

Photochemistry – development and achievements

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Abstract: Photochemistry has been subjected to the enormous development within the last two centuries. This development has been driven mainly by two key factors: inherent scientific thirst for knowledge and worldwide foodstuff and energy needs. Within the development of photochemistry, mutual conditionality of global needs, progress in theory, improving of existing and birth of qualitatively new experimental techniques can be identified. Photochemistry has found its application in various fields of our life, development and protection of the nature.

Keywords: applications, energy needs, experimental techniques, history, photochemistry

Photochemistry – definition

Photochemistry is defined as the branch of chemistry concerned with the chemical effects of ultraviolet, visible, or infrared radiation (Braslavsky, 2007). Photochemistry cannot be separated either from photophysics investigating processes occurring without changes in chemical identity of the involved compounds, or from ground-state chemistry not involving formation and deactivation of electronically excited states. Taking these facts into account, a broader definition of photochemistry can be formulated as follows: photochemistry is the branch of chemistry dealing with causes and courses of chemical deactivation processes of particles from their electronically excited states, usually with the participation of ultraviolet, visible or near-infrared radiation (Šima, 2015). Anyway, an inherent feature both of photochemistry and photophysics is the involvement of electronically excited state(s).

The term *photochemistry* is composed of parts *photo*, meaning light, and *chemistry*. Along with this term it seems to be worth mentioning that the term *photon* was coined neither by Planck nor Einstein who introduced the concept of light quantum (*das Lichtquant* as in the original German language). Instead, it was used by Lewis in his paper *The conservation of Photons* published in *Nature* (Lewis, 1926). In his paper Lewis presented the following hypothesis “*we are dealing here with a new type of atom, an identifiable entity, uncreatable and indestructible, which acts as the carrier of radiant energy and, after absorption, persists as an essential constituent of the absorbing atom until it is later sent out... I therefore take the liberty of proposing for this hypothetical new atom, which is not light but plays an essential part in every process of radiation, the name photon*”. It is a classical scientific paradox that his theory and explanation about the light failed but the word photon has survived.

Photochemistry – stages of its development

Human beings have known the impacts of light on various aspects of life from the beginning of their existence. This knowledge has been based on experience. In the field of therapy, sunlight was used in the treatment of skin diseases over many centuries and the method was named heliotherapy. More than 3,500 years ago, ancient Egyptian and Indian healers used the ingestion of plant extracts or seeds in addition to sunlight for treating leucoderma. Natural desire not only to notice light-induced phenomena but also to understand them has led to gradual formation of photochemistry, photophysics, and photobiology as scientific disciplines.

In an introduction to photochemistry, brief information of photography cannot be missing. The existence of photography has roots in the fact that some substances are visibly altered by exposure to light. The coining of the word *photography* is attributed to Sir John Herschel (1839) and it is composed from the Greek *phōtós* (meaning light) and *graphé* (meaning drawing or writing). Following previous experiments, Nicéphore Niépce was the first managing to fix an image that was captured with a camera after several hours of exposition in 1826 or 1827. It was made on a polished sheet of pewter and the light-sensitive substance was a thin coating of bitumen.

As a pioneering stage of photochemistry, the purposeful investigation of chemical processes induced by sunlight may be declared. When introducing this stage, the name Giacomo Ciamician cannot be omitted. Due to the variation of the intensity and wavelength of solar radiation this stage was of empirical nature with missing quantitative aspects. The main goals of the research consisted in preparing new

organic compounds through the impact of sunlight on investigated systems (Ciamician, 1912).

The invention of discharge and fluorescent tubes and filters, as well as spectral methods allowed specifying and determining radiation intensity and wavelength. This was a condition to follow wavelength-dependence of photochemical processes. Photochemical experiments were still of steady-state nature using continuous irradiation, the main parameter obtained being the quantum yield of final product(s) of photoreactions. Along with searching for final reaction products, attention was paid to the mechanism of photochemical processes identifying intermediates, e.g. radicals in photoredox processes through their ground-state reactions and spectroscopic techniques. This stage continued as the dominant mode of photochemical investigation till the 1960s.

The advent of fast flash techniques working from microsecond to femtosecond timescale has opened a qualitatively new chapter in investigating photochemical and photophysical behaviour of chemical species. Flash photolysis was developed in 1949 and Eigen, Norrish and Porter won the 1967 Nobel Prize in Chemistry “for their studies of extremely fast chemical reactions, effected by disturbing the equilibrium by means of very short pulses of energy”. In the field of chemistry, this stage started with Porter’s introduction of microsecond flash photolysis allowing him to monitor reaction intermediates (van Houten, 2002). Over four decades the instrumentation has evolved up to the femtosecond timescale – nine orders of magnitude faster. The concept of (ultra)fast flash techniques is in principle simple – to distort the system at equilibrium using a high-energy flash of (usually monochromatized) radiation and detect how fast the system restores to the equilibrium. It should be noted that at the time being also attosecond (subfemtosecond) technique is at disposal, however, it is exploited mainly to follow physical processes (Schultz and Vrakking, 2013). We thus have femtochemistry (no chemical process is faster) and attophysics. In this connection it is worth mentioning that the first papers describing femtosecond experiments originated not from a university but from AT&T Bell Laboratories (Shank and Ippen, 1974) and orientation to solve tasks of practical importance can be demonstrated, e.g. by investigation of thermal energy dissipation after excitation of silicon (111) surface by 80-fs optical pulses (Shank, 1986). The field of academic research focused on the intimate mechanism of chemical processes is associated with Zewail’s pioneering works (Zewail, 2003). Femtosecond techniques provide valuable information about both physical processes (kinetics of

electronic deactivation and vibrational relaxation) and chemical reactions (formation and reactions of intermediates). It should be pointed out that current techniques allow scientists also to determine the structure of electronically excited molecules and nanoparticles (Coppens et al., 2002; Coppens et al., 2014). It should be pointed out that outcomes of attosecond (photo)physics penetrate to chemistry providing valuable information on the electron dynamics connected to chemical processes (Nisoli et al., 2017; Kumpulainen et al., 2017).

Down of photochemistry as a science

Any field of human activity to be called scientific must be covered by consistent terminology, laws or principles, and hypotheses and scientific aims. As for terminology of photochemistry, IUPAC publishes Glossary of Terms in Photochemistry, the latest one in 2007 (Braslavsky, 2007). The glossary forms terminological and matter-of-fact basis of photochemistry and photophysics.

Photochemistry is based on just two photochemical laws dealing more with the absorption of radiation (photophysical phenomenon) than with its photochemical consequences. The first one is called according to its inventors the Grotthuss-Draper law (for chemists Theodor Grotthuss 1817 and John W. Draper 1841) and states that only radiation that is absorbed by a molecule can produce a photochemical change in that molecule.

The development of the quantitative aspects of photochemistry began with the enunciation of the quantum theory by Max Planck in 1900. The second law of photochemistry (Stark, 1908 and Einstein, 1912) states that for each photon of light absorbed by a chemical system, only one molecule is activated for its subsequent reaction. This photochemical equivalence law was definitely derived by Einstein during his development of the quantum (photon) theory of light. It should be noted that irradiation of a system by very intensive lasers can cause that one molecule absorbs simultaneously two (in general even more) photons. Such a non-linear optical process was predicted originally in 1931 (Goeppert-Meyer, 1931), observed thirty years later (Keiser, 1961) and are of practical importance.

The Bunsen-Roscoe Law of Reciprocity (1862) stating that a photochemical effect is directly proportional to the total energy dose, irrespective of the time required to deliver the dose, is not included into fundamental photochemical laws. It is true for chemicals in a test tube, but the response of cells to radiation usually involves a sequence of interacting biological reactions, making a linear “dose × time” relationship highly unlikely. There is no reciprocity

when a damage (e.g. of DNA) is produced (Schindl et al., 2001).

Along with the mentioned, generally valid laws, there are a few rules and principles describing and explaining particular photochemical and photophysical processes. Kasha's, Vavilov's, Adamson's etc. rules can be introduced as examples, detailed discussion is, however, beyond the aims of this contribution and can be found in specialized literature (Klán and Wirz, 1999; Turro et al., 2009; Šima, 2008, Adamson and Fleischauer, 1975).

There has been a systematic approach to unveil principles and ways to purposefully modify or, in the best case, optimize parameters of photochemical and photophysical processes based on easily available ground state parameters. As for photochemistry, three reactivity parameters have been investigated, namely the rate constant, threshold energy and quantum yield of photochemical reactions. Detailed study of several ground-state and photochemical electron-transfer processes finally has led to the conclusion based on Marcus theory of electron-transfer reactions (Marcus, 1993) that the relations between the rate constant k_q (as a parameter of excited state reactivity) and the electrode potentials $\Delta E_{1/2}$ of the reactants or ΔG of reactions (as ground-state parameters) are both theoretically rationalizable and experimentally verified. The knowledge of such relations allows manipulating the composition of the predicted reactants to reach the rate constant of desirable value. This knowledge is of enormous theoretical importance, its practical value is, however, very limited (Šima, 2008).

Quantum yield Φ is the most frequently used and easily determinable excited-state reactivity parameter. It is also the most important one from a practical point of view because it represents a measure of the efficiency of a given deactivation mode and, when using radiation as a reactant, it can be taken as an economic parameter (electricity-based artificial radiation is not a cheap matter) too. Quantum yield is not correlable with any ground-state parameters of involved compounds. The reason for this sad statement is obvious taking its definition and hardly influenceable course of secondary reactions accompanying the primary photochemical step into account.

In practice, quantum yield of the i -th process, Φ_i is usually defined in two modes:

$$\frac{n(P_i)}{I_{\text{abs}}(R)} = \Phi_i = \frac{k_i}{\sum_j k_j}$$

where $n(P_i)$ represents the amount of the product P_i formed per unit time; $I_{\text{abs}}(R)$ is the amount of photons absorbed by the reactant R per unit time;

k_i is the rate constant of the i -th deactivation mode; denominator represents the sum of the rate constants of all deactivation modes. Quantum yield is a wavelength-dependent quantity. It is obvious that the value of Φ_i does not depend just on the rate constant of the followed i -th deactivation mode (e.g. redox decomposition of excited molecule or fluorescence) but significantly depends on the rate constants of all parallel competitive deactivation modes.

As for secondary processes, they can reduce the photochemical efficiency of a given process next to zero due to very fast reactions (back electron transfer; radical-pair recombination, electron-hole recombination in heterogeneous photocatalysts; secondary reaction with surrounding molecules etc.) of the primary products. The same effect – no net change – can be caused by physical deactivations. As a classical example, several iron(II) and iron(III) complexes for which the rate constants of ultrafast electronic and vibrational deactivation processes were determined, the complexes are, however, photochemically stable (Šima et al., 2013). The threshold energy E_{th} of a given deactivation process is a quasi-thermodynamic quantity understood as the photon energy at which the quantum yield of the process approaches zero value (Endicott, 1977). At intramolecular redox processes of a few systems of structurally similar compounds, the threshold energy is correlable mainly with optical electronegativity of the ligand undergoing photooxidation. To accept more well-founded conclusions, much more detailed experiments must, however, be done.

It should be mentioned that there have been tendencies to tune (optimize) the efficiency of photophysical deactivation modes too; the effort in this field is also in progress (see e.g. Ford, 2016).

Any emerging scientific branch tries to introduce itself via publishing original papers and conference presentations, then to systemize the acquired knowledge first through review papers and finally through monographs or textbooks. Inorganic photochemistry can serve as an example. Up to 1962 dozens of original papers were published. The first review systemizing data of about 250 original papers appeared in 1962 (Szychliński, 1962). This stage was concluded by issuing the excellent monograph Photochemistry of Coordination Compounds (Balzani and Carassiti, 1970) which was of comprehensive nature and included all the then known works and data. Enormous upsurge of the photochemistry of inorganic compounds at the end of the 20th century does not allow to write a further comprehensive monograph and a number of books has appeared covering, however, just particular aspects of this field.

As for photochemistry in general, the first book (446 pages) was, according to the author's best knowledge, published in 1914 (Sheppard, 1914).

Driving forces for development of photochemistry – a historical view

Utilization of photochemical processes may be divided into two fundamental groups. One of them comprises natural processes occurring without human intervention. Photosynthesis and processes in the environment may be introduced as examples. The other group consists of human governed processes, such as conversion of solar radiation energy into thermal, electrical and chemical energies; synthesis of chemical compounds (mainly those hardly preparable from ground-state reactants); photoprocesses of pharmacological, medical and cosmetical nature; photodegradation of harmful compounds in the environment. In this part the attention will be focused on the latter mentioned group.

The above mentioned heliotherapy led to the effort to understand the matter and exploit the accumulated knowledge. In the 20th century modern phototherapy evolved. Among the pioneers, the Nobel Prize (1903) winner Niels Finsen who treated patients with skin tuberculosis (lupus vulgaris) by visible light irradiation may be mentioned. However, it took several decades until phototherapy was introduced anew into the dermatological armamentarium by means of photochemotherapy (PUVA) in 1974 that marked the beginning of a huge upsurge in photodermatology. The subsequent development of high intensity UV sources with defined spectra facilitated an optimized therapy for psoriasis and led to an expansion of indications for photo(chemo)therapy also in combination with topical and systemic agents. The introduction of extracorporeal photophoresis in 1987 for cutaneous T-cell lymphoma and of topical photodynamic therapy widely expanded the therapeutic possibilities in dermato-oncology (Hönigsmann, 2013).

Application of radiation to perform photoinduced transformation of organic compounds was in scientific literature first recorded in 1834 (Trommsdorf, 1834). It is worth mentioning that the mechanism of the Trommsdorf's original observation of crystal-to-crystal transformation of α -santonin was explained only a few years ago (Natarajan et al., 2009). As a milestone in inorganic photochemistry the observation of the Swedish chemist Carl Wilhelm Scheele (the discoverer of seven chemical elements) in 1777 that the light causes decomposition of silver chloride to silver and chlorine can be mentioned. In inorganic photochemistry the first publication

can be traced down to 1790, when photochemical synthesis of FeCl_2 from etheric solution of FeCl_3 was described (Macquer, 1790). Photochemical synthesis (performed at rather unusual conditions) was used to answer the questions on the existence of some "exotic" compounds. Three examples can illustrate the matter.

The elements of Group 12 (Zn, Cd, Hg, Cn) were generally considered post-transition metals with filled $(n - 1)d$ shell. Irradiation of Hg and F_2 dispersed in solid neon or argon matrixes ($T \leq 10$ K) with 240 – 380 nm radiation emitted from a mercury arch led to the formation of square-planar HgF_4 molecules identified by IR spectroscopy (Wang et al., 2007). Involving its $5d$ orbitals in bonding, at least mercury may thus be declared a true transition metal.

Iron(III) iodide was characterized as a non-existing compound even in modern textbooks (Wulfsberg, 1991; Moody, 1991). In the pure state it was prepared (Yoon and Kochi, 1988, 1990) photochemically irradiating a hexane solution of $[\text{Fe}(\text{CO})_4\text{I}_2]$ and I_2 at -20 °C.

Xenon and krypton fluorides were prepared via irradiation of Xe or Kr and F_2 with ultraviolet radiation. The best yield and purity of the KrF_2 were obtained by a photochemical process occurring at -196 °C when Kr was a solid and F_2 a liquid (Kinkead et al., 1994).

It should be pointed out that any photochemical reaction yields new chemical species. From the viewpoint of exclusivity, three kinds of photochemical processes and their products are of interest:

- those leading with high efficiency and purity to the desired products (economical aspect);
- those hardly preparable through a ground-state reaction due to kinetic reasons (high activation energy of a ground-state process is overcome by excitation);
- those thermodynamically disfavoured products non-preparable through a ground-state reaction due to thermodynamic reasons ($\Delta_r G \gg 0$ for the corresponding ground-state reaction).

Probably the strongest driving force for the development of photochemistry were the 1970s energy crises when major industrial countries of the world faced substantial petroleum shortages as well as elevated prices. The two worst crises were the 1973 oil crisis and the 1979 energy crisis, when the Yom Kippur War and the Iranian Revolution triggered interruptions in Middle Eastern oil exports. All these events stimulated the search for new, renewable energy sources, in optimal case independent on political plays. One of the most promising sources was the energy of solar radiation. The reason for such orientation is obvious. Every hour the Sun

beams onto Earth more than enough energy (about 4.3×10^{20} J) to satisfy global energy needs for an entire year (about 4.1×10^{20} J) (Anwar et al., 2013, Mutmaz et al., 2015). The fundamental question is how to harness the Sun's energy and make it usable, i.e. how to convert it efficiently into electrical, chemical and thermal energy.

Speaking in a nutshell, solar-to-thermal energy conversion has become still more and more applied for heating of industrial, agricultural and residential buildings. Solar-to-electrical energy conversion is accomplished mainly through solid, semiconductor-based or organic photovoltaic devices (Ahn et al., 2016; Bazilian et al., 2013). Solar-to-chemical energy conversion seems to be the least advanced area in the field of utilizing solar radiation energy. This is a paradox since the Nature clearly demonstrates by means of photosynthesis how to do it. It is estimated that about ten photons should be absorbed to fix and reduce one CO₂ molecule as the key step in biomass formation (Pessarakli, 2016; Wilson and Hunt, 2014). The ambition of scientists has not been focused primarily on artificial biomass production (foodstuff-problem solving) but rather on photochemical decomposition of water to hydrogen and oxygen. It is due to the facts that sunlight is free of charge and the Earth is abundant in water which is thus a very cheap reactant. Moreover, hydrogen is ecologically the most friendly and best chemical fuel since within its reaction with oxygen the substantial amount of energy is produced (for liquid water $\Delta_r G^0 = -273.1 \text{ kJ} \cdot \text{mol}^{-1}$) without contaminating the atmosphere with greenhouse gases and other pollutants. For comparison, at burning of 1 g of hydrogen and 1 g of carbon, 136 kJ·mol⁻¹ and 32 kJ·mol⁻¹ of Gibbs energy is released, respectively (Haynes, 2015). To acquire the ability to effectively convert solar-to-chemical energy, much research must be done in the future.

Experimental equipment of photochemistry

The first source of radiation applied in photochemistry was the Sun. Giacomo Ciamician, generally recognized as the father of photochemistry did his experiments using solar radiation on his laboratory balcony of Bologna University where hundreds of bottles and glass pipes containing various substances and mixtures were exposed to the sun rays (Venturi et al., 2005). Later on artificial sources have been introduced, the first one being a mercury vapour lamp developed by John Thomas Way who received a British patent on it in 1857 (Way, 1857). Gradually several radiation sources of UV, visible and NIR radiation were constructed. In

most continuous irradiation experiments, five types of radiation sources have been applied, namely incandescent tungsten-filament lamps, discharge lamps containing xenon gas or mercury vapours (depending on the vapour pressure, low, medium and high-pressure arcs are employed), narrowly light-emitting diodes (LED), near-monochromatic excimers, and monochromatic lasers (Mutmaz et al., 2015). All these sources of radiation have been used in various types of photoreactors, marry-ground equipment, or optical benches.

Advances in laser technology have enabled lasers to deliver monochromatic, coherent and intense pulses of ultrashort duration of the order of femtosecond. The most frequently types of lasers employed in ultrafast flash techniques are solid-state lasers (ruby laser, neodymium doped yttrium aluminium garnet, denoted as Nd-YAF, and titanium-sapphire lasers), gas lasers (He-Ne or Ar⁺ lasers), and dye lasers containing coloured fluorescent dye dissolved in a nonabsorbing solvent (for more details on radiation sources, see Wardle, 2009).

Fields of application of photochemistry

The relevance of photochemistry and driving forces of its development lie, along with theoretical aspects, in various fields of the applied science and technology. The application fields are so numerous that all of them cannot be even mentioned in this paper. Details can be extracted from a huge number of monographies, conference proceedings, scientific and patent literature. Based on the author's selection, top ten (in some cases overlapping) areas are as follows.

1. Photochemical synthesis of organic and inorganic compounds, mainly those hardly preparable by ground-state processes due to thermodynamic and/or kinetic reasons (Pape, 1974; Pfoertner, 1984; Knowles et al., 2012, Klán and Wirz, 2009; Sýkora and Šima, 1990).
2. Radiation-induced polymerization and preparation of polymeric materials (Pape 1974; Chatani et al., 2014; Fouassier and Lalevée, 2014; Dietliker et al., 2010; Nakamura, 2015), in particular preparation of photoresists (materials crucial in the whole electronic industry) and UV curing (a photochemical reaction generating a crosslinked network of polymers).
3. Preparation of nanoparticles (Lu, 2016) of desired size, shape and properties. Synthesis, incorporation on surfaces and light-driven utilization of quantum dots (Mosconi et al., 2015).
4. Application of semiconducting materials in protecting the environment and purifying

water via (photo)Fenton and photochemical advanced oxidation processes (Katagi, 2004; Byrne et al., 2015).

5. Photocatalysis (Kaneko and Okura, 2002; Schneider et al., 2016; Nosaka and Nosaka, 2016).
6. Photodynamic therapy for cancer treatment and light-involving treatment of dermatological diseases (Hönigsmann, 2013; Lee and Baron, 2011).
7. Solar-to-electrical energy conversion mainly by means of solid state semiconducting materials (Smets et al., 2015; Bauer, 2015).
8. Solar-to-chemical energy conversion including photochemical preparation of compounds of high chemical energy content, mainly hydrogen and other fuels production through catalytic photolysis of water and other compounds (Smestad and Steinfeld, 2012; Han and Eisenberg, 2014).
9. Photoinduced production of biomass and artificial photosynthesis (Sugiyama et al., 2016; Alim and Bak, 2016; Barber and Tran, 2013).
10. Deepening the knowledge of photochemical and photophysical properties of chemical compounds and materials and its implementation in the formulation of photostabilizers and skin-protective sun lotions and creams (Parker, 2013; Barrow and Barrow, 2005).

Note: Highly appreciated results have been obtained in the field of molecular machines driven by light absorption. The appreciation can be documented by the Nobel Prize in Chemistry 2016 awarded to Jean-Pierre Sauvage, Sir J. Fraser Stoddart and Bernard L. Feringa “for the design and synthesis of molecular machines” (Sauvage et al., 2016; Stoddart, 2009; Lerch et al., 2016). In spite of the attractiveness and future potential of such machines, their inclusion into the top ten list of applied of photochemistry would be at the time being too premature.

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