoichiometric reaction.

$$Cl_2 \xrightarrow{h\nu} 2Cl^{\bullet}$$

Quantum yield and quantum efficiency

(25)

- Experimental determination:
  - Determining the concentration of a product or reactant is often a simple analytical task.
  - Determining the concentration of an intermediate is not! It can decompose even when it is created.
  - Measurement of the number of absorbed photons is also possible by physical (*e.g.* light intensity measurement) or chemical (actinometry) methods.
  - **Quantum yield** is relatively **easy** to determine, **quantum efficiency** is quite **difficult**.
- All primary processes can rarely be observed experimentally.
  - If luminescence is not detected, the quantum efficiency of the primary chemical process is often assumed to be 1.

The interaction between photons and molecules

(26)

- If we want to know more about molecules, we often investigate their interaction with light (electromagnetic radiation):
  - UV-Vis spectrophotometry
  - IR spectroscopy
  - X-ray diffraction
  - ESR, NMR
- If we want to know the nature of light, we examine its interaction with certain materials:
  - Diffraction
  - Photoelectric effect

Physical description of electromagnetic radiation

(27)

- The change of **electric field** strength in time and space:
  $$E_y = E_0 \sin\left[2\pi\left(\frac{vt - x}{\lambda}\right)\right]$$
  - E_y is the vector of electric field strength in direction y,
  - E_0 is a value constant in time and space: the amplitude of vibration,
  - v is the frequency,
  - λ is the wavelength.
- The direction of movement of the electric field vector is the **direction of polarization**.
- The plane that includes this vector is the **plane of polarization**.

Physical description of electromagnetic radiation

(28)

- The vibrating electric field produces a **magnetic field** (H) perpendicular to it. This vibrates in the same phase as the electric field, *i.e.*:
  $$H_z = H_0 \sin\left[2\pi\left(\frac{vt - x}{\lambda}\right)\right]$$
  - The ratio of the amplitude of the two oscillating fields is determined by the magnetic permeability (μ) and permittivity (ε) of the material:
  $$\frac{E_0}{H_0} = \sqrt{\frac{\mu}{\varepsilon}}$$
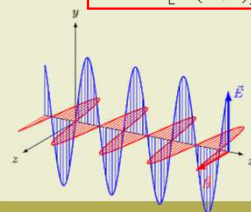
Physical description of electromagnetic radiation

(29)

- The electric and magnetic fields can be divided into different components:
  - electric dipole,
  - electric quadrupole,
  - magnetic dipole,
  - magnetic quadrupole.
- In the interaction between matter and light, the electric dipole component is the determining factor, only $5 \cdot 10^{-6}$ times its value is the electric quadrupole and 10^{-6} times its value the magnetic dipole interaction.
- When the light and material interact, the energy eigenvalue of the photon-absorbing molecule changes:
  $$E_1 \rightarrow E_2$$

The Franck–Condon principle

(30)

- Molecules can take different quantized rotation and vibration states so within a given electron state, different rotation and vibration states are possible.
- Their energy levels are determined by the rotational (J) and vibration (v) quantum numbers:
  $$E_{rot} = J(J+1)\frac{h^2}{8\pi^2 I}$$
  $$E_{vibr} = \left(v + \frac{1}{2}\right)\frac{h}{2\pi}\sqrt{\frac{k}{\mu}}$$
  - μ is the reduced mass of the molecule,
  - I is the moment of inertia ($I = r^2\mu$).

The Franck–Condon principle
(31)

- The vibration-rotation spectrum of gaseous molecules shows a characteristic fine line structure.
- Selection rules:
  - ○ Diatomic diamagnetic molecules (*e.g.* HCl): $\Delta J = \pm 1$ and $\Delta v = \pm 1$
  - ○ Paramagnetic molecules with non-zero magnetic momentum: $\Delta J = 0, \pm 1$ and $\Delta v = \pm 1$

The Franck–Condon principle
(32)

○ Diatomic diamagnetic molecules (*e.g.* HCl): $\Delta J = \pm 1$ and $\Delta v = \pm 1$

Transitions where the vibrational energy increases (n = 0 → 1) and the rotational angular momentum decreases (j → j − 1)

Transitions where the vibrational energy increases (n = 0 → 1) and the rotational angular momentum increases (j → j + 1)

Center frequency for n = 0 → n = 1

The Franck–Condon principle
(33)

- In the electron excitation spectrum of **gaseous molecules**, **fine structure** appears due to vibrational transitions (and also rotational transitions at higher resolutions).
- In the **condensed phase** – due to intermolecular interactions – there is no fine structures but **bands**, but their shape depends on the vibrational transitions.
- The shape of the fine structure or the bands can be interpreted on the basis of the **Franck–Condon principle**…

A Franck–Condon-elv
(34)

- **Franck–Condon principle**:

○ *The change of the electron state is much faster than the movement of the nuclei (due to the much smaller mass of the electrons).*

○ *The electronic transition causes a change in the equilibrium nuclei distances, but the actual nuclei distances are the same as before the electronic transition, so when we excite the electron state of an electron, not only its electron state but also its vibration state will be excited.*

○ *At the edge of the PES…*

A simple model of light absorption
(35)

- If there are two states, the energy of which differs by $E_2 - E_1 = \Delta E$, then using the conservation of energy for the absorption gives $\Delta E = h\nu$.
- Whether this happens or not is given by **Einstein's transition probability**:

$B_{12} = \dfrac{8\pi g_2}{3h^2 c}[M]^2$

  - ○ g_2 is the degree of degeneration of excited state,
  - ○ M is the transition momentum, which is (for two different quantum states): $M = \int \Psi^* \mu \Psi \, d\tau$
  - ○ Ψ^* and Ψ are the wave functions for the excited and ground states,
  - ○ μ is the operator of the dipole momentum, which includes changes depending on the coordinates of the nuclei, the coordinates of the electrons, and the spins.

A simple model of light absorption
(36)

- The **oscillator strength** can be calculated from Einstein's transition probability:

$f = \dfrac{8\pi^2 cm_e \omega_{1/2}}{3he^2} g_{12}[M]^2$

  - ○ m_e is the mass of an electron,
  - ○ $\omega_{1/2}$ is the wavenumber of the transition.
- The oscillator strength can be calculated from experimental results (from the absorption band):

$f = 4{,}32 \cdot 10^{-9} F \int \varepsilon(\omega) \, d\omega$

  - ○ F is a factor depending on the refractive index of the medium: $F = 9n/(n^2+2)^2$
  - ○ $\nu_{1/2}$ is the half-width readable from the spectrum.

$\boxed{f = 4{,}32 \cdot 10^{-9} F \varepsilon_{max} \Delta \nu_{1/2}}$

- The oscillator strength of a fully permitted electronic transitions is 1.