Under the influence of light

New chromatographic tools for elucidating photodegradation mechanisms

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CHAPTER 0

Prologue

'To develop a complete mind: Study the science of art; Study the art of science. Learn how to see. Realize that everything connects to everything else.' (Leonardo da Vinci)

Throughout history, chemistry and art always went hand in hand. As a painter, one was limited by the resources available. Organic dyes, *i.e.* dyes with structures consisting mainly of carbon and other light elements, used to dye textiles were extracted from natural resources, such as plants (*e.g.* roots, leaves, wood) or animals (insects, mollusks), and inorganic pigments, such as earth pigments and minerals, were available to prepare paint. Pigments were also discovered in a more accidental way. For example when paint maker Diesbach made a red lake pigment of cochineal, a scale insect used for the dye carmine, he accidentally discovered Prussian blue while using a sample of potassium contaminated with iron.

As a painter before the 1820s, you had several choices for pigments ranging in quality and price. While some pigments were derived from rare materials and were very expensive, other ones were cheaper, because of their high abundance. In those days the colorants used were never mass produced. They were created in workshops, studios, and small laboratories. This all changed during the first industrial revolution (mid-18th century to mid-19th century). In this period, the iron-production process grew enormously after charcoal was replaced by cokes. The latter material was also used to fuel stoves and forges. Cokes is made in the coking process, in which coal is heated in the absence of oxygen. This process resulted in three main products, *i.e.* coke, coal tar, and coal gas. The latter was used to heat the furnace, but the coal tar was an unused waste product. Scientists currently know that coal tar, which has a high concentration of polycyclic aromatic hydrocarbons (PAHs), constitutes a great health risk. Although a feared substance in current society, scientists in the 19th century were trying to make something out of this waste.

August Wilhelm von Hoffman was one of these scientists. He discovered a way to convert benzene and xylene obtained from coal tar to their nitro and amine derivatives. The resulting product, aniline, was already known to man, but it was only prepared from the dye indigotin, which was retrieved from different types of indigo plants. Because aniline was known to be one of the building blocks of indigotin, it was then used as a starting material to produce more-useful products.

One of Von Hoffmans students, William Henry Perkin, was trying to synthesize quinine, which was used as a medicine to treat malaria. While these attempts failed, Perkin discovered a purple colorant, later identified as the first synthetic (*i.e.* man-made) organic dye. Although Perkin at 18-years old may have been just in the right place at the right time, he made history with one of the great examples of serendipity in science by showing persistence after obtaining the disappointing result. He later perfected the synthesis route of mauveine to obtain a patent in 1856. He then decided to market his discovery, offering a cheaper and better alternative to the purple dyes extracted from natural sources, which were less bright than mauveine.

Within 5 years, 'mauve' was a fashion trend, both in France and in England, especially after its display at the 1862 International Exhibition. Perkin eventually made a fortune with its production and started the 'race on dyes'. Scientists tried to make other colorants from aniline, creating a new class of aniline-dyes, of which we can still see the influence in companies such as BASF (Badische Aniline- & Soda Fabrik) and Bayer. Some of the colorants discussed in this thesis, such as crystal violet and fuchsin, were synthetized shortly after the discovery of mauveine and are still used today in many fields.

Perkin's invention started a revolution in organic chemistry and started a whole new industry that produced a rainbow of colours, but also fertilizers, explosives, and plastics, and so on. Eventually, the lightfastness and the production-yield of mauveine were lower than that of newly produced colorants. As a result, the production of mauveine could not keep up with the demand. Later, it was also found to be carcinogenic, which makes another science-history story.

What I love about this story is that we, as chemists, often do not realize how variable our field is. Only in the 19th century, scientists started to mass produce chemicals and to slowly understand molecular structures. Many of the compounds we study contain more information than only their molecular structure or lightfastness. An example may be how these components were used and how they were synthesized. I believe it is important to know the history of our chemical world to put our research in a broader perspective. After all, without Perkin (and his supervisor!), mauveine would have been just a (group of) undiscovered molecules that faded when exposed to light.