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The Absorption Spectrum of Malachite Green Leucocyanide and the Mechanism of the Dark Reaction after Photolysis

BY LOUIS HARRIS, JOSEPH KAMINSKY AND ROGER G. SIMARD

Colorless alcoholic solutions of the leucocyanides of triphenylmethane dyes have been found[1] to become deeply colored when illuminated with ultraviolet light. The photolysis of crystal violet leucocyanide has been studied and its use suggested as an actinometer for the ultraviolet.[2,3,4] The present investigation deals with malachite green leucocyanide, the photolysis of which is proposed as the basis for a precision actinometer. The use of this actinometer requires a knowledge of the absorption spectra of the leucocyanides and of the products of photolysis. Such data are presented in this paper together with the results of some qualitative experiments which assist in the use of these compounds and indicate the mechanism of the dark reaction, namely, the fading of the color of the compound formed on illumination of the leucocyanide solutions. Hereafter, the colored compound will be designated as the "photo-compound."

I. Preparation of Materials

A. Malachite Green Series

1. The leucocyanide (*p,p'*-di-dimethylaminotriphenylacetonitrile) was prepared by two methods,[5,6] the original material being the oxalate. In each case the resultant products were recrystallized five times from an ethyl alcohol–benzene mixture, in the dark, and finally were washed with *n*-hexane. The Hantzsch method yielded the product less contaminated with potassium cyanide; it was purified further by a series of continuous extractions with cold ethyl alcohol (95%) for a period of ten weeks, fresh solvent being used every seven days. The m. p., taken with a thermometer calibrated against a platinum resistance thermometer, was 173.7 to 174.5° (corr.). An alcoholic solution showed less than 10^{-8} g. mole per liter of dye. A semi-micro analysis gave the results: C, 81.29; H, 7.02, 7.04; N, 11.68, 12.08; calculated, C, 81.08; H, 7.10; N, 11.83.[7]

2. The carbinol (or base) was prepared according to previous[8] directions, slightly modified, using sodium hydroxide and substituting *n*-heptane for ligroin. The melting point on crystallization from ether was found to be 109.0–109.5°; from *n*-heptane, 119.5–120°.

3. The chloride (dye) was prepared only in alcoholic solution by adding a slight excess (1.8×10^{-2} to 3.6×10^{-4} *N*) of hydrochloric acid to the carbinol.

4. The photo-compound was formed by illumination of the leucocyanide solution with ultraviolet light sufficient to produce a maximum coloration when viewed in a visual colorimeter.

B. Crystal Violet Series

1. The leucocyanide was prepared by the Hantzsch method.[6] The m. p. was 294.0–295.6° (corr.); coloration began at 290° and decomposition occurred on melting.[9] A solution of the leucocyanide showed less than 10^{-8} g. mole per liter of dye.

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[1] Lifschitz, *Ber.*, **52**, 1919 (1919); **61**, 1463 (1928).

[2] Weyde, Frankenburger and Zimmermann, *Naturwissenschaften*, **18**, 206 (1930).

[3] Weyde and Frankenburger, *Trans. Faraday Soc.*, **27**, 561 (1931).

[4] Weyde, Frankenburger and Zimmermann, *Z. physik. Chem.*, **17B**, 276 (1932).

[5] Lifschitz and Joffé, *ibid.*, **97**, 426 (1921).

[6] Hantzsch and Osswald, *Ber.*, **33**, 307 (1900).

[7] We are indebted to Mr. R. T. Armstrong for the nitrogen determination.

[8] Villiger and Kopetschni, *Ber.*, **45**, 2916 (1912).

[9] Staudinger and Stockmann, *ibid.*, **42**, 3494 (1909).

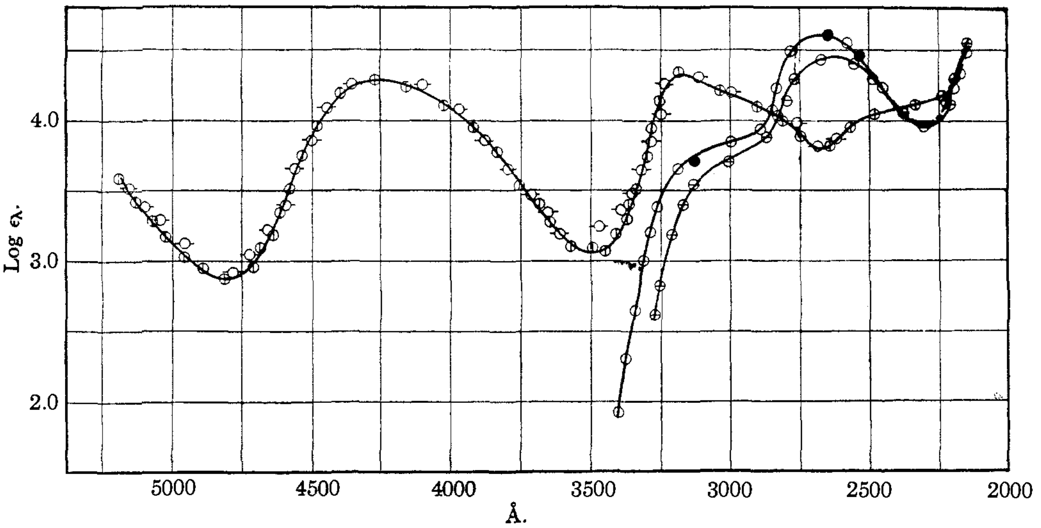

Fig. 1.—Plot of logarithm of absorption coefficients of malachite green series *vs.* wave length: -O-, photo-compound; ⦶, chloride; ⊖, carbinol; O, leucocyanide; ●, leucocyanide (thermopile). Alcoholic (95%) solutions.

2. The carbinol was prepared in the same manner as the malachite green carbinol (solvent being benzene). The m. p. was 205–207°; coloration began at 190° and decomposition occurred on melting.[10]

3. The chloride (dye) was prepared by repeated solution of a sample of biological stain in ethyl alcohol, followed by precipitation with ether. Its purity was checked against the carbinol.

4. The photo-compound was prepared in the same manner as above.

Alcohol.—Grain alcohol (95%) was used without purification. The absolute alcohol was prepared according to the directions of one of the authors.[11]

Measurement of Absorption Spectra

The measurements were made with a Hilger E 315 quartz spectrograph and a Spekker photometer, using Eastman 33 plates. The cell lengths varied from 2.03 to 60.0 mm. The alcoholic (95%) solutions of the leucocyanides were renewed every twenty seconds during the measurements, to reduce the absorption by the photo-compound. The measurements of the carbinol and leucocyanide of malachite green and the crystal violet leucocyanide for wave lengths greater than 3000 Å. were repeated using a glass filter for the same purpose. Both sets of measurements were in good agreement. Transmission measurements were made at three wave lengths using monochromatic light with a thermopile–galvanometer system. The results are presented in Figs. 1 and 2.

Discussion of Transmission Measurements.—The measurements with thermopile are in good agreement with the spectrographic measurements. The absorption spectra[12] of the colored compounds formed upon illumination of the leucocyanides are the same in the visible and ultraviolet as those of the respective colored dyes. Similar results have been reported for the crystal violet series.[3,13]

The spectrographic measurements in the visible show that the colorimetric analysis for the photo-compound is dependable. The addition of hydrochloric acid to malachite green leucocyanide solutions caused a slight broadening of the absorption bands and increased the value of ϵ_λ slightly; similar treatment of the chloride produced no observable change in the visible.

In the crystal violet series our data for the chloride are in agreement with those reported.[3] We found that the addition of hydrochloric acid to the chloride produced a slight change in the absorption at 3130 Å. accompanied by a very noticeable change in the visible. Our ϵ_λ values for the leucocyanide are lower than those reported.[3] Sufficient illumination converted a leucocyanide solution of known concentration quantitatively into the photo-compound, as determined by colorimetric analysis. Our results seem to indicate that the ϵ_λ values reported for crystal

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(10) Noelting and Saas, *Ber.*, **46**, 954 (1913); Kovache, *Ann. chim.*, [9] **10**, 247 (1918).

(11) Harris, THIS JOURNAL, **55**, 1940 (1933).

(12) ϵ_λ, the molal absorption coefficient is calculated from the relation $I/I_0 = 10^{-\epsilon_\lambda cl}$, where c is the concentration in moles per liter and l is the length in cm.

(13) A. Hantzsch, *Ber.*, **52**, 509 (1919).

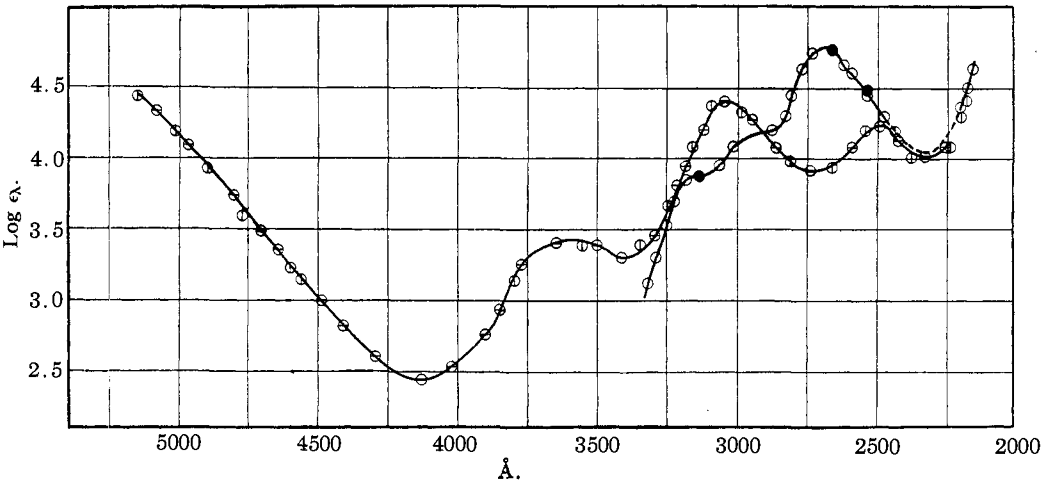


Fig. 2.—Plot of logarithm of absorption coefficients of crystal violet series *vs.* wave length: ⦶, photo-compound; ⊖, chloride; ○, leucocyanide; ●, leucocyanide (thermopile). Alcoholic (95%) solutions.

violet leucocyanide[3] are in error and hence the depth of solution necessary for 99% absorption of light is considerably greater than indicated there.

Mechanism of the Dark Reaction Following the Photolysis

Lifschitz and Joffé[5] proposed a mechanism for the dark reaction (fading) of the illuminated leucocyanides (photo-compound), which has been accepted[3,4] for crystal violet leucocyanide. We found that the mechanism suggested was inadequate for malachite green leucocyanide. On the basis of a series of conductivity measurements of the photolyzed and unphotolyzed solutions Lifschitz and Joffé represented this reaction as

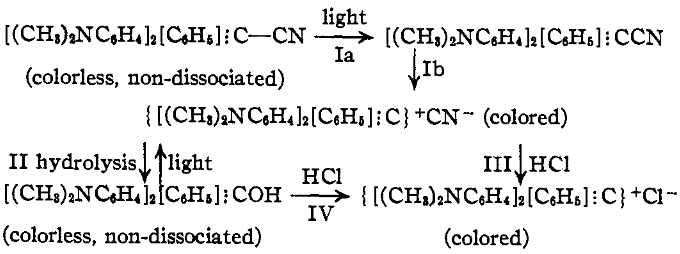
$$\underset{\text{(colorless, non-dissociated)}}{[(CH_3)_2NC_6H_4]_2[C_6H_5]\vdots C{-}CN} \underset{\text{dark}}{\overset{\text{light}}{\rightleftarrows}} C\vdots[(CH_3)_2NC_6H_4]_2[C_6H_5]CN \underset{\text{dark}}{\rightleftarrows} \underset{\text{(colored, dissociated)}}{\{C\vdots[(CH_3)_2NC_6H_4]_2[C_6H_5]\}^+CN^-}$$

They assumed that solvolysis of the colored compound was of secondary importance.

With a colorimeter, we observed the rate of fading of the malachite green leucocyanide photocompound, in absolute ethyl alcohol (99.9%), in grain alcohol (95%) and in photolyzed solutions in alcohol (95%) to which known quantities of potassium cyanide, potassium hydroxide and hydrochloric acid had been added immediately before or after the photolysis.

We obtained about the same rate of fading in absolute alcohol as reported.[5] We found that the addition of water to the 95% alcohol solutions increased the rate of fading. Potassium hydroxide and potassium cyanide each accelerated the fading similarly. The reillumination of a partially-decolorized photolyzed solution regenerated the photo-compound. No resultant dark reaction was observed if the hydrochloric acid was added before or after the photolysis. The addition of hydrochloric acid to partially decolorized photolyzed solutions restored the color completely, but only 95–97% restoration was obtained for water content greater than 20%. No coloration appeared if hydrochloric acid was added to an unexposed leucocyanide solution. This indicates that the product of the dark reaction in ethyl alcohol (95%) is not the original leucocyanide and therefore the above mechanism is not applicable here.

The following mechanism is offered for the photolysis of malachite green leucocyanide and for the dark reaction. Primary importance is given to the hydrolysis of the photo-compound.



$$\begin{tikzcd}
\underset{\text{(colorless, non-dissociated)}}{[(CH_3)_2NC_6H_4]_2[C_6H_5]\vdots C{-}CN} \arrow[r, "\text{light}", "\text{Ia}"'] & {[(CH_3)_2NC_6H_4]_2[C_6H_5]\vdots CCN} \arrow[d, "\text{Ib}"] \\
& \{[(CH_3)_2NC_6H_4]_2[C_6H_5]\vdots C\}^+CN^-\ \text{(colored)} \arrow[dl, shift right, "\text{II hydrolysis}"'] \arrow[d, "\text{III}"', "\text{HCl}"] \\
\underset{\text{(colorless, non-dissociated)}}{[(CH_3)_2NC_6H_4]_2[C_6H_5]\vdots COH} \arrow[ur, shift right, "\text{light}"'] \arrow[r, "\text{HCl}", "\text{IV}"'] & \underset{\text{(colored)}}{\{[(CH_3)_2NC_6H_4]_2[C_6H_5]\vdots C\}^+Cl^-}
\end{tikzcd}$$

The final product of the dark reaction in the absence of hydrochloric acid is assumed to be the colorless carbinol, not the original leucocyanide.

The effects of HCl, H_2O, KCN and KOH are at once evident on this scheme. The fact that the colored product is regenerated upon reillumination of partially decolorized solution is understandable when it is realized that the carbinol now undergoes photolysis reproducing the colored compound. We assume that Reaction I is instantaneous. (We have no evidence of an intermediate compound formed in Reaction Ia.) Reaction III may be slow or moderate, while IV is known to be comparatively slow from measurements with the pure carbinol. Reactions II plus IV were found to be fast compared to the time of measurement if hydrochloric acid was used during the photolysis. The dark reaction had a positive temperature coefficient.

Stability of Solutions

Neutral alcoholic (95%) solutions of malachite green oxalate and crystal violet chloride faded when stored in glass bottles. The former faded much more rapidly than the latter. Reliable color standards were obtained by addition of hydrochloric acid (in slight excess) to solutions of malachite green carbinol and crystal violet chloride. The mechanism proposed above affords a satisfactory explanation of the fading.

Solubilities

The solubility of the purified leucocyanide in ethyl alcohol (95%) was determined at several temperatures using precautions to approach equilibrium from over- and under-saturation. The rate of solution was slow. The solubility at 24.5° was 3.1×10^{-3} g. mole per liter. The concentration of the solution after saturation at 24.5° and after standing for five days at 0° in contact with the solid was 1.6×10^{-3} g. mole per liter. The concentration of leucocyanide in an absolute alcohol solution, originally 1×10^{-3} g. mole per liter, was 8.6×10^{-4} after remaining five days at $-78°$ in contact with solid. (The solubility of crystal violet leucocyanide in ethyl alcohol (95%) at 24.5° was found to be 9.3×10^{-5} g. mole per liter, about 50% greater solubility than reported.[4])

Summary

The absorption spectra of the malachite green and crystal violet series have been presented and discussed. A study was made of the fading of the compound formed by photolysis of the leucocyanides, and of salts of malachite green. On the basis of these experiments a new mechanism for the "dark reaction" is proposed, in which the hydrolysis of the photo-compound is given the primary importance.

The solubility of malachite green leucocyanide was found to be about thirty times as large as that of crystal violet leucocyanide, a property indicating its preference for use in actinometry.

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A Precision Actinometer for the Ultraviolet Region (Including an Exact Test of the Einstein Equivalence Law)

BY LOUIS HARRIS AND JOSEPH KAMINSKY

The coloration produced on illumination of alcoholic solutions of crystal violet leucocyanide by ultraviolet light has been proposed[1,2] as the basis of quantitative measurements of ultraviolet energy. We[3] have found that malachite green leucocyanide possesses some important advantages over crystal violet leucocyanide for use in actinometry. Our results indicate that an alcoholic solution of malachite green leucocyanide is admirably suited for a precision actinometer for the spectral region between 3340 and 2480 Å. The fact that malachite green leucocyanide is thirty times[3] more soluble than crystal violet leucocyanide (at 25°) permits a shorter cell length to be used and a certainty of 99.9% absorption. Furthermore, the correction for inner filtration by the photo-compound of the former is less than that by the photo-compound of the latter. The colorimetric measurements can be made more accurately for the green dye. Standard solutions

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[1] Weyde, Frankenburger and Zimmermann, *Naturwissenschaften*, **18**, 206 (1930).

[2] Weyde and Frankenburger, *Trans. Faraday Soc.*, **28**, 561 (1931).

[3] Harris, Kaminsky and Simard, THIS JOURNAL, **57**, 1151 (1935).