Angelo Albini

Photochemistry

Past, Present and Future

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Photochemistry

Preface

The chemical changes induced by light on substances have been long known. The advancement of this discipline has been somewhat irregular, however, with an outburst at the beginning of the twentieth century corresponding to the first in-depth preparative studies on one hand and to the development of quantum physics on the other hand, and a much more consistent development after 1950 when the general framework of this science was recognized.

As we now understand this phenomenon, absorption of a photon leads to an electronically excited state, characterized by high energy and a strongly perturbed electronic structure. The result often is an in-depth—but selective—chemical transformation. As everyone can easily appreciate, photochemistry has a key role in nature (e.g., chlorophyll photosynthesis, vision) and in a variety of applications. Photography and other methods of reproducing an image, the fast hardening of varnishes and of dental cement, and many other applications are based on photochemical reactions.

Furthermore, photochemistry has a particular role in learning and teaching chemistry, as was recognized already in 1926 (see Sect. 2.5), in that it concerns *all* of the electronic states of a given species, in particular the lowest singlet excited and triplet states, not only the lowest-lying (ground) one as does normal (thermal) chemistry. Thus, not only one but at least two new dimensions are added to chemistry by light absorption, and learning how to exploit and direct the system toward a specific goal is one of the main issues of future time's chemistry. Retracing the path that has led to the present state of photochemistry may give some hints of those that still lay open to exploration.

What has been attempted here is to understand the actual experiments and the intellectual effort that have led to the development of this wonderful discipline, and perhaps to extend the enthusiasm of scientists already engaged in the field toward new facets of it.

I would have not expected writing this book to be such a hard task. I am grateful to the many scientists from whom I had the opportunity to learn over the years and I hope that the many inefficiencies of the manuscript will be indicated to me. The colleagues who helped me in this adventure are thanked for their enthusiasm and competence (prof. Maurizio Fagnoni, drs Stefano Protti, Davide Ravelli, Stefano Crespi, and prof Elisa Fasani). My sons and my friends, in particular Mr Nicola Scuro, are likewise thanked for their help.

Pavia, Italy Angelo Albini

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Chapter 1
Early Times of Photochemistry

1.1 Introduction

The perception of light is one of the fundamental experiences of living beings and its power to reveal the world has always been recognized. In Genesis, creation of matter is immediately followed by creation of light that allows to detect the created world through its forms and colors:

And God said:
Let there be Light,
and there was Light.
And God saw the Light, that it was good;
and God divided the Light from the darkness.
(Genesis I: 1–4)

Similar tales are present in the oldest texts of other cultures. The deepest impressions are expressed as an overwhelming flood of light, as Dante mentions for the vision of Paradise:

I think the keenness of the living ray
Which I endured would have bewildered me,
If but mine eyes had been averted from it
(Paradise XXXIII: 76–78)

Light reveals matter through what is the most powerful sense for humans, sight, and indeed the more so in contemporary society where the other senses have in part lost their role. Not only that, light is also able to modify living beings, and this in a way that is vital for them. Thus, mankind always perceived the relation between the long days of solar irradiation in summer and the abundance of the fruits Earth produced in that time and has attempted to exploit in the best way such an inexhaustible source of energy and of materials. This has been achieved through

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agriculture, the science and technique that improves the harvest unperturbed nature produces, arriving at much better results (from men point of view). The beginning of modern human culture is generally taken as the moment when previously nomadic populations permanently settled. A more abundant harvest has been necessary for the increasing population and has always been sought by mankind, whether through ceremonies and sacrifices to the god sun in ancient times or by introducing innovative agrochemical techniques in the modern ones.

The advancement of society has seen a more and more pervasive role of light. Indeed, light was often taken as the symbol itself of progress guided by science. This was enlightenment, out of the darkness of earlier, less technologically advanced times. A celebrated example is the ballet "Excelsior" that was staged at La Scala theatre in Milan in 1881 (story by Manzotti, music by Marenco) that culminated in the triumph of light. Or at least, this was the predominating view (at least among the upper classes) in the rapidly growing western world, in particular during the industrial development from the eighteenth century up to the early years of the twentieth century. Although an optimistic overall attitude based on the confidence in a continuous improvement of mankind conditions may be no more predominating 100 years afterward, vision-based communication develops at an increasing pace and is more and more at the basis of society, with such media as the net and television pervading everyday life.

As mentioned above, light has a strict relation with the modification of matter and thus with the science that studies it, that is chemistry, through a dedicated discipline, photochemistry. This has extended to an unbelievable variety of applications, certainly primarily concerned with the reproduction of images, but involving many other cases where the characteristics of light, that is, the high-energy of UV and visible quanta and the possibility to deliver them when, where, and how desired offer a decisive advantage, from building and operating "intelligent" materials or machines to carrying out complex manipulations (including surgery) at the submicroscopic level and to innumerable further applications.[1]

As illustrated in Sect. 2.5, already in 1926 it was remarked [1] that photochemistry is concerned with all of the electronically states of chemical entities, and thus in a sense it is photochemistry that includes chemistry and not vice versa, since ground states are but a particular case of electronic states. Furthermore, comparing the reactivity of excited states with that of the corresponding ground states makes particularly apparent the direct relation between chemical properties and electronic structure of each species and thus the role of the electronic structure in the reactions of chemical species. In view of this situation, it may be thought that all chemistry, through photochemistry, is included in atomic physics, the science that studies the intimate structure of the matter and thus the electronic structure of atoms and molecules. This peculiar relation endows photochemistry both with a particularly

[1] Sensu stricto, if the prefix photo is taken etymologically, this science should be limited to the effect of visible light, but of course the affinity of UV and visible-light photochemistry is too strict for allowing a separate treatment.

rich approach for understanding and teaching chemistry - and science in general - as well as with a rich vision toward innovation.

As a matter of fact, the applications of photochemistry are so rich and diverse that the relation with a common basic discipline tends to be lost. This is unfortunate, because the abovementioned central role of photochemistry is a continuous source of inspiration and there is much to gain from conserving a unified point of view. In this sense, some historic knowledge is helpful, as always in science. The present volume is not a proper history of photochemistry, but rather a discussion of some turning points during the formation of the basic postulates of photochemistry and an attempt to present some directions of future development.

1.2 Light and Chemistry

Of the two parts of the word photochemistry, the former one refers to the discipline that arrived first at a fully scientific description. The advancement of the understanding of what is light advanced rapidly from the experiments on the dispersion of (visible) light and the corpuscle theory of colors by Newton (1704) [2] and the discovery of ultraviolet (Ritter, 1801) [3] and infrared (Herschel, 1800) [4] components to the formulation by Maxwell of the equations for the electromagnetic field (1862–1864) and then to the theoretical contributions by Planck that concluded that a black body emits light only in discrete bundles (quanta, 1900) and by Einstein that viewed all quanta of light as actual particles (1905). These were later called photons (as proposed by G. N. Lewis, 1926) in analogy to other elementary particles that had been discovered, such as electrons and protons (and then phonons, plasmons). The study of light-related effects is the core of modern physics and set the stage for a particular role of photochemistry in that it combines photons with molecular structure and thus with the properties of electrons and protons. Lewis conceived photons as actual particles, different from the light they transported.

"Whatever view is held regarding the nature of light, it must now be admitted that the process whereby an atom loses radiant energy, and another near or distant atom receives the same Energy, is characterized by a remarkable abruptness and singleness. We are reminded of a process in which a molecule loses or gains a whole atom or a whole electron but never a fraction of one or the other... Had there not seemed to be insuperable objections, one might have been tempted to adopt the hypothesis that 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 again bearing a new amount of energy. If I now advance this hypothesis of a new kind of atom, I do not claim that it can yet be proved, but only that consideration of the several objections that may be adduced shows that there is not one of them that can not be overcome. It would seem inappropriate to speak of one of these hypothetical entities as a particle of light, a corpuscle of light, a light quantum, or a light quant, if we are to assume that it spends only a minute fraction of its existence as a carrier of radiant energy, while the rest of the time it remains as an important structural element within the atom. It would be also cause confusion to call it merely a quantum, for later it will be necessary to distinguish between the number of these entities present in an atom and the so called quantum number. 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." Lewis postulates that the total number of (intrinsically identical) photons was constant in an isolated system. Serious objections against this idea of the conservation of photons could be raised on the basis of the thermodynamics of radiation and of the laws of spectroscopy. As mentioned, Lewis thought that they could be overcome, but this theory was never accepted and seems unpalatable today, although this is the last manifestation of the view of light as one of the "imponderables" that can be accumulated in matter, a representation that has a long tradition (see Sect. 2.3). The name photon, however, remained and became of general use [5, 6].

1.3 Historic Notes

As mentioned, the observation of chemical effects of light is as old as mankind itself. Accounts of the earlier history of photochemistry have been presented by several authors. Long erudite lists of reference are of little usefulness, however. Here, it has been chosen to present a brief historic profile based on a document itself of historic value, the introduction written by a great authority, professor Ivan Plotnikov. This well-known Russian-born scientist published in 1910 a book on photochemistry which was followed in 1936 by a second, much extended, edition of over 900 pages. The view he had on this science, or at least on some aspects of it, in particular the unconditioned refusal of the Stark–Einstein "equivalence law," appeared obsolete at the time of the second edition, as it is discussed in Sect. 2.3. However, Plotnikov can certainly not be accused of insufficient knowledge of the matter or of insufficient exploration of the literature and his book is a rich mine of data and thoughts [7].

The chapter devoted to the historic aspects of photochemistry in Plotnikov's book may thus offer a convenient approach. The key early events are presented and discussed with reference to three periods, by adopting a scheme that he thinks had general validity. The first one, during which much experimental material was collected and progressively acquired a scientific character, lasted, he thought, until the first third of the nineteenth century. Apart the role sunlight had in monotheistic religions and cultures, he lists a series of important events, of which some are reported below, as characterizing this period:

- 50 BC—Vitruvius mentions the light-induced fading of paintings.
- 1342 AC—Petrus de Alexandria describes the camera obscura (in principle, already known to Aristotle's).
- 1575—Niccolò Monardes in Venice reports the fluorescence of lignum nephriticum.

- 1602—Casciarolo in Bologna reports the phosphorescence of feldspar.
- 1674—Brand in Homburg reports the chemical luminescence of phosphor.
- 1725–1757—Several reports on the light sensitivity of inorganic salts appear ($FeCl_3$, $AgNO_3$, AgCl) and applications for sympathetic inks and for reproducing images are published.
- 1782—After several partial reports (by Priestley, Bergmann, Scheele, Ingenhousz), Senebier publishes a comprehensive and successful book on the effect of solar light on plants, oils, dyes, wood, etc. This not only mentions that silver chloride blackens at light but also that this darkening depends on the color of the light.
- 1785—Berthollet reports the photocleavage of HCl.
- 1790—Saussure builds the first photochemical photometer, based on the development of gas by irradiation of chlorine water.
- 1802—The first photographs on silver paper by Wedgwood and Davy.
- 1814—Nièpce and Daguerre begin their work on photography.
- 1817—Grotthuss formulates the law that only absorbed light has a chemical effect while studying the photodecomposition of iron salt solutions.

After this period, the moment would have been mature for the full blowing of photochemistry as a science, as it happened with most disciplines. Unfortunately, at least in the opinion of Plotnikov, a major stumbling block intervened, viz., the enormous success of photography that concentrated the effort on technical aspects of the chemistry of the silver salt emulsion, the sensitization, the stability of images, and so on. Therefore, this is named the "technical–photographic period" and the purely scientific advancement had been less significant that it may have otherwise be. Furthermore, when a scientific issue was confronted, then the topic was ill chosen. Thus, the first photochemical kinetic study was devoted to the formation of hydrogen chloride from the components by Bunsen and Roscoe in the1850s [8, 9].

These authors found in their initial study that the progress of the reaction was proportional to light intensity and time of irradiation. Unfortunately, this held only under the conditions they had chosen, that is, under removal of the product and by maintaining constant the concentration of the reagents. Then, they found a more complex course in the presence of moisture and air and furthermore observed an induction period. The authority of Bunsen spurred a large number of scientists to concentrate their efforts on the study of this really complex reaction, perhaps retarding the development of photochemistry in general. Apart from these considerations, Plotnikov lists several key events of this second period lasting until the last years of the nineteenth century, some of which are indicated below:

- 1838—Preparation of the first daguerreotype.
- 1839—Ponton discovers the sensitivity to light of paper tramped with a potassium bichromate solution.
- 1843—Draper rediscovers, independently from Grotthuss, that only absorbed light is chemically active.
- 1850—Regnault discovers the development of images by pyrogallol.
- 1851—Archer discovers the properties of collodium.

- 1852—Beer formulates the light absorption law.
- 1869—Fritsche discovers the dimerization of anthracene and other substances.
- 1869—Timiriaseff and Engelmann study quantitatively the assimilation of carbon dioxide by green plants.
- 1872—Baumann discovers the photopolymerization of vinyl chloride.
- 1875—Balmer discovers the line structure of the hydrogen spectrum.
- 1879—Eder describes a mercury-oxalate photometer and establishes that photochemical reactions have no temperature coefficient.
- 1894—Joly reports the first trichromatic print.

In the third part of his historic introduction, Plotnikov notices that, as it is generally the case for a mature science, the development of contemporary photochemistry was characterized by the advancement in theory coupled with the advancement in experimental methods and instruments. The possibility of obtaining quantitative data about the amount of light and matter in photochemical reactions and the availability of convenient mercury arcs in substitution of solar light opened the way for new applications. The initial phase of the development of every discipline, "in which an accumulation of experimental data takes place, and confusion of opinion prevails," had been overgrown and photochemistry had arrived where fundamental laws are established. This phase "always represents a turning-point in the history of a given branch of science... characterized by great intellectual exertion on the part of the leading investigators, as well as by the sharp clash of mutually opposing tendencies." A number of books were printed [10–12], besides Plotnikov's own, that related on the whole of photochemistry, whereas in previous periods these had been practically limited to photography [13]. Single events that Plotnikov considered important included:

- 1897—Kinetic characterization of the HI photolysis by Bodenstein.
- 1900—Ciamician and Silber begin their work on organic photochemistry.
- 1905—Trautz formulates a theory of chemiluminescence.
- 1904–1907—van't Hoff suggests and Lazareff demonstrates the proportionality between absorbed light and reaction (quantitative application of the Grotthuss law).
- 1907—Warburg publishes the first paper on energy measurements in a photochemical reaction.
- 1908—Plotnikov builds his light thermostat.
- 1908—Stark suggests that a molecule requires a quantum for reacting.
- 1908—Stobbe discovers the photochromism in the case of fulgides.
- 1910—D. Berthelot begins his studies on the photochemistry of organic compounds.
- 1912—Einstein gives a thermodynamic base to the Stark hypothesis on the light quantum.

Although a lessening of the rate of the scientific advancement in photochemistry after the war was noticeable, Plotnikov hoped that this would have not lasted long and the discipline would early find a shared, comprehensive theory as well as new applications (he thought particularly of biology and medicine).

Plotnikov had been somewhat hasty in judging that photochemistry had become a mature science in 1930. In fact, many seeds were close to germinate, the paradigms of photochemistry had been not yet formulated, the number of known photochemical reactions was too small for reaching generalizations, and apart from the fact that in many cases it was difficult to recognize which chemical change occurred upon irradiation, key instruments that were able to afford a more detailed view of excited states had yet to be devised and assembled.

In the present case, further extending his list of key dates would lead to a treatise of photochemistry that may be conveniently found elsewhere. This will not be attempted, therefore, and only a few indications are given of the main instrumental advancements that made possible to understand the complex mechanism of photochemical reactions. A list of dates can at any rate be found in the Webster's timeline history [14]:

- 1933—Jabłonski proposes a metastable electronic state for the long-lived emission of some dyes.
- 1940–1946—Lewis and Kasha recognize the role of triplet state and introduce the state diagram.
- 1950—The role of triplet states in photochemical reactions is recognized.
- 1950—Flash photolysis instrument.
- 1950—The availability of modern chromatographic and spectroscopic techniques makes possible to discover (and sometime rediscover) many photochemical reactions; quantum yields are routinely determined.
- 1955—Steady-state luminescence routinely investigated for the role of excited states, excited complexes, electron/energy transfer, and intermediates; steady-state luminescence in rigid media.
- 1965—Time-correlated single-photon counting techniques for determining the lifetime of short-lived excited states.
- 1970—Laser flash photolysis.
- 1970—Photochemical reactions in rigid matrix (rigid solvent, codeposition with inert gas) with spectroscopic detection.
- 1980—Laser flash photolysis with IR detection.

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