1
Introduction

1.1
A Brief History of Photochemistry

Photochemistry, which means chemical changes induced by absorption of light, constitutes the basis of human life. This is linked to the property of a green leaf to absorb the blue and red components of sunlight and generate carbohydrates and oxygen. Only water and carbon dioxide are necessary for that unique process of unprecedented selectivity, considering that only carbon dioxide is reduced even though the competitive and much more reactive oxygen molecule is present in about 600-fold excess. Thus, photosynthesis[1] supports mankind with food to eat and oxygen to breathe (Equation 1.1). Therefore, it is not surprising that in the very earliest human cultures

$$nH_2O + nCO_2 \xrightarrow[\text{green leaf}]{\text{sun}} (CHOH)_n + nO_2 \tag{1.1}$$

the sun was worshiped as a god. A prominent example is Egypt, where in the fourteenth century BC pharaoh Ikhnaton rejected the many old gods and introduced a monotheistic religion based on the sun-god Aton. Also, in the Christian genesis God said, “let there be light,” after he had created the earth and heaven (Genesis, verses 3–4). Besides photosynthesis, sunlight controls also the growth of plants through the protein phytochrome [1]. The complicated action mechanism can be broken down to an olefinic cis–trans isomerization. In the protein rhodopsin, the same molecular process forms the basis of human vision.

Light absorption by other eye proteins controls the concentration of hormones such as melatonin relevant for circadian rhythms, the immune system, and seasonal defective disorders such as the “winter blues.” In the eyes of some migratory birds, another protein, cryptochrome, upon light absorption generates a short-lived triplet ion pair having a magnetic moment. Interaction with the terrestrial magnetic field seems to be the underlying mechanism of these birds’ admirable

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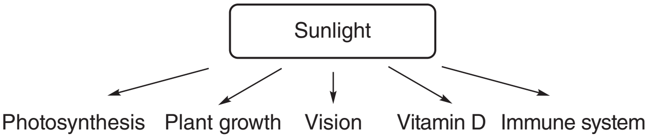
[1] Throughout this book, the word *photosynthesis* refers to photosynthesis of green plants. Artificial reactions are called *photochemical syntheses*.

Semiconductor Photocatalysis: Principles and Applications, First Edition. Horst Kisch.

navigation capability. A similar type of light-induced magnetic sensing is invoked also for the spawn-migration of some salmons (*Oncorhynchus nerka*) [2].(2)

The well-known synthesis of vitamin D in human skin is based on a sunlight-driven electrocyclic ring opening of a 1,3-cyclohexadienyl fragment. Sufficient supply of this vitamin seems to have also a positive influence on various types of cancer. Contrary to this direct chemical action of sunlight, which is localized in the skin, there is also an indirect one on the skin surface. Already, Egyptian physicians were curing skin cancer by smearing bergamot oil onto the tumor and exposing the patient to sunlight. This indirect effect is based on the oil-photosensitized formation of the very reactive singlet oxygen and is utilized nowadays under the name of *photodynamic therapy* (PDT) in cancer treatment. The use of artificial light sources such as optical fibers allows conducting PDT also on internal tumors. Scheme 1.1 summarizes the biological actions of sunlight.



Scheme 1.1

In addition to this unique relation with human life, photochemistry is important because of its distinct influence on natural and artificial matter.(3) An early example is the photochromic effect induced by a cis–trans photoisomerization of olefins. It has been claimed that the Macedonian troops of Alexander the Great carried rag bands around their wrists that contained a photochromic dye. The color change observed after a specific time of sunlight exposure probably was the visual command for attack. This early device for "optical communication" was referred to as "Alexander's Rag Time Band." Until the end of the eighteenth century, the interaction of light with matter was limited to qualitative observations such as the darkening of colors and silver salts. Around 1790, J. Priestley observed a red colorization when he exposed nitric acid ("spirit of niter") to sunlight. He also reported that in photosynthesis a reaction of water is responsible for gas evolution and that a green compound is necessary for that. And in 1804, N.T. de Saussure observed the mandatory provision of water and carbon dioxide for the formation of oxygen. In early nineteenth century, the explosive action of light on hydrogen/chlorine mixtures (R. Bunsen, H. Roscoe, J. W. Drapers, and W.C. Wittwers) and the reduction of iron(III) to iron(II) upon exposing oxalic acid solutions to sunlight (J.W. Döbereiner) were reported. Performed with artificial light under well-defined conditions, the latter reaction became the basis for ferrioxalate actinometry(4) (C.A. Parker). From the observation that mixtures of

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2) For a short summary, see I. Solov'yov and K. Schulten at *http://www.ks.uiuc.edu/research/cryptochrome/*

3) Unless otherwise cited, the following historical considerations are taken from Ref. [3].

4) An actinometer is a chemical system for the measurement of the number of photons emitted by a light source.

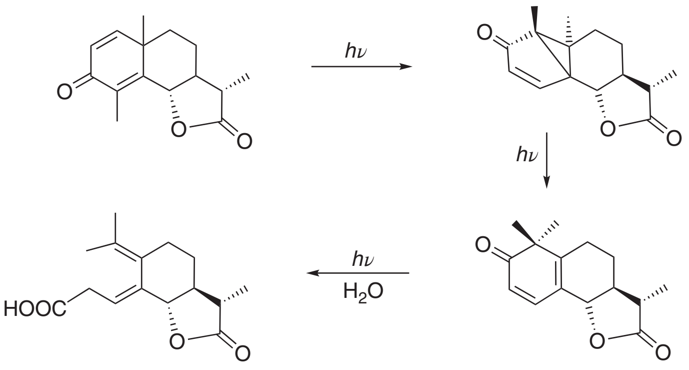
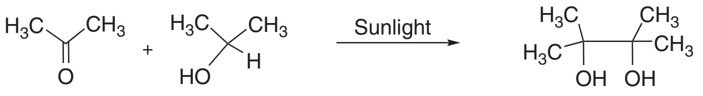


Figure 1.1 Photorearrangement of santonin to photosantonic acid.

silver salts and chalk darken when left in daylight (J.H. Schultz), silver halide photography was developed (N. Niépce, L. Daguerre, and W.F. Talbot). In the second half of that century, organic photochemical syntheses became a central topic. The earliest example is a photorearrangement of santonin (Figure 1.1), an anthelmintic sesquiterpene lactone present *Artemisia* plants (F. Sestini, S. Cannizzaro).[5] Other reactions are the photodimerizations of anthracene (C.J. Fritzsche) and thymoquinone (C.T. Liebermann). The latter constitutes the first solid-state (2 + 2)-cycloaddition. Further examples are geometric isomerizations of olefins such as cinnamic acids (W.H. Perkin, C.T. Liebermann). It was proposed that the absorption of light "causes a weakening of the double bond, so that the formerly doubly bound carbon atoms become temporarily trivalent. This leads to a migration of groups, then to rotation, and then to renewed bonding of the carbon atoms" (K. Wislicenus). Another noteworthy reaction is the addition of benzaldehyde to benzoquinone affording 2-benzoylhydroquinone, which is probably the first example for a synthetically useful photoreaction. This and analogous reactions were referred to as *syntheses by sunlight* and assumed to be similar to photosynthesis of green plants (H. Klinger). To probe this similarity, even wavelength-dependent irradiations were conducted as early as in 1888 using inorganic filter solutions. It was found that quinones reacted fastest with blue light, whereas the green plant preferred red light.

At about the same time, the photochemical reduction of nitrobenzene to aniline by ethanol and the hydrodimerization of aldehydes and ketones to pinacols in alcohols were reported (Equation 1.2; G.D. Ciamician, P. Silber).



(1.2)

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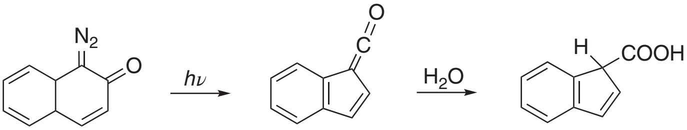
[5] In such types of formula drawings, a single bond without an attached atom label symbolizes a methyl group. The second photochemical step of the rearrangement contains migration of a methyl group. For mechanistic details, see p. 273 of Klan and Wirz [4].

Long before the first oil crisis in 1973, the splitting of water into hydrogen and oxygen, the "holy grail" of photochemistry, was discussed as an inexhaustible energy source. About 100 years earlier, Jules Verne wrote in his book *The Mysterious Island*: "Yes, my friends, I believe that water will one day be employed as fuel, that hydrogen and oxygen which constitute it will furnish an inexhaustible source of heat and light. Water will be the coal of the future." And Ostwald wrote in 1911 that mankind should cover a maximum part of its energy demand from solar energy [5]. The use of sunlight for organic syntheses was visionary predicted in 1912 by G.D. Ciamician stating that "On the arid lands there will spring up industrial colonies without smoke and without smokestacks; forests of glass tubes will extend over the plants and glass buildings will rise everywhere; inside of these will take place the photochemical processes that hitherto have been the guarded secret of the plants, but that will have been mastered by human industry which will know how to make them bear even more abundant fruit than nature, for nature is not in a hurry and mankind is" [6]. However, this vision still awaits fulfillment.[6] But an organic reaction became the basis of an industrial process conducted with artificial light. That is the photolithographic process for the manufacture of positive photoresists employed in the integrated circuit industry. It consists of the photorelease of dinitrogen, subsequent Wolff rearrangement of the generated carbene to a ketene, and the addition of water (Scheme 1.2).



Scheme 1.2

In the second half of the twentieth century, mechanistic aspects prevailed, especially in organic chemistry. Because of the development of time-resolved emission and absorption spectroscopy, the direct observation of *excited states,* that is, molecular states generated by absorption of light in the wavelength range from approximately 300 to 700 nm, became feasible. The initially obtained time resolution of nanoseconds (Norrish and G. Porter) was gradually improved to pico-, femto-, and attoseconds through the replacement of conventional flash lamps by gradually improving laser systems [4, 8, 9]. Together with theoretical calculations, the chemical properties of excited organic compounds could be explored in great detail including physical primary processes such as energy transfer.[7] This applies also for the fast developing areas of atmospheric photochemistry and photosynthesis, which are major topics in physical chemistry. Mechanistic photochemistry of organometallic and inorganic compounds

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[6] For a realistic state-of-the-art review, see Esser *et al.* [7].

[7] In photochemistry, the processes occurring directly from the excited state are called *primary processes*. They are divided into *photophysical* and *photochemical* primary processes, depending whether the process generates the same chemical entity in its ground state or a new and stable one, respectively.

developed much more slowly because of the more complicated electronic structure of metal complexes. It started with the analysis of absorption and emission spectra through the application of crystal and ligand field theory and molecular orbital calculations. These theoretical concepts were primarily used to understand the stereoselectivity and wavelength dependence of photochemical substitution and isomerization reactions of octahedral coordination compounds. The other classical research area deals with photoredox reactions, which became the major topic after the first oil crisis in the early 1970s. This is due to the fact that the chemical utilization of solar energy in general relies on photocatalysts capable of absorbing visible light and converting it into high-energy redox equivalents. Transition-metal complexes fulfill this requirement much better than organic compounds since, owing to their easily exchangeable d electrons, they can exist in various stable oxidation states. The most prominent example are d^6-configured tris(bipyridyl)ruthenium(II) complexes employed in hydrogen-evolving systems [10].

Except the solid-state dimerization of thymoquinone, all the reactions were conducted in homogeneous solutions. However, initiated by the light-to-current-conversion capability of semiconductor single-crystal electrodes in contact with a liquid electrolyte, that is, photoelectrochemistry, also semiconducting inorganic powders such as titania turned out to photocatalyze redox reactions of dissolved substrates without the need of applying an electric field. These heterogeneous systems combine classical photochemistry with electrochemistry and heterogeneous catalysis. They constitute the most promising systems for the chemical utilization of visible light [11, 12].

1.2
Catalysis, Photochemistry, and Photocatalysis

Catalysis is one of the most important phenomena both in nature and chemistry. According to the generally accepted definition, a *catalyst* is *a substance that increases the rate at which a chemical system approaches equilibrium, without being consumed in the process.*[8] And *catalysis* is therefore the phenomenon of a catalyst in action. According to reaction rate theories, the difference between a stoichiometric (uncatalyzed) and catalytic reaction can be described in the form of a potential energy diagram (Scheme 1.3). There, the reaction coordinate (RC) describes a characteristic property of the reacting molecule R, such as a bond length or bond angle, that changes significantly with progressing reaction. In an uncatalyzed process, the activation energy E_a has to be provided to the system in order to reach the geometry of the transition state, located at the maximum of the diagram. According to collision theory, the rate constant k is given by Equation 1.3:

$$k = P \times Z\,(\exp -E_a/RT) \tag{1.3}$$

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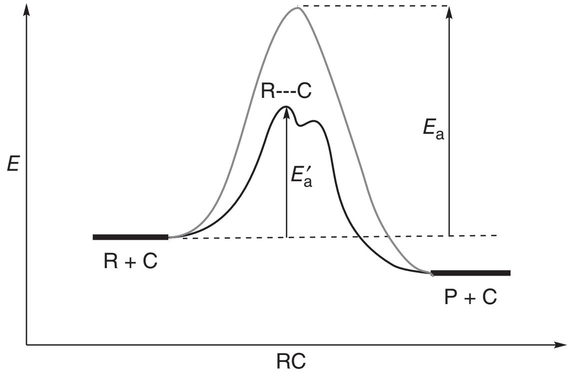
[8] It is noted that the catalyzed reaction may be *exothermic* or *endothermic.*

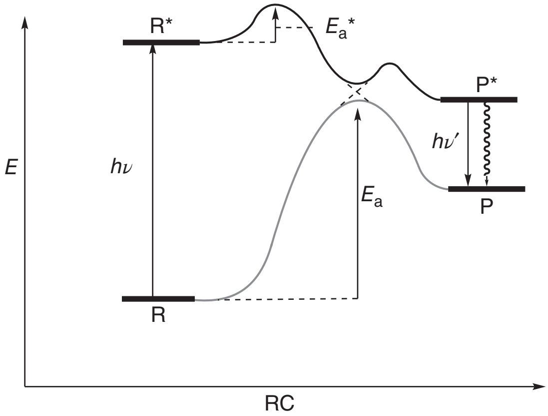


Scheme 1.3 Potential energy diagram of the stoichiometric (thin line) and catalytic (bold line) exothermic reaction of reactant R to product P. RC = reaction coordinate.

In the equation 1.3, P is a steric factor, Z is the collision frequency, R is the gas constant, and T is the absolute temperature. In the presence of a catalyst C, the activation energy becomes much lower ($E_a{}'$) because of the interaction with the reactant R, leading often to an intermediate (R⋯C) of very low stability, as indicated by the shallow energy minimum.

According to the definition of catalysis, a catalyst must not be consumed during the reaction. This is usually evidenced by calculating the *turnover number* (TON), which is defined as the ratio of concentration of product formed divided by the catalyst concentration. Only if this number is greater than 1, the reaction is catalytic. While the calculation can be easily performed for homogeneous systems, it is difficult for heterogeneous ones. Now, the *catalyst concentration* is given by the surface concentration of active sites present on the solid catalyst. That number is known in rather rare cases and usually the catalytic nature is proven by the repetitive use of the catalyst without significant decrease in the reaction rate.

Before discussing a photocatalytic reaction, we first treat the more basic case of thermal and photochemical stoichiometric reactions (Scheme 1.4). As mentioned, a supply of thermal energy E_a is necessary to reach the transition state, from where product formation proceeds without activation. This differs drastically from a photochemical reaction, in which absorption of light in the range 200–700 nm, corresponding to energies of 40–150 kcal, generates an excited state R*. Since activation energies of thermal reactions in condensed phases are typically in the range 4–25 kcal mol^{-1}, the energies of excited states are usually far above these values. The conversion of R* to the product P has therefore, if at all, only a very low activation energy $E_a{}^*$ (in the range of a few kcal mol^{-1}). The product may be formed via two classical pathways. The most common is the *diabatic* path, that is, the system passes from the photochemical potential curve to the thermal curve in the area indicated by the dashed cross and continues directly to the product. The probability of that crossing is the larger, the smaller the energy difference between the two curves. When R* does not change the potential curve but



Scheme 1.4 Potential energy diagram of the thermal (thin line) and photochemical (bold line) endothermic reaction of R to P.

transforms to the product in its excited state P* followed by radiative ($h\nu'$) or nonradiative deactivation to the ground state, the photoreaction is called *adiabatic*. According to Scheme 1.4, there is also a certain possibility that a thermal reaction when reaching its transition state may change to the photochemical potential energy surface and finally end up at the excited product P*. If the latter reaches the ground state by a radiative process, that is, by the emission of light, the reaction is called *chemiluminescence* in artificial systems and *bioluminescence* in natural systems, respectively. A prominent example is the firefly, which attracts her mate by sending out pulsed light flashes.[9)]

No general agreement exists on the definition of the term *photocatalysis.* According to the IUPAC (International Union of Pure and Applied Chemistry) *photocatalysis* is defined as "change in the rate of a chemical reaction or its initiation under the action of ultraviolet, visible, or infrared radiation in the presence of a *substance* – the *photocatalyst* – that absorbs light and is involved in the chemical transformation of the reaction partners" [14]. The reaction fulfilling this requirement is then called *photocatalytic*.[10)] This definition includes *photosensitization,* "a process by which a photochemical alteration occurs in one *molecular entity* as a result of initial absorption of radiation by another molecular entity called photosensitizer," since the *substance* mentioned above may be a "*molecular entity*" or a nonmolecular solid such as an inorganic semiconductor. Note that in these definitions no difference is made between heterogeneous and homogeneous systems. Thus, the general field of catalysis can be divided into *thermal catalysis* (usually just named *catalysis*) and *photocatalysis.* Both fields include homogeneous and heterogeneous reactions. The terms *Photokatalyse* and

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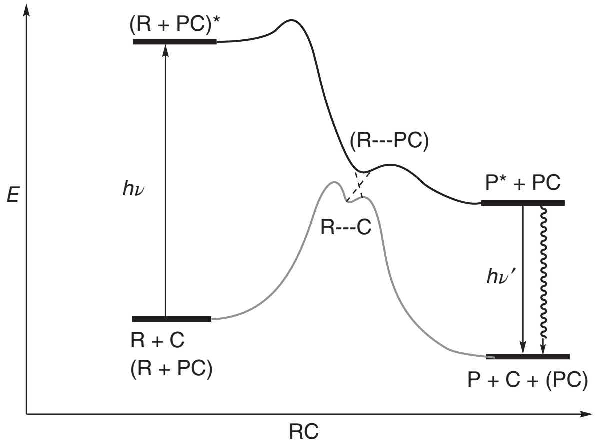
9) In the case of Japanese *Hotaria parvula*, both sexes produce precisely timed flash signals containing information on species identity and sex. Once a female responds by flashing, a reciprocal courtship dialog ensues in which males and females exchange flash signals [13].

10) Although *photocatalytic* in a strict sense signals that the reaction is catalytic in photons, this is not the case!

photokatalytisch appeared probably the first time in the textbook *Photochemie*, published by Plotnikov in 1910 [15].

A simplified reaction diagram is depicted in Scheme 1.5 for a thermal catalytic (R + C) and photocatalytic (R + PC) reactions. Different from an uncatalyzed photoreaction (Scheme 1.4), now, in general, the photocatalyst is absorbing the light. But this is not a stringent condition since also the reagent R or a weak R ⋯ PC surface complex may be the absorbing species (see Chapter 5). In addition to this direct effect of light, the original surface may be restructured to a catalytic surface during an induction period, a process well known from thermal heterogeneous catalysis. In general, photocatalytic reactions follow a diabatic pathway.



Scheme 1.5 Potential energy diagram of a thermal (thin line) and photochemical (bold line) catalytic reaction of R to P. C symbolizes a thermal catalyst, and PC a photocatalyst.

As discussed for the case of heterogeneous thermal catalysis, also in heterogeneous photocatalysis the catalytic nature is proven by the observation of an increased reaction rate and repetitive use of the photocatalyst. In some cases, a reliable estimation of the number of active sites may be also possible. Quite often, the reported reaction is claimed to be photocatalytic, although only the rate increase but not the repetitive use has been demonstrated. This applies especially for the many reactions producing very small amounts of products in presence of rather large photocatalyst concentrations.