Lecture 3. Photochemistry. Kinetics of photochemical reactions.

The purpose of the lecture: to provide information on photochemistry, its laws and kinetics of photochemical reactions.

Expected results: students receiving information about the characteristics of photochemical reactions, the laws and kinetics of photochemical processes.

Photochemistry deals with the laws of reactions occurring under the influence of light. Light can be scattered and absorbed. Absorption is described by the Lambert-Bouguer-Beer law and depends on λ of the light, the nature of the absorbing substance, the path length of light in it l, and its concentration C. The intensity I of the monochromatic light transmitted through a homogeneous medium is

$$I = I_0 \bullet 10^{-\varepsilon\lambda/C}$$

where I_0 - incident light intensity, $\varepsilon\lambda$ - molar extinction coefficient at a wavelength λ. $\varepsilon\lambda/C$ is also called optical density. Molecules upon absorption of a quantum of light usually go into an electronically excited state.

The electronic state of a diatomic molecule is characterized by:

1) by the projection Λ of the total orbital momentum L onto the axis passing through the nuclei, and the states are denoted $\Sigma(\Lambda=0)$, $\Pi(\Lambda=1)$ and Δ ($\Lambda=2$);

2) spin multiplicity 2S + 1, where S - total spin of the molecule. If all the electrons are paired, then S = 0, and the multiplicity is 1 (singlet state). If, upon excitation, an electron transfers to a higher energy level, then its spin becomes parallel to the spin of the electron remaining at the lower level, S = 1, and the multiplicity is 3 (triplet state);

3) the even (g) or odd (u) state of the wave function (if, when the sign of all the coordinates of the electrons changes, the wave function changes sign too, then the state is odd, and vice versa);

4) the sigma Σ states Σ^+ and Σ^- are distinguished by the fact that when reflected in a plane passing through the nuclei, the wave function of electrons for Σ^+ does not change sign, but for Σ^- it reverses.

Example: ground state H_2 - $^1\Sigma_g^+$; O_2 - $^3\Sigma_g^-$.

Selection rules. With a weak interaction between the spin and the orbital momentum (in light nuclei), such rules:

1) $\Delta\Lambda=0, \pm1$;

2) $\Delta S=0$ (that is, between states of the same multiplicity);

3) necessarily odd terms combine with even and vice versa: $u\rightarrow g$; $g\rightarrow u$;

4) positive terms combine with positive and negative with negative: $+ \rightarrow +$; $- \rightarrow -$.

For molecules with strong spin-orbit interaction (in the presence of heavy nuclei), only the first condition remains.

The Frank Condon Principle. When the electronic-vibrational state is excited, there are mainly transitions between those vibrational levels of two electronic states in which the nuclear configurations are the same. Transitions at turning points are more likely when the vibrational energy is concentrated in the form of potential energy, and the kinetic is close to 0.

Photophysical processes. Absorbing a quantum of light, the molecule passes from the ground singlet state to the excited electronic-vibrational singlet state:

$$A\ (S_0) \xrightarrow{\ h\upsilon_1\ } A^*(S_1^\upsilon)$$
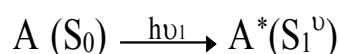
After some time, excited molecules become normal either by emitting an absorbed photon (radiative transition), or by converting excess energy into heat as a result of collisions (non-radiative conversion), or transferring it to another molecule, which therefore dissociates

(quenching). In addition, an electronically excited molecule can enter into a reaction, and then its excess energy passes to the reaction products.

Both singlet and triplet states can occur in <u>nonradiative transitions of the cascade type</u>: the molecule gradually passes from one vibrational state to another to a lower electronic level. The energy released in this case is transmitted non-radiatively to other molecules of the medium: this is vibrational relaxation
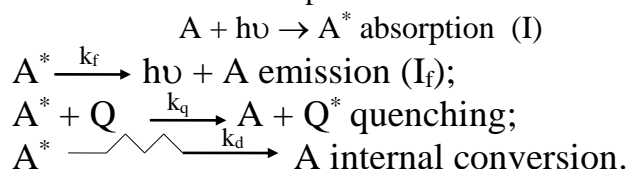
$$A^* (S_1^\upsilon) \rightarrow A^* (S_1).$$
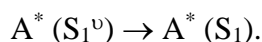
Nonradiative transitions between states of the same multiplicity are called internal conversion:

$$A^* (S_1) \xrightarrow{\quad\wedge\wedge\wedge\quad} A^* (S_0^\upsilon)$$

and further $\rightarrow A (S_0)$. Radiative transitions with the emission of photons between singlet states are called <u>fluorescence</u>:

$$A^* (S_1) \xrightarrow{\quad k_f \quad} A (S_0) + h\upsilon_1$$
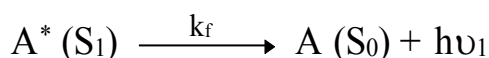
Usually $k_f \approx 10^6\text{-}10^9 \text{ c}^{-1}$. If emission is the only way to deactivate an electronically excited molecule (first order reaction), then the inverse of the emission rate constant k_f is called the natural lifetime t_0 of the excited state. Fluorescence pattern:

$$A + h\upsilon \rightarrow A^* \text{ absorption (I)}$$
$$A^* \xrightarrow{k_f} h\upsilon + A \text{ emission (I}_f\text{)};$$
$$A^* + Q \xrightarrow{k_q} A + Q^* \text{ quenching;}$$
$$A^* \xrightarrow[k_d]{\quad\wedge\wedge\wedge\quad} A \text{ internal conversion.}$$

<u>Stern-Volmer equation</u>:

$$I_0/I = 1 + k_q t[Q]$$

Can be written as $I_0/I = 1 + K [Q]$.

Life time of a fluorescent molecule $t = 1/(k_f + k_d + k_q[Q])$.

<u>Intercombination transitions</u> (between states with different multiplicities) are prohibited according to the selection rules. But, since real states are not purely singlet or purely triplet, these transitions occur, but with a lesser probability ($10^3\text{-}10^6$ times) than transitions between states of the same multiplicity, and play a large role in the deactivation of electronically excited particles. An intercombination (or intersystem) transition usually occurs from one electronic singlet level to the vibrational level of the same energy of the triplet state:

$$A (S_1) \xrightarrow{\quad\wedge\wedge\wedge\quad} A^* (T_1^\upsilon).$$
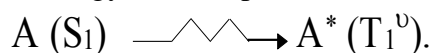
This process is adiabatic. Such a non-radiative transition is called intercombination conversion. Usually triplet states are metastable; residence times in these states are longer than in singlet ones. Reverse non-radiative transition is also possible:

$$A^* (T_1) \rightarrow A (S_0).$$
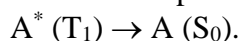
More important is the radiative transition

$$A^* (T_1) \xrightarrow{\quad k_p \quad} A (S_0) + h\upsilon_2$$
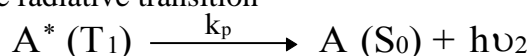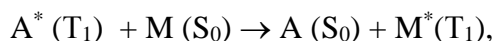
which is called phosphorescence. The lifetimes of such a transition are large: from 10^{-3} s to 10 s. In organic molecules, a transition usually takes place from the lowest vibrational level of the triplet state to some vibrational level of the ground singlet state.
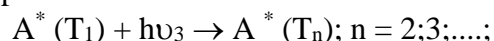
Singlet-singlet energy transfer is also possible.

$$A^* (S_1) + M (S_0) \rightarrow A (S_0) + M^*(S_1)$$
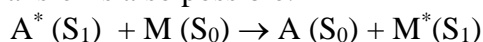
triplet-triplet energy transfer
$$A^* (T_1) + M (S_0) \rightarrow A (S_0) + M^*(T_1),$$
as well as triplet-triplet absorption
$$A^* (T_1) + h\upsilon_3 \rightarrow A^* (T_n); n = 2;3;....;$$
the consequence of which are two-stage (two-quantum) photochemical reactions.

The transition of an electron from one level to another can be interpreted as a transition from one molecular orbital to another. Organic molecules are characterized by 3 types of single-electron orbitals: σ, π and n. π and σ-orbitals are binding and loosening (the latter are denoted by an asterisk). The n-orbital is called non-binding. σ-orbital corresponds to a single simple bond. σ-electrons are strongly binding electrons and are largely localized. The π-orbital corresponds to one of the bonds in the atomic group with a multiple bond.

Each σ and π-orbitals correspond to loosening (free in the ground state) σ^* and π^*-orbitals. The n-orbital is occupied by a lone pair of electrons of the heteroatom that are not involved in the formation of a chemical bond. Such a pair can be localized on the n-orbitals (for example, in carbonyl compounds) or can participate in conjugation with π-electrons (for example, in aniline, furan). Usually binding σ-orbitals have lower energy than π and n orbitals. Electronic transitions in a molecule often denote $n\rightarrow\pi^*$, $\pi\rightarrow\pi^*$, $\sigma\rightarrow\pi^*$, etc. The excited state resulting from such transitions is called a state of the type corresponding to the transition, for example, $Sn\pi^*$ is a singlet state of an $n\pi^*$ type.

The types of transitions can be determined from the electronic absorption and emission spectra. Electron-excited states in photochemistry play a huge role, since in such states molecules have a higher energy and a different distribution of electrons and are therefore more reactive.

If the difference in the energies of the singlet and triplet states is small, then the excited singlet and triplet molecules in chemical reactions can behave identically, i.e. may have the same reactivity, although their physical properties (para- or diamagnetism) will differ.

In both states there is a certain separation of charges. When two electrons with parallel spins are located in a molecule at a great distance from each other, such a molecule behaves like a biradical. If unpaired electrons are close to each other, then the differences between the singlet and triplet states of the molecule are not very obvious.

Kinetics of photochemical reactions

The Grotius-Draper law: those rays that are absorbed during the reaction are photochemically active (without exception, but the converse is not true, since absorption does not always lead to a reaction).

Bunsen-Roscoe law: the quantity of products of a photochemical reaction is proportional to the intensity of the incident light and the time of its exposure to the substance (approximate, since not all absorbed energy is spent on the chemical process).

The main quantitative character of Einstein's law of photochemical equivalence: each absorbed quantum of light causes the transformation of one molecule. Hence, the quantum yield Φ is the ratio of the number of reacted molecules to the number of absorbed quanta (more convenient in moles). The photochemical process is composed of a primary (a quantum is absorbed, and the molecule decays to form free radicals and atoms) and secondary processes (reactions of atoms and free radicals, or their recombination, or deactivation of molecules).

Primary processes (truly photochemical) always obey Einstein's law, i.e. F = 1.
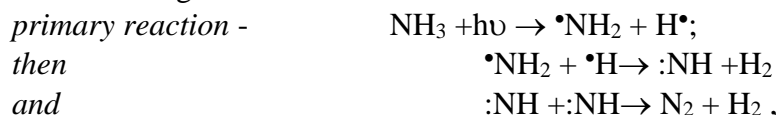
Deviations from this value are encountered due to secondary processes without irradiation.

For example, $\Phi = 1$ for a gas-phase reaction $H_2 + O_2 \rightarrow H_2O_2$.

Often $\Phi < 1$ for reactions in solutions or in the gas phase at low pressures. In gas - if excited molecules are deactivated before reaction (for example, $2NH_3 \rightarrow N_2 + 3H_2$).
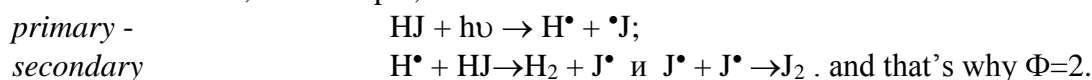
In solutions - both due to deactivation by solvent molecules and due to increased recombination - the effect of the cell (for example, $CH_3COOH \rightarrow CH_4 + CO_2$ in aqueous solution).

Φ often depends on temperature: so when NH_3 photolysis temperature changes from 20 °C to 500 °C Φ grows from 0.2 to 0.5.

primary reaction - $\qquad$ $NH_3 + h\upsilon \rightarrow {}^\bullet NH_2 + H^\bullet$;

then $\qquad$ ${}^\bullet NH_2 + {}^\bullet H \rightarrow :NH + H_2$

and $\qquad$ $:NH + :NH \rightarrow N_2 + H_2$,

*but there is recombination* $\qquad$ ${}^\bullet NH_2 + H^\bullet \rightarrow NH_3$,

the probability of which at room temperature is 3 times more than secondary processes; therefore, 3/4 of the active products of photolysis returns to its original state, and $\Phi < 1$; with increasing temperature, the probability of recombination decreases, and Φ increases.

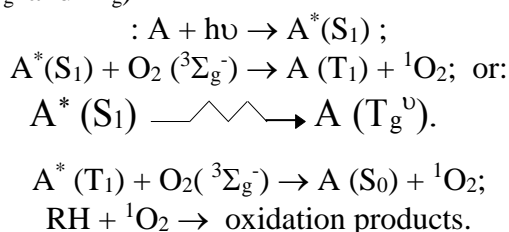Often $\Phi = 2$, for example, for a reaction $2HJ \rightarrow H_2 + J_2$

primary - $\qquad$ $HJ + h\upsilon \rightarrow H^\bullet + {}^\bullet J$;

secondary $\qquad$ $H^\bullet + HJ \rightarrow H_2 + J^\bullet$ и $J^\bullet + J^\bullet \rightarrow J_2$. and that's why $\Phi = 2$.

It happens $\Phi = 3$, for example, for the reaction $O_2 + 2O_2 + h\upsilon \rightarrow 2O_3$.
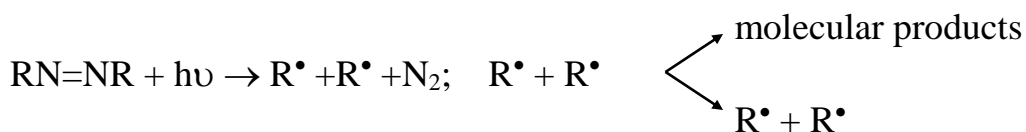
For the photochemical polarization of C_2H_2 in the gas phase, Φ reaches 9.2. If $\Phi \gg 1$ - a characteristic experimental sign of chain reactions. Sometimes Φ depends on the concentration of the starting materials (for example, photodimerization of anthracene). Sensitized reactions that occur not with light-absorbing particles, but with neighboring particles, insensitive to radiation with a given wavelength λ, which receive energy directly from the molecules that absorb it, are close to the primary processes. For example, gas-phase photolysis of hydrocarbons that do not absorb UV at $\lambda = 253.67$ nm, but are absorbed by Hg atoms, and in their presence there is a process:

$$Hg + h\upsilon \rightarrow Hg^*;$$
$$Hg^* + RH \rightarrow Hg + RH^*;$$
$$RH^* \rightarrow {}^\bullet R' + {}^\bullet R''.$$
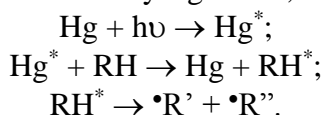
Photosensitizers can themselves enter into a cycle of reactions that initiate a radical reaction and again give the original sensitizer molecule. In photosensitized oxidation, most often the role of a sensitizer is reduced to the transfer of energy to O_2 and the formation of chemically active singlet oxygen ${}^1O_2$ (states ${}^1\Delta_g$ and ${}^1\Sigma_g$)

$$: A + h\upsilon \rightarrow A^*(S_1) ;$$
$$A^*(S_1) + O_2 ({}^3\Sigma_g^-) \rightarrow A (T_1) + {}^1O_2; \text{ or:}$$
$$A^* (S_1) \longrightarrow\!\!\wedge\!\!\vee\!\!\wedge\!\!\longrightarrow A (T_g^\upsilon).$$

$$A^* (T_1) + O_2({}^3\Sigma_g^-) \rightarrow A (S_0) + {}^1O_2;$$
$$RH + {}^1O_2 \rightarrow \text{ oxidation products.}$$

The photoinitiator decays into radicals under the action of an absorbed photon, i.e. each of its molecules is involved in the initiation once:

$$RN{=}NR + h\upsilon \rightarrow R^\bullet + R^\bullet + N_2; \quad R^\bullet + R^\bullet \begin{cases} \text{molecular products} \\ R^\bullet + R^\bullet \end{cases}$$

Literature

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