Teaching Photochemistry with Microscale Experiments.
A Contribution for the Ongoing Curriculum Modernisation

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Rationale (Why Photochemistry?)

A fundamental demand on chemical education today is to communicate core principles of chemistry closely linked to everyday life experiences of students as well as to convincing applications from science, technology and environment. Photochemical and photophysical processes are *par excellence* suitable to fulfill this requirement.

Therefore research in chemistry education is challenged to develop experiments, teaching concepts and teaching materials which all together help to interpret and communicate photochemistry in a manner, that it is both, *exciting* and *understandable.* According to this idea educational materials have been developed and published [1-4]. It should be pointed out, that most photochemical experiments can be designed as microscale versions. The examples reported below are part of the workshop given during the summer 2003 at the Universidad Iberoamericana in Mexico City. The theoretical interpretation of these experiments is embedded in a conceptual framework for teaching photochemistry which is as simple as possible, but able to explain all basic phenomena involving light in a reasonable first approximation for students in high school, college and university. The paradigm needed for this conceptual framework can be summarized as *N. J. Turro* wrote in 1968: "… excited states of molecules are the heart of all photoprocesses" . In accordance with this we have to distinguish between the electronic ground state and the electronically excited state of a molecule.

Experimental Section

1. Photochromism of Spiropyrane

Equipment/Materials: Cuvette with teflon stopper (or small test tube with screw-type cap), slide projector (with 200-W halogen lamp), projection area; glass filters (red and blue); chronometer; crystallisation dish; microscope slides; aluminium foil; green ore blue laser pointer (if available).

Chemicals: Spiropyrane (6-Nitro-1',3',3'-trimethyl-spiro[2H-1-benzopyrane-2,2'-indoline, available from *Aldrich*), toluene, ice, water, colorless nail polish.

a) Basic experiment: About 10 mg of spiropyrane are dissolved in 1.5 mL of toluene. The pale-yellow (almost colorless) solution is filled into a cuvette. The

Merocyanine blue   darkness ⇌ light   Spiropyrane pale-yellow
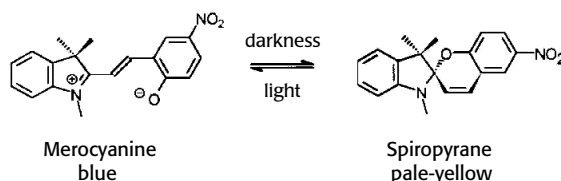
cuvette should be closed with a teflon stopper. The solution is irradiated with the light of a slide projector (see Fig. 1). Immediately one can observe on the projection area a dark blue coloration of the solution. The photostationary state is reached after 3-5 seconds. Now the cuvette containing the blue solution is stored in darkness. After about 30 seconds at room temperature the color of the solution has changed back from blue to the initial pale yellow. This cycle can be repeated more than 1000 times.

b) Influence of light filters: The solution from the basic experiment (a) is used to investigate the
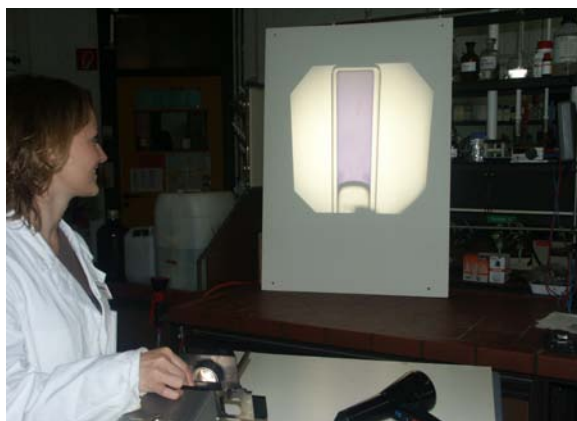
Figure 1. The basic equipment for photochemical microscale experiments consists of a slide projector and cuvettes.

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color respectively the wavelength of the light needed for the photochemical reaction of spiropyrane. Therefore different light filters, i.e. blue and red, are inserted in the slide projector and the behavior of the spiropyrane solution (blue coloration or no change in color) is observed. Whereas irradiation with blue light leads to the same effect as in the basic experiment (a), irradiation with red light does not cause any change in color of the pale yellow spiropyrane solution in toluene. But the irradiation with red light accelerates the back coloration from blue (merocyanine) to pale-yellow (spiropyrane).

c) Influence of temperature: The spiropyrane solution from the basic experiment (a) is cooled in an ice-water bath at about 0 °C. This solution is irradiated to produce the photostationary mixture. This is achieved in the same time as in basic experiment a) after about 5 seconds of irradiation. The blue solution is immediately placed in darkness and the reaction time needed for the decoloration (the recolorarion from blue to pale- yellow) is measured. Depending on the actual temperature the decoloration takes from 100 seconds to 200 seconds.

d) Influence of the solvent (the matrix): 3 drops of colorless nail polish are placed on a microscope slide (or another small plate of glass). Using a spatula some crystals of spiropyrane are introduced into the nail polish and well mixed on the glass until a homogeneous mixture is obtained. This mixture is then distributed over the glass to give a thin film. Using a blow-dryer the nail polish is gently heated until a thin solid film on the glass plate is obtained. This film consists of an acrylic polymer with spiropyrane molecules in it. The layer obtained is colored pale yellow.

This thermochromic/photochromic glass plate is heated on an electrical heating plate at about 90 °C from the opposite side of the polymer matrix. Heating leads to a change of color to dark red-violet across the entire film on the plate. Keeping the plate in the dark the red coloration is maintained for weeks. But the irradiation of a part of the plate with the light of a slide projector leads to a change in color in the irradiated area from dark red to pale yellow within several seconds.

To obtain a yellow picture on the red plate irradiation should be carried out through a mask made of aluminium foil or of black paper. By using a green laser pointer it is possible to write or draw yellow signs on the red layer

2. Photoprotection with β-Carotene

Equipment/Materials: Erlenmeyer flask (100 mL or more); rasper (to chop Carrots); quartz cuvette (or quartz test tubes); test tubes with screw-type cap; UV-hand lamp; fluorescent screen with fluorophor F_{254} (or thin layer chromatography foil with fluorophor F_{254}); slide projector with a 200-W halogen lamp; projection area; glass filters (red and blue).

Chemicals: carrots, heptane, acetone, toluene, water, tetraiodoethylene, β-carotene

a) Extraction of β-carotene: If authentic β-carotene is not available it can be extracted from chopped carrots using heptane (or acetone, or toluene) as solvent.
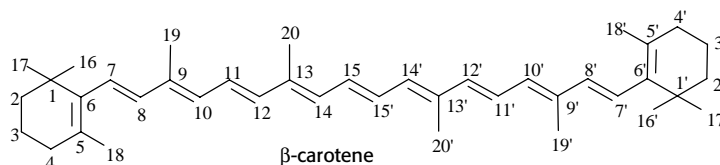
β-carotene

b) UV-absorbance: 3 mL of β-carotene solution in heptane is filled in a quartz test tube (or a quartz cuvette) and 3 mL of water are added. The test tube is placed at a distance of about 2 cm in front of the fluorescent screen between the screen and the UV-hand lamp. The screen is illuminated from a distance of about 15 cm at $\lambda = 254$ nm.

The whole screen shows a bright green-yellow fluorescence except the zone exactly behind the upper β-carotene layer. In the back of the β-carotene layer a distinct shadow can be observed on the screen. No shadow appears behind the layer of water. To make sure that β-carotene (and not heptane!) is the UV-absorbing species, the experiment is carried out with pure heptane in a quartz tube. In this case no shadow is produced on the luminescence screen.

c) β-carotene as photoprotector for chlorophylls: First about 15 mL of an extract from green leaves in methanol or acetone are prepared. This solution is divided into 3 samples. The first sample is kept dark. T the second sample 1 mL of saturated β-carotene solution in acetone is added. The second and the third sample are placed into UV-penetrable cuvettes (or test tubes) and irradiated simultaneously with the light of a slide projector (200-W halogen lamp) from a short distance of about 3 cm for 3 minutes.

Then all three samples are analysed by thin layer chromatography using a silica gel coated aluminium foil (dimensions: 8×3 cm^2) divided into 3 tracks (paths). As mobile solvent for the chormatography a mixture of petroleum ether (40-70°C): petroleum

benzene (100-140 °C): isopropanol in a ratio of 5:5:1 (volume parts) is used.

The non irradiated sample taken in darkness and the irradiated sample where β-carotene was added, show all characteristic pigment bands from the green leaf: β-carotene, chlorophylls and xanthophylls. In the second sample the β-carotene band appears even more intensive. No damaging of chlorophylls a and b can be observed in the chromatograph of this irradiated sample. The result from the irradiated samples No. 3 (without addition of β-carotene) is very different. The β-carotene band has completely disappeared and no green bands of chlorophyll a and b can be observed. Gray or brown bands can be seen instead.

d) β-carotene as radical trap: 50 mg of tetraiodoethene are dissolved in 10 mL of heptane. If necessary it can be heated at 40 °C to dissolve the complete amount of tetraiodoethene which consists of yellow crystals. The solution is divided into two test tubes (or cuvettes).To one of the samples 1 crystal of β-carotene (or 3 drops of a saturated solution of β-carotene in heptane or toluene) are added.

Both samples are irradiated simultaneously with a slide projector (200-W halogen lamp) and the color is observed on the projection area. After 30 seconds th color of the sample without β-carotene turns violet whereas the color of the sample with β-carotene remains unchanged. It turns violet after longer irradiation time.

Discussion andTeaching Applications of the Experiments

All experiments should be seen in connection with the following four questions:

i. Are they any links to the everyday life of students?

ii. Is the experiment suitable as classroom experiment? (…as teacher-demonstration experiment?) (…as student-group/demonstration experiment?)

iii. What can we learn from the experiment? What theoretical principles of chemistry can we teach on the basis of this experiment?

iv. What applications of the phenomena and/or the theory from the experiment actually exist and what can be expected for the future?

Concerning **photochromism experiments** (see No. 1 in Experimental Section) the questions mentioned above could be answered using the following **key words**:

i. light sensitive glasses, windows and windshields for automobiles.

ii. teacher experiment (to demonstrate the effect), student experiments (to investigate the influence of parameters)

iii. (see further indications above) photochemically driven (or induced) reactions; electronical ground state-excited state; energetic pathway of a photochemical reaction *vs.* a thermal reaction (see Fig. 2); photo-steady state *vs.* thermodynamical equilibrium (see Fig. 2); relation color of light ↔ energy (quantum ↔ photochemical effect; relation color of a substance ↔ wavelength of the absorbed light ↔ molecular structure; influence of the molecular environment on the actual color of a chromophore

iv. light sensitive materials (glasses, windows, optical devices…); data storage systems (computers, bank cards…); molecular switches (in nanomachines)

Inasmuch as it represents a simple isomerisation, the photochromism of spiropyrane described in experiment No. 1 can be excellently used to emphasize the basic difference between a photochemical reaction and a thermal reaction. The **ground state GS** and the **excited state ES** of the molecular system are drawn in Fig. 2 as energy curves.

The abscissa in this diagram represents the so-called reaction coordinate that concerns changes of the nuclear geometry during the reaction, the ordinate represents the energy of the reacting system.

The black (blue) curve describes the energetic pathway of a thermal reaction that always occurs exclusively in the GS. It starts from the energetic minimum of a molecule and leads over an energy barrier to the energetic minimum of another molecule. The activation energy E_a must be supplied as heat. The situation represented in Fig. 2 indicates that the reaction from A to B is endergonic and needs a higher activation energy than the reverse reaction from B to A which in fact is exergonic. In this case even environmental heat at room temperature may be sufficient to drive the reaction from B to A. Of course it can be accelerated by heating whereas it is broken down by cooling as in experiment No. 1c.

The diagram in Fig. 2 helps to understand why the reaction from A to B can not be carried out by heating. Due to the fact that the reaction from A to B needs more activation energy, A should be heated at higher temperatures to react. Upon supplying heat the vibrations in the spiropyrane molecule become faster and the amplitudes of vibrations increase. Therefore somewhere along the black curve,

before the transition state in Fig. 2 has been reached, the spiropyrane molecule breaks into fragments instead of isomerizing to B. But if on the other hand the spiropyrane molecule is shot up into the ES by absorption of a light quantum of adequate energy (!) and if it doesn't fall down immediately into the GS via emission of a fluorescence quantum, then the excited molecule can move along the gray (red) curve in Fig. 2. "The molecule moves along an energy curve in Fig. 2" means that the atoms gradually adopt new geometrical configurations in the molecule, in other words the molecule undergoes a rearrangement (isomerization). The movement along the energy curve of the ES occurs towards the indicated energy minimum (energy funnel). From the bottom of that funnel the molecule falls down into the GS landing close to the energy maximum of the GS energy curve. From there it can slide to the energetic valley of the product.

From the basic version of the photochromism experiment one can learn that photochemistry opens new possibilities for chemical reactions because it makes products available that are not available through a thermal reaction. Using this experiment one can teach also the difference between the thermodynamic equilibrium and the photosteady state (photosteady equilibrium) of a chemical system. In our case the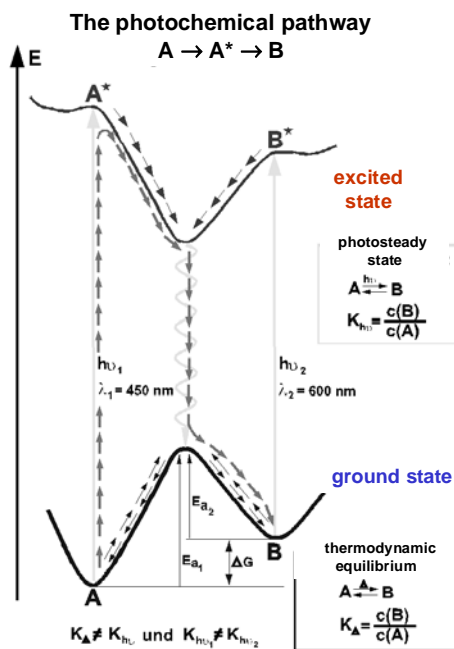 thermodynamic equilibrium (see Fig. 2) almost exclusively contains the thermodynamically more stable pale-yellow spiropyrane, whereas the photosteady state contains a considerable amount of the blue merocyanine isomer

Note that the photosteady state always can be reached and maintained only by irradiation with light. The light needed for a certain photoreaction must be of an adequate wavelength, more precisely the energy of the absorbed photon must exceed the energy difference between the

lowest unoccupied and the highest occupied energy level (or molecular orbital) in the molecule. This LUMO-HOMO energy difference depends on the extension of the system of conjugated double bonds (delocalised π-electron system) as well as on the geometry of the molecule. The sp³-hybridisation of the "spiro"-carbon atom causes a non-planar arrangement of the benzopyrane- and the indole-system in the spiropyrane molecule A. Consequently the energy difference is comparatively high as shown in Fig. 2. The molecule absorbs at relatively low wavelengths ($E = h\nu = hc/\lambda$) in the blue and violet region of visible light, and spiropyrane appears a pale-yellow color or even colorless. Because of the non-interrupted conjugation in the merocyanine molecule (completely sp²-hybridised) the LUMO-HOMO energy difference is lower than in the spiropyrane molecule A, the molecule absorbs at higher wavelengths and the substance shows a dark blue color. As a result of these molecular structures and energetic features not only the real colors of the isomers A and B can be explained, but also the photoreactivity as it can b   investigated or demonstrated in experiment No. 1b.

Finally it is also possible – but not as simple as above – to understand and explain the different colors of the spiropyrane-merocyanine system in the toluene solution and in the polymer matrix. For this it should be taken into consideration that toluene is a non-polar solvent whereas the polyacrylate matrix represents a polar environment of very high viscosity. Thus in the polyacrylate matrix the zwitterionic merocyanine-system seems to be more stable at room temperature than the non polar spiropyrane molecule. Because of the solvatochromic effect merocyanine does not appear in the same dark blue color as in toluene. Instead it shows the dark red-violet color described in experiment No. 1d.

In fact the investigated system spiropyrane-merocyanine works like a molecular switch. If a molecular switch of this or a related type is integrated in a supramolecular system, not only the color, but further properties of a material can be controled by irradiation with light. One of the most important examples is rhodopsine in the retina of our eyes. A photochemical *cis-trans* isomerization of retinal represents the first step in the vision process. Molecular switches open interesting perspectives for some technical applications, for example new materials with special optic, electronic and magnetic properties. One should be able to determine and control the proper-

The photochemical pathway
A → A* → B

Fig. 2. Photochemical reaction vs. thermal reaction see formula of A and B above in experiment No. 1).

ties of the material if photochromic molecular units were integrated in supramolecular systems.

Relating to the **experiments with β-carotene** question i to iv (see above) can be answered by the following **key words**:

i. β-carotene in carrots, egg yolk, feathers of flamingos, orange peels, … foods, cosmetics etc.

ii. student experiments (extraction, chromatography, photoprotection), student/teacher demonstration (UV absorbance, radical trap)

iii. demonstrating and explaining that macroscopic properties (solubility, color, UV-absorbance, photoactivity) are determined by the molecular structure of β-carotene, multiple biochemical functions of β-carotene (see below)

iv. β-carotene as provitamine A, as colorant in foods (European identification No.: E 160), β-carotene in cosmetics, sun protection pills, cancer prevention and therapy

Only a few facts on β-carotene needed for the described experiments are given here. For further information see literature [4]. β-carotene, a tetraterpene $C_{40}H_{56}$ with 11 conjugated double bonds, is the most important carotenoid, an important class of natural colorants. Green plants produce about 100 million t of β-carotene per year. The polyenic molecular structure causes an absorption over the complete UV domain (see experiment No. 2b) as well as an absorption maximum in the visible region at $\lambda_{max} \approx 450$ nm. Because of the non-polar molecular structure, β-carotene is insoluble in water, moderately soluble in ether, heptane and acetone, and well soluble in benzene, toluene and chloroform (see experiment No. 2a). The chemical and photochemical reactivity of β-carotene is determined especially by the "weak point" in the molecule (see Fig. 3).

Experiment No. 2d is a very simple but impressive demonstration of the radical capture property of β-carotene. Irradiation with visible (blue) light induces the homolysis of C-I bonds in tetraiodoethylene molecules $I_2C=CI_2$ leading to iodine radicals (iodine atoms), which combine to iodine molecules. This solution turns violet. In the sample containing β-carotene the iodine radicals are trapped by β-carotene molecules preventing the generation of molecular iodine.

Experiment No. 2c should be discussed in connection with the various functions of β-carotene in green leaves. In this respect β-carotene is a real all-rounder. If only little light is available, it acts as
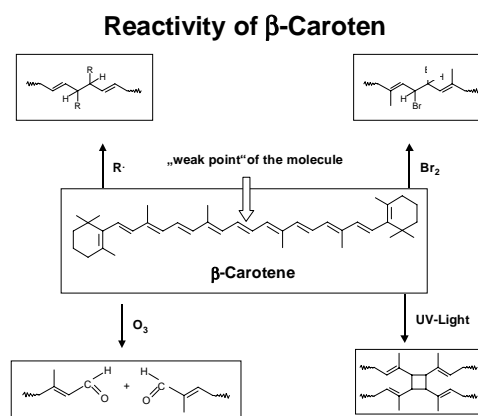
Reactivity of β-Caroten

Fig. 3. Possible reactions of β-carotene.

sensitizer for chlorophyll molecules, improving the photosynthesis efficiency. In this case the absorption of a photon produces an excited singlet state $^1Car^*$ of a β-carotene molecule. Energy transfer from $^1Car^*$ to a chlorophyll molecule in the ground state ^1Chl leads to an excited singlet chlorophyll $^1Chl^*$ which becomes active in the photosynthesis process. If green leaves are exposed to an excess of light, β-carotene acts as photoprotector for chlorophylls as it can be observed in experiment No. 1d. In this case energy transfer processes are involved, too. But now the energy transfer occurs from other excited states, namely triplet chlorophyll $^3Chl^*$ and/or singlet oxygen $^1O_2$ (both cell poisons, generated if too much $^1Chl^*$ is produced by light absorption) to β-carotene. The excited β-carotene molecules finally reach the ground state through vibrational relaxation. As a result the excess of light is transformed into heat saving chlorophylls and other substances in the green leaf from degradation. ◤

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