

Fiat lux!

Edwin C. Constable*

Abstract: Photochemistry made the transition from a natural observable to a scientific discipline in the latter half of the 19th Century CE. This short article looks at the development of the discipline in its first 100 years with a particular emphasis on the participation of Swiss scientists.

Keywords: History of Science · Photochemistry · Switzerland



Edwin (Ed) Constable is professor of chemistry at the University of Basel. He studied chemistry at the University of Oxford before migrating to “the other place”, holding fellowships and a lectureship at the University of Cambridge. He moved to Basel in 1993. His interests in chemistry are broad-ranging with a particular emphasis on the role of metals in

modifying the properties of materials. He was one of the founders of metallocsupramolecular chemistry and his current interests centre on the development of a sustainable materials chemistry. He has long been interested in the history of science, believing that we need to understand how modern science developed to enable further progress.

1. Introduction

In the 21st Century CE, photochemistry and the underlying photophysics are mainstream disciplines in the scientific world. On the other hand, despite phenomenological origins before recorded history, photochemistry is a relative newcomer to the mainstream of chemical science. For a more complete discussion of the history of the discipline, the reader is referred to the excellent book by Albini.^[1] This article traces the development of photochemistry with a particular emphasis on the involvement of Swiss scientists up to the beginning of the second world war, a point which we could consider the beginning of modern instrumental chemistry. We are concerning ourselves only with photochemistry, in which chemical change is initiated by light absorption.

2. The Earliest Days

2.1 Colours Fade

Probably the earliest societal impact of photochemistry is to be found in the fading of natural dyes upon exposure to sunlight. One of the earliest records of the phenomenon is given by Vitruvius around 50 BCE, who recommended that “picture galleries, embroiderers’ work rooms, and painters’ studios” should face north “in order that the fixed light may permit the colours used in their work to last with qualities unchanged”.^[2]

A very early contribution to the scientific study of the phenomenon was made by Jean Senebier (1742–1809, Fig. 1a) who was the chief librarian of the Republic of Geneva and an early pioneer in photosynthesis research. In 1782, he published a book entitled “*Mémoires physico-chimiques sur l’influence de la lu-*



Fig. 1. Two important Genevans (a) Jean Senebier (1742–1809) the Swiss pioneer of photosynthesis and photochemical research who described the effect of light of different wavelengths on silver chloride (https://commons.wikimedia.org/wiki/File:Jean_Senebier.jpg) and (b) Horace-Bénédict de Saussure (1740–1799) (https://commons.wikimedia.org/wiki/File:Horace-B%C3%A9n%C3%A9dict_de_Saussure.jpg).

mière solaire pour modifier les êtres des trois règnes de la nature, et sur-tout ceux du règne végétal” which contained an overview of the effect of light on inorganic and organic materials.^[3] About five years later, his Genevan contemporary Horace-Bénédict de Saussure (1740–1799, Fig. 1b) noted that the effect of light on an aqueous solution of chlorine (to generate HCl and HOCl) was proportional to the time and intensity of the exposure.^[4]

My emphasis in this article is not on colour, but it would be disingenuous to mention that the present day Swiss chemical and pharmaceutical industry is the linear descendent of the dyestuff industry that developed in and around Basel. The transition from natural dyes to synthetic dyes transformed the region and industrialized the city. The importance to the region was commemorated by the involvement of Ciba and Sandoz in the 1948 establishment of the Institut für Farbenchemie in Basel under the leadership of Robert Wizinger.^[5]

2.2 Enter Silver!

Silver nitrate turns black in sunlight and probably the earliest description of this phenomenon is due to Angelo Sala (1576–1637) who, in 1604, lived in Ponte, Switzerland.^[6] In “*Septem planetarum terrestrium spagirica recensio*” published in Amsterdam in 1614, Sala states “*Si lapidem lunareum pulveratum ad solem exponas instar atramenti niggerimus*” (When you expose powdered silver nitrate to sunlight, it turns black as ink).^[7] In 1717, Johann Heinrich Schulze (1687–1744) showed that the same phenomenon occurred when silver nitrate was mixed with, or absorbed on, various substrates – and thus began the story of photography.^[7] In

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passing, I note that Senebier reported the same phenomenon in silver chloride in his 1782 work. Although Schulze produced images on a chalk substrate, it was for Thomas Wedgwood (1771–1805) and Humphry Davy (1778–1829) around 1800 to extend the concept to ceramic, glass, leather or paper treated with silver salts. However, they could not capture images from a *camera obscura*, although they succeeded in making photograms.^[7] Even the photograms had to be kept in the dark to prevent further blackening as the process of ‘fixing’ had not been discovered.

Modern photography had its beginnings in the improved technologies introduced by Joseph Nicéphore Niépce (1765–1833), Louis-Jacques-Mandé Daguerre (1787–1851) and William Henry Fox Talbot (1800–1877). Although the artistic and aesthetic aspects of photography were embraced by the Swiss community, probably first by Johann Baptist Isenring (1796–1860), there appear to have been few contributions to the development of the fundamental technology. The first female photographer active in Switzerland was Franziska Möllinger (1817–1880), who worked in the 1840’s and produced daguerreotypes of rural and urban scenes.

The Talbot calotype process utilized paper sensitized with silver iodide and generated a stable negative image after stabilization by treatment with either KBr or sodium thiosulfate. The daguerrotype was more common in the 1840’s and 1850’s and used light sensitive silver halide-coated copper which was developed with mercury vapour and subsequently fixed with sodium thiosulfate. The daguerrotype process was inconvenient and dangerous and was largely replaced from 1850 onwards by the wet (and dry) collodion processes. Once again, this utilized silver halides for the generation of the latent image, but our interest lies in the solution known as collodion.

In 1845–46, one of my predecessors as professor of chemistry at the University of Basel, Christian Friedrich Schönbein (1799–1868), developed a safe way of nitrating cellulose to prepare guncotton (*Schiessbaumwolle*). Some kinds of guncotton were soluble, or partially soluble, in ether-alcohol mixtures and these solutions became known as collodion. To this day, collodion is used in medicine to form protective films on wounds. Although the discovery and use of guncotton and collodion were, and remain, contentious, the contribution of Schönbein to the development of photography is undeniable.

The collodion process was replaced, in turn, by the gelatine dry-plate, which was succeeded by roll film, introduced by Eastman in 1885. By 1889, our old friend cellulose nitrate (a.k.a. guncotton) was being used as the base flexible plastic roll film – another connection to Schönbein. Naturally, the use of a potentially explosive and highly inflammable material in the roll film was not optimal and the cellulose nitrate was replaced by cellulose acetate in 1908.

3. The 19th Century CE

We have got ahead of ourselves in this story by our digression into photography. In general, photochemical studies were sporadic in the 19th Century CE and appear to have been largely unknown to, or ignored by, the Swiss chemical community. This section summarizes the most important developments in this period.^[1,4,8,9]

3.1 The Fundamental Laws

The most basic law of photochemistry was discovered by Christian Johann Dietrich Theodor von Grotthuss (1785–1822) in 1817 when he recognized that only light absorbed by a solution or a substance can lead to a chemical effect.^[10] This observation was not widely known and was rediscovered by John William Draper (1811–1882) in 1843^[11] and is immortalised in the Grotthuss-Draper law. The attenuation of light in a coloured solution and the quantification of light absorption was discovered a number of times by Pierre Bouguer (1698–1758),^[12] Johann Heinrich Lambert (1728–1777) in 1760^[13] and by August Beer (1825–1863) in 1852^[14] and is still known eponymously as

the Beer–Lambert law, Beer’s law, the Lambert–Beer law or the Beer–Lambert–Bouguer law.

Also relevant to photochemistry were the observations of John Dalton (1766–1844)^[15] and Wilhelm Constantin Wittwer (1822–1908)^[16] that the rate of a photochemical reaction was proportional to the amount of radiation absorbed. Dalton noted of the reaction of hydrogen with chlorine (oxymuriatic acid in his nomenclature): “it was ... placed in the direct rays of the sun, and the diminution was rapid as before. Upon repeating the experiment with sundry variations, it was confirmed, that Light is the occasion of this rapid combustion of hydrogen in oxymuriatic acid gas; that the more powerful the light, the more rapid is the diminution of the mixture”.

3.2 Inorganic Photochemistry

Some of the earliest studied photochemical reactions involved inorganic chemistry. By 1790, Joseph Priestley (1733–1804) had shown that nitric acid was decomposed to NO₂ upon exposure to sunlight.^[17] Johann Wolfgang Döbereiner (1780–1849), today better remembered as one of the pioneers attempting to bring order to chemistry through a nascent periodic system, described the photoreactions of various metal salts, particularly iron(III), in the presence of organic substances, particularly carboxylates. These were the same types of reaction that had led Grotthuss to the formulation of the fundamental law of photochemistry.

3.3 Organic Photochemistry

Whilst the developments in photography were fascinating the watching world, organic photochemistry was developing in its own quiet way.

The obscure compound santonin plays an important role in early photochemical studies stemming from Hermann Trommsdorff’s 1834 observation that colourless crystals of santonin turn yellow in sunlight and subsequently “explode”.^[18] Over the next 70 years, studies on the irradiation of solutions of santonin by Heldt, Fausto Alessandro Sestini (1839–1904) and Stanislaw Cannizzaro (1826–1910) made important contributions to understanding the transformations and to the development of the familiar methods of photochemistry (Fig. 2). The first publication by Sestini in 1866^[19] marked the beginning of an involvement of Italian chemists with photochemistry, particularly those in Bologna where it continues to flourish to this day.

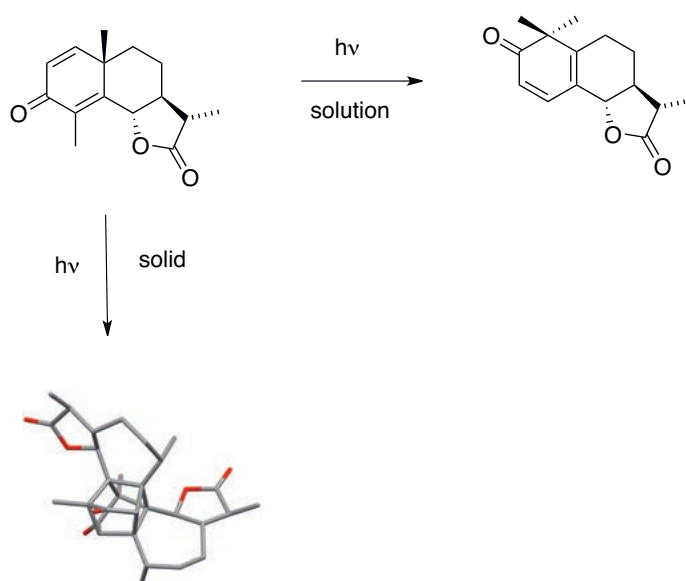


Fig. 2. Santonin gives different photoproducts upon irradiation in the solid state and in solution. The solid state species is the product after the crystals “explode”. Structure generated from coordinates as published in *J. Am. Chem. Soc.*, **2007**, 129, 9846.

This is the point to draw attention to the enormous contribution of the Bologna group from the early to mid-1880's onwards, in particular Giacomo Ciamician (1857–1922) and Paul Silber (1851–1932), who used sunlight to initiate numerous photochemical reactions of organic compounds.^[20] This work by their southern neighbour does not appear to have stimulated interest within the Swiss chemistry community.

In 1867, Carl Julius Fritzsche (1808–1871) discovered the dimerization of anthracene upon irradiation and in subsequent work showed the formation of other photodimers (Fig. 3a).^[21] Carl Theodor Liebermann (1842–1914) extended the study of photodimerization to [2+2] cycloadditions (Fig. 3b).^[22]

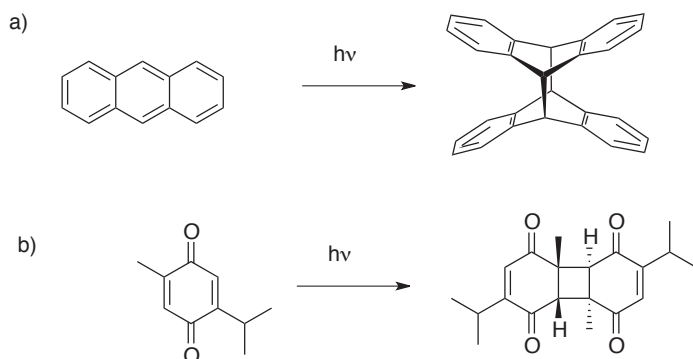


Fig. 3. Dimerization reactions were identified early in the history of photochemistry.

Another important photochemical observation dates to 1872, when Eugen Baumann (1846–1896) observed the formation of a white solid in a container of vinyl chloride that had been left in sunlight^[23] – polyvinyl chloride (PVC) remains one of the key polymers used in the plastics industry.

Another important photochemical reaction discovered in the 19th Century CE is the isomerization of alkenes, which was first reported by William Henry Perkin (1838–1907) in 1881 as part of his study of cinnamic acid derivatives.^[24] Now we can finally identify a contribution with a tenuous connection to Switzerland. Johannes Wislicenus (1835–1902) was active at the University of Zurich and the Swiss Polytechnic Institute (later ETH) from 1860–1872. Wislicenus described the formation of photostationary states containing both maleic and fumaric acid from the irradiation of maleic acid in aqueous solution in the presence of bromine, although this work was performed after he had succeeded Hermann Kolbe to the chair at Leipzig in 1885.^[25]

In general, photochemical studies were sporadic in the 19th Century CE and appeared to have been largely unknown to, or at least not integrated within, the Swiss chemical community.

3.4 The Methods

The laboratories of the 19th Century CE were often interesting places! This holds in the field of photochemistry as in many others. Remember that convenient electrical sources of intense light, such as discharge lamps, were not available. Some workers describe the use of burning magnesium ribbon as a light source, which conjures a picture of laboratories covered with a snow-like dust of MgO. The light source of choice was often sunlight, perhaps concentrated using a lens. Today we think of solar power as being safe and efficient – however, explosions appear to have been commonplace when sealed tubes of reactants were left in sunlight for long periods.^[9]

4. The Twentieth Century CE

The first decade of the 20th Century CE is relatively thin in terms of Swiss contributions to photochemistry. A number of

researchers published manuscripts dealing with aspects of photochemistry, although research groups with primary interests in photochemistry were only established in Zurich and Neuchâtel. The development of photochemical research in Switzerland is characterized by the involvement of scientists who are better known for their other activities!

4.1 Starting in the West

Aleksei Nikolayevich Bach (1857–1946) had broad interests in redox enzymes and peroxy compounds and in the early part of the 20th Century CE published from a private laboratory in Geneva and subsequently Moscow. He had links with the University of Geneva through collaborations with Robert Hippolyte Chodat, the director of the botanical institute. As part of a broader study on the photochemical reduction of carbon dioxide, Bach reported that solutions of uranyl acetate were stable in sunlight but when CO₂ was passed through the solution they became turbid.^[26]

Frédéric Reverdin (1849–1931) was also active in Geneva, originally in a private laboratory but from 1907 at the University School of Chemistry. He published extensively on dyestuffs and the chemistry of aromatic amines. He published a single paper specifically on photochemistry, in which he described the conversion of a nitroamine to an amine by the action of sunlight (from “24th September to 16th November 1912”) (Fig. 4).^[27]

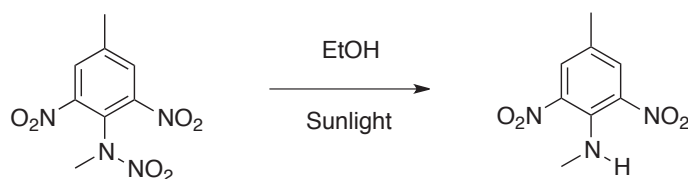


Fig. 4 The photoreaction discovered by Reverdin after seven weeks in sunlight.

Moving Eastwards, we come to Lausanne where Jean Jules Amann (1859–1939), a pharmacist who ran a private analytical laboratory and also taught microscopy in the pharmacy department of the university, reported ultramicroscope studies of photochemical reactions of colloids formed from iron(III) salts and carboxylic acids as well as of various photoreactions of sulfur and sulfur compounds.^[28] Another early contribution from the University of Lausanne describes the photoreaction of yellow arsenic with sulfur in CS₂ solution.^[29]

Continuing our journey, we reach Neuchâtel, where one of the early research schools involving photochemistry was established by Alfred Berthoud (1874–1939) at the University. Berthoud was consecutively professor of physical chemistry (1908–1925) and inorganic chemistry (1925–1939). His research output was impressive, primarily being concerned with the photochemical reactions of halogens and halogen compounds^[30] and his book on photochemistry provided a masterly summary of the state-of-the-art in 1928.^[31]

4.2 The View from Lugano and Athens

A series of papers on the photochemical properties of metal compounds was published by Carl Renz in the period 1919–1920. Originally the work was performed in his private laboratories in Lugano and Athens and subsequently he was associated with the ETH.^[32] As ever, Carl Renz was not known primarily as a photochemist, or even a chemist, but was a highly respected geologist holding a chair at the University of Breslau. Nevertheless, the publications describe some extremely interesting photoreactions of main group compounds and also the use of metal oxides as photosensitisers.

4.3 Meanwhile in Basel

Werner Kuhn (1899–1963) is best remembered for his pioneering contributions to the understanding of polymer solutions. Kuhn was Swiss, studied chemical engineering at the ETH followed by a doctorate in physical chemistry from the University of Zurich, and then held positions in Copenhagen, Heidelberg, Karlsruhe and Kiel before accepting the chair of physical chemistry at the University of Basel in 1939. In his period in Heidelberg, Kuhn demonstrated for the first time that in photochemical reactions of solutions of racemates using circularly polarized light for the irradiation, one of the two enantiomers reacted faster leading to modest enrichment of the slower reacting species.^[33] A few years after these publications, Remy Cantieni from the University of Basel described the UV photolysis of solutions of biomolecules including amino acids, glucose and fructose^[34] following studies in his doctoral thesis submitted in 1932.

4.4 Pioneering Photons in Zurich

Eugen Bamberger (1857–1932) was professor at the ETH between 1893 and 1905 and continued to work in a private laboratory after this period. In 1910, a report from Eugen Bamberger (1857–1932) and Franz Elger at the ETH described a reinvestigation of the photochemical conversion of 2-nitrobenzaldehyde in ethanol to ethyl 2-nitrosobenzoate, previously reported by Ciamician and Silber, and also the analogous photoconversion of 2-nitrobenzyl alcohol in ethanol to 2-nitrosobenzaldehyde (Fig 5).^[35] These appear to be the only formal photochemical studies in his extensive scientific output.

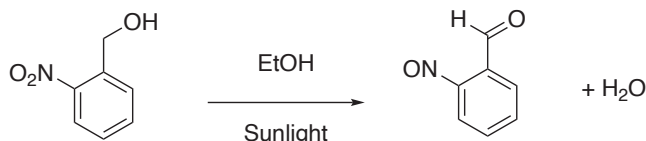


Fig. 5 The photoconversion of 2-nitrobenzyl alcohol in ethanol to 2-nitrosobenzaldehyde.

Emil Baur (1873–1944) was professor of physical chemistry at the ETH from 1911 to 1942 and is best remembered today for his work on fuel cells. However, in the first volume of *Helvetica Chimica Acta*, he published a paper entitled ‘*Photolyse und Elektrolyse*’ in which he correlates photophysical and photochemical processes with redox change, starting from classical observations on uranyl salts;^[36] in a series of some 35 papers he subsequently reported photochemical studies of a variety of organic and inorganic compounds, including photosensitization by semiconducting materials and unsuccessful attempts at photoelectrochemical water splitting.^[37]

Karl Meyer (1899–1990) is best known as a biochemist who worked extensively on connective tissue and hyaluronan, but he worked with Richard Kuhn at the ETH 1927–1930 on a Rockefeller Foundation Fellowship studying the sensitized photooxidation of unsaturated compounds using hemes.^[38]

Also from the first volume of *Helvetica Chimica Acta* is a short note on chemiluminescence from J. Lifschitz at the University of Zurich which begins optimistically “Just like the study of light absorption and the chemical effects of light, the study of light emission in chemical reactions promises significant insights into the relationship between radiant and chemical energy and the nature of chemical forces” and subsequently described studies of photochemical reactions involving triphenylmethane dyestuffs.^[39] However, some of the earliest work at the University of Zurich was performed by Oskar Baudisch (1881–1950), who had worked with Perkin in Manchester and subsequently obtained his habilitation in Zurich with Alfred Werner. He was interested in the photochemistry of nitromethane^[40] and published a long series of

papers on the photochemical interconversion of nitrate and nitrite with particular relevance to the transformation of nitrogen compounds in living systems.^[41]

An important development in the 20th Century CE was the establishment of the Department (later Institute) of Physical Chemistry at the University of Zurich under the leadership from 1920–1930 of Victor Henri (1872–1940). Henri is today best remembered for his derivation of what is now known as the Michaelis-Menten equation, but at Zurich he concentrated upon photochemistry and molecular spectroscopy. His major contributions to photochemistry and photophysics in this period include the identification of photochemical chain reactions (in which one quantum of light initiates the reaction of a large number of molecules) and the phenomenon of predissociation, although he also studied the photochemical decomposition of a wide range of biomolecules.^[42] Henri was succeeded by Hans Ritter von Halban (1877–1947) and his broad research portfolio included studying the photoreactivity of 1,1,2,2-tetrabenzoyl ethene. The photochemical theme continued after the second world war, in particular in the group of Hans Schmid (1917–1976).^[43] The legacy of Henri is seen in two publications from Felix Almasy (1900(?)–1984), who was a titular professor of physical chemical biology and describing the photochemistry of phosgene.^[44]

Two publications from K. Zuber at the University of Zurich describe the partial photochemical separation of mercury isotopes, relying on the gas phase reaction $\text{Hg}^* + \text{O}_2 \rightarrow \text{HgO} + \text{O}$.^[45]

It seems appropriate to finish this section with one of Switzerland’s adopted sons, Albert Einstein, who variously held positions at the Universities of Bern and Zurich as well as the ETH. If the Grothuss-Draper law is the ‘first law of photochemistry’, then the second law is certainly the Stark-Einstein law. Einstein’s formulation of his ‘photochemical equivalent law’ which states that in a photochemical reaction, one quantum of active light is absorbed per molecule of absorbing and reacting substance which disappears, was formulated when he was active in Switzerland.^[46]

5. Post-war

Today photochemistry is a healthy and flourishing discipline in Switzerland, as evidenced by the other contributions to this issue. It is interesting to see how our modern photochemistry developed from a disjointed and fragmentary research activity in Switzerland in the first part of the last century. It is interesting to note that the third IUPAC Symposium on Photochemistry was held in Switzerland in 1970 and returned in 1984. The importance of the discipline is seen in the biennial award of the Grammaticakis-Neumann Prize by the Swiss Chemical Society to a scientist under the age of 40 for outstanding accomplishments in the field of experimental or theoretical photochemistry. Finally, I note with pleasure that ICP2021 was held (virtually) this year in Geneva.

Acknowledgements

I apologise in advance for any omissions in the chemical history. The early part of the 20th Century CE is not especially well documented and to identify Swiss contributions to the chemical literature it was necessary to manually check the ‘Bibliographic list of Swiss works in chemistry’, published between 1901 and 1936 by the *Archives des sciences physiques et naturelles* or *Helvetica Chimica Acta*. The efficiency of this search depended on my ability to spot likely titles! I have certainly missed important organic contributions where a photochemical transformation is buried in a synthetic manuscript – mea culpa! There is an English expression regarding needles and haystacks that appears pertinent. I would particularly like to thank the usual suspects at the University Library in Basel for assisting me in locating obscure journals, Susan Grulich and Hermann Wichers in Basel and Heinz Berke in Zurich for assistance with Remy Cantieni and Lifschitz respectively. I also thank Joggi Wirz for assisting with his memories of earlier photochemical studies in Switzerland.

