



# Impact of medium and ambient environment on the photodegradation of carmine in solution and paints



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## ABSTRACT

The fundamental chemistry underlying the photo-induced degradation of cochineal (carmine), a red dye extracted from South American scale insects and used as an artist colorant, and its stability in solution and as a lake pigment in different paint media exposed to light in various ambient environments is examined. The influence of oxygen on the photodegradation was examined for dye solutions and for solid paint samples containing the lake pigment, and the effect of ambient humidity was assessed for the paint samples. The degradation was followed using absorbance spectroscopy, and characterized using IR and LC-MS. Results indicate lower reaction rates of the carminic acid chromophore in solution and in oil paints during light exposure in anoxic conditions; whereas watercolor paints demonstrated a stronger dependence of the rates on the ambient humidity. A ring opening of the anthraquinone core is suggested in the breakdown of the dye and pigment. This study illustrates that solution phase systems may serve as simple models to assess the kinetics and mechanism of photochemical breakdown of organic-based pigments in solid samples.

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## 1. Introduction

Fundamental photochemical studies can provide significant insight into the aging of cultural artifacts and provide potential means to best conserve items [1]. Photodegradation of pigments may be dependent upon properties of a paint medium or the ambient environment, such as paint additives, the atmosphere, or the pH. For example, environmental exposure to acidic gases, such as nitric oxide, or oxygen may induce the chemical breakdown of pigments or dyes [2–7]. Understanding how the environment impacts the photostability of a dye in solution may help to inform techniques used to preserve the artifact.

This study focuses upon the UV-induced degradation of carmine or cochineal lake pigment, and carminic acid, Fig. 1, the constituent organic molecule that contains the chromophore structure. Carmine or cochineal lake is a naturally derived pigment with a metal, typically aluminum, complexed to two carminic acid molecules at their central carbonyl and adjacent hydroxyl positions [8]. Carmine lake pigment is naturally derived from the aqueous extracts of a scale insect harvested primarily in Central America.

Depending upon the preparation and metal used to complex the dye, the resulting pigment can take on a scarlet red or purple hue [9]. The pigment is found in artifacts from the Aztec and Incan civilizations, and the dyestuff was brought to Europe for use in textiles and paints following the Spanish exploration of the Americas [10]. This natural dye has been found to be comparably stable to other natural red dyes, but not as stable as modern synthetic alternatives. The light instability of carmine lake, particularly in watercolors, has led to its replacement by other pigments in art works intended for permanent display [11,12]. Another primary use of the dye currently is in the food and cosmetic industries, as a natural source of red color [13].

Studies of the impact of anoxic conditions on the photodegradation of carmine lake have shown conflicting results. A study of the stability of the dry pigment, monitored using vibrational spectroscopy, indicated enhanced photodegradation under anoxic conditions [14]. In contrast, anoxic conditions were found to stabilize or slow the photo-induced degradation of carmine lake in paint samples [6,7,15]. The latter investigation also indicated that the medium plays a role in the lightfastness of the pigment, under anoxic conditions, with the smallest color change observed for the oil color, followed by the watercolor and pure dye on paper [6].

A fundamental study of a series of anthraquinone dyes with varying hydrogen-bonding motifs indicated that hydrogen-

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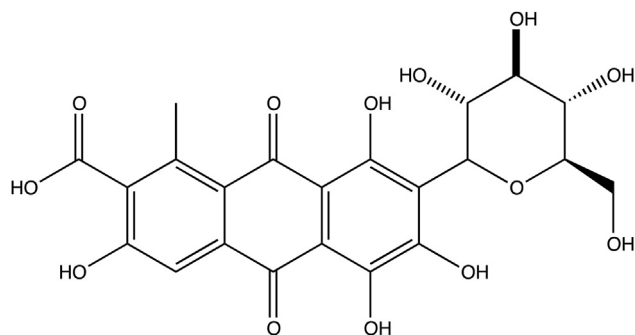


Fig. 1. Structure of carminic acid.

bonding influences photo-stability and the oxidative processes that lead to degradation [16]. Hydrogen-bonding motifs with two intramolecular hydrogen bonds from the central carbonyl moiety to a hydroxyl on the same side ring, such as that found in carminic acid, exhibited greater lightfastness than motifs with only a single intramolecular hydrogen bond or a hydrogen bond to both side rings of the anthraquinone. The latter motifs are found in alizarin and anthrarufin, respectively. Additionally the anthraquinones with hydrogen bonding motifs similar to carminic acid were destabilized by the presence of oxygen or water in the ambient environment, with a greater dependence on the presence of oxygen [16].

The mechanism for the photo-induced chemical breakdown of carminic acid is less well known. Changes in the vibrational spectra suggest that anthraquinones undergo aromatic ring opening and that adsorbed water on the sample can enhance the degradation [14]. Examination of the decolorization mechanism of dyeing effluent by a fungus has provided some insight into the degradation process, showing the fungus degrades the carminic acid via a two-step process of glucose cleavage followed by a ring cleavage reactions [17]. The dependence of the degradation kinetics on pH and oxygen content has been examined in solution, relating to its use in food products, and was fit well to first order-kinetics [18]. Past studies of paint photostability find a linear correlation between oxygen concentration and degradation rate for oil color paints, but a more complex dependence in the case of watercolor or dyes on paper [6]. Additionally, Feller and coworkers carried out some of the initial studies regarding the impact of vehicle and relative humidity (RH) on the lightfastness of organic pigments. The fading rate of carmine lake was tested in coatings prepared with poly(vinylacetate) and cellulose. The rate of fading was directly related to the RH in both coatings, with a greater enhancement of the fading rate in the more hydrophilic (cellulose) coating [19].

Our investigations seek to understand the fundamental chemistry of the photo-induced degradation of carminic acid in solutions, and carmine lake pigment in oil and watercolor paints. For both the solution and solid paints, the impact of oxygen on the degradation was examined; the influence of ambient humidity was assessed only for the solid paint samples. The degradation was followed using absorbance spectroscopy, with spectral changes assigned to the disappearance of the parent compound and appearance of photoproduct(s). Characterization of the samples before and after irradiation by vibrational spectroscopy and mass spectrometry provided a means of evaluating potential decay mechanisms. Understanding the impact of environment on the lightfastness of these model systems can provide further insight into the proper care of cultural objects containing these substances.

## 2. Experimental

### 2.1. Sample preparations

#### 2.1.1. Solution samples

Carminic acid (Sigma Aldrich) was dissolved in deionized water and stored in amber containers. For irradiation studies, samples were  $ca. 1 \times 10^{-4}$  M for kinetic analysis and  $1 \times 10^{-3}$  M for photoproduct analysis.

#### 2.1.2. Paint samples

All paint samples were prepared using Carmine Naccarat (Kremer), and the paints were studied as films applied to clean quartz slides for irradiation. The fluid paints were drawn down in a thin strip using a razor blade, with the thickness established by strips of Scotch® magic tape (0.0625 mm). The concentration of the pigment in the paints was adjusted so the paint films were transparent, and the absorbance in the range of 500–600 nm, measured by UV–VIS spectroscopy, did not exceed 1. For the oil paints the pigment was ground into stand oil (a thickened linseed oil purchased from Utrecht) and the applied films were dried in an oven for at least 40 h at 60 °C. The watercolor paints were prepared using gum Arabic (Winsor & Newton Watercolor Medium Gum Arabic Solution) and a few drops of ox gall as a wetting agent for the pigment dispersion. Samples of only the pure medium, stand oil or gum Arabic, were prepared as dried films on quartz plates by the same method as for the paint samples, as controls.

### 2.2. Irradiation

#### 2.2.1. Solution phase irradiation

Sealed cuvettes (Starna Cell fluorimeter quartz cuvette with septum top, 3-Q-10-GL14-S) containing the carminic acid solution were irradiated and monitored throughout the irradiation using absorbance spectroscopy. For anoxic conditions the solution was bubbled with dry nitrogen, in the sealed cuvette, for at least 5 min. Absorbance spectra were recorded on a Cary 50 UV–VIS from 200 to 800 nm at a speed of 600 nm/min and baselined to water. Irradiation was carried out using a Rayonet mini-reactor, RMR-600, equipped with a merry-go-round sample holder, a cooling fan (run temp  $ca. 28$  °C), and 8 UV light bulbs, UVA at 350 nm or UVB at 300 nm. The fluence of the light chamber was measured at each experimental time point up to 24 h. Four trials were carried out for each type of light. Linear regression of the data based upon integrated rate laws was carried out in MS Excel to determine the rate constants and the integer-order that best fit the degradation based upon the R-squared values.

#### 2.2.2. Solid phase irradiation

Three dried paint films and a blank of the unpigmented medium were tested under each condition in a given trial. Three ambient conditions were tested: air, dry nitrogen, or dry air (low RH). The air samples were in a container open to the outside atmosphere. For the dry conditions a sealed container with a UV-transparent Teflon film cover and fittings for connection to a gas flow, was purged with the respective gas for a period of at least 5 min prior to sealing. The samples were exposed in a light chamber in a controlled environment room at 23 °C and 50% RH. The light chambers were equipped with 8 UVA or UVB fluorescent lamps (Qlab UVA-340 or UVB-313 EL) and a fan. Samples were removed and their absorbance spectra were recorded periodically throughout the irradiation. The dry air and nitrogen sample containers were purged with the respective gas before sealing and returning to the light chamber. The light fluence was monitored in the chamber throughout the exposures. Absorbance spectra were recorded on a Perkin Elmer

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