[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF COLORADO]

Studies on the Reactions of the Leucocyanides of the Triphenylmethane Dyes. I. The Mechanism of the Dark Reaction Following the Photolysis of Malachite Green Leucocyanide

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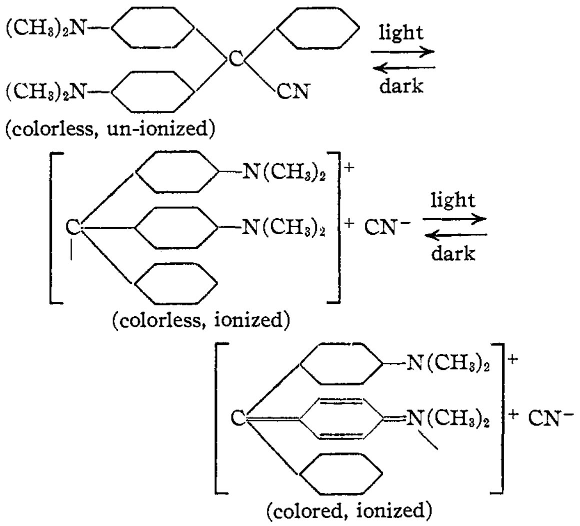
An alcoholic solution of malachite green leucocyanide has been shown to become deeply colored when exposed to ultraviolet light. This solution again becomes colorless when placed in the dark. Two mechanisms have been proposed for this "dark reaction." Lifschitz and his co-workers[1] proposed the following equation for the photolysis and dark reaction of malachite green leucocyanide in absolute alcohol



The final product of the dark reaction was assumed to be the original leucocyanide.

Harris, Kaminsky and Simard[2] found that photolyzed and subsequently partially faded solutions of malachite green leucocyanide in alcohol containing some water recovered their color when treated with dilute hydrochloric acid. Leucocyanide solutions which had not been irradiated did not become colored when treated with the acid. They therefore suggested that the final product of the dark reaction may be the corresponding leucocarbinol, the hydroxyl ion being obtained from the water. This carbinol could be transformed into colored malachite green chloride when treated with hydrochloric acid. If exposed to ultraviolet light, this leucocarbinol would produce the colored ion of malachite green just as does the leucocyanide.

Villiger and Kopetschni[3] had at an earlier time reported that the acid always present in ordinary ethyl alcohol can quantitatively cause the removal of the ammonia from malachite green leucoamine upon warming. The end-product suggested for this reaction was $Ar_3C{\cdot}OC_2H_5$. Neutralization of the alcohol with sodium hydroxide prevented the reaction.

The purpose of the present investigation was to check these proposals of Harris, Kaminsky and Simard and of Villiger and Kopetschni by means of absorption studies of the photolyzed and then faded alcoholic solutions of malachite green leucocyanide which had been neutralized before irradiation. If the leucocarbinol were the end-product of the dark reaction, the absorption curve should shift from that of the pure leucocyanide to that of the leucocarbinol, in going from the photolyzed to the faded solutions, the amount of shift depending upon the time of irradiation.[4] Such results were not obtained.

Experimental

Preparation of Materials.—The malachite green leucocyanide was prepared from the oxalate by the Hantzsch[5] method and was purified as suggested by Harris, Kaminsky and Simard.[2] However, only five week-long extractions with ethyl alcohol were performed. The melting point of the purified crystals was found to be 174.6–175.8°. The measurements were made with a thermometer calibrated against a Bureau of Standards standard thermometer. In contrast to this Harris, *et al.*, state that they carried on extractions for ten weeks and obtained a melting point of 173.7–174.5°.

The "95%" ethyl alcohol used was the standard laboratory grade of grain alcohol. Density measurements showed the actual percentage of alcohol in the solution to be 92.6 to 92.8%. This alcohol was found to be definitely acidic. It was determined that 1 ml. of sodium hydroxide solution in "95%" alcohol of approximately 0.004 molarity was required to neutralize 50 ml. of the stock alcohol to the neutral tint of brom thymol blue. All the alcohol used in this experiment was neutralized in this manner except the absolute alcohol and the alcohol used in the purification of the leucocyanide.

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[1] Lifschitz, *Ber.*, **52**, 1919 (1919); **58**, 2434 (1925); **61**, 1463 (1928); *Z. physik. Chem.*, **97**, 426 (1921).

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

[3] Villiger and Kopetschni, *Ber.*, **45**, 2910 (1912).

[4] Darmois, *Compt. rend.*, **197**, 1120 (1933).

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

Procedure.—A Hilger E-3 quartz spectrograph with rotating sector was used for all spectrographic measurements. The light source was an under-water arc with tungsten electrodes. Wratten and Wainright Panchromatic plates were used for the photographs. A spectrum extending to a wave length of 2500 Å. was obtained with accurate comparisons possible to about 2700 Å. Absorption tubes one centimeter long were used throughout the experiment. The solution in the absorption tube was never allowed to be exposed to the light of the arc for more than twenty seconds, in order to avoid absorption due to the photocompound.

Fresh solutions of the leucocyanide in the neutralized 92.7% alcohol of 5×10^{-4}, 1×10^{-4}, 5×10^{-5} and 1×10^{-5} molarity were prepared in the dark and absorption spectra obtained. The absorption curve checked closely with that given by Harris, Kaminsky and Simard, which for comparison purposes has been reproduced in Fig. 1.

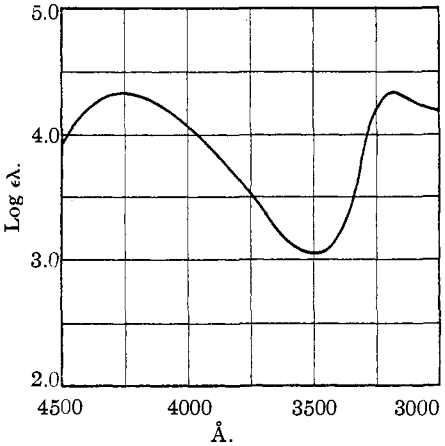

Fig. 1.—Section of curve of Harris, Kaminsky and Simard for photo-compound and chloride.

For the studies of the absorption spectra of the photocompound, the following solutions were used: (A) 5×10^{-5} *M* leucocyanide in 92.7% neutralized ethyl alcohol; (B) 5×10^{-5} *M* leucocyanide in 99.2% unneutralized ethyl alcohol; (C) 5×10^{-5} *M* leucocyanide in 84.6% ethyl alcohol (prepared by addition of water to 92.7% neutralized ethyl alcohol).

Different portions of these three solutions were illuminated for fifteen hours, ten hours, five hours and one hour in quartz flasks. The source of light was a "Bruleur Gallois" mercury vapor lamp (Type HG). After irradiation, the solutions were allowed to fade in the dark room for at least a week. At the end of that time all portions of solutions A and B were absolutely colorless. However, solutions C, even after only one hour of exposure to ultraviolet light, retained some green color after a month in the dark room. Absorption studies of solutions C were therefore not attempted.

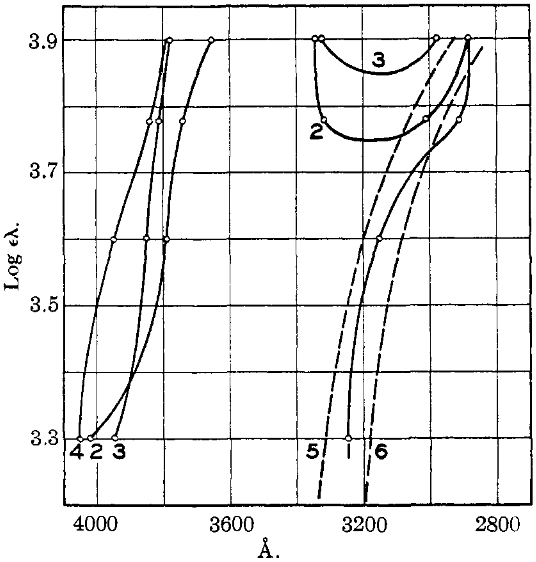

Fig. 2.—Absorption spectra of 0.00005 *M* malachite green leucocyanide in 92.7% ethyl alcohol completely faded after irradiation: curve 1, illuminated for one hour; curve 2, for five hours; curve 3, for ten hours; curve 4, for fifteen hours; curve 5, unilluminated cyanide; curve 6, unilluminated carbinol. Curves 5 and 6 are taken from the work of Harris, Kaminsky and Simard.

Unfortunately, absorption bands for the faded photolyzed solutions were obtained only at low extinction (sector reading) and hence are not as accurate as they might have been. However, the appearance of a new absorption band in the region of 3400 Å. to 3700 Å. was quite evident for the solutions studied. The absorption curves obtained from the faded photolyzed solutions are shown in Figs. 2 and 3. In Fig. 2, we have inserted in curves 5 and 6 the absorption data for the leucocyanide and carbinol as taken from Harris, Kaminsky and Simard. These

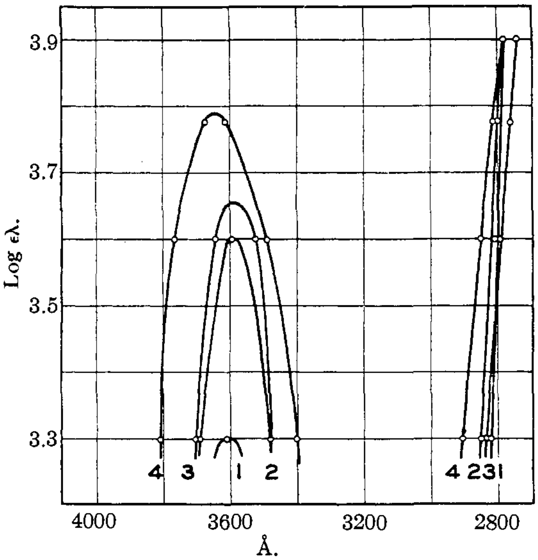

Fig. 3.—Absorption spectra of 0.00005 *M* malachite green leucocyanide in 99.25% ethyl alcohol completely faded after irradiation: curve 1, illuminated for one hour; curve 2, for five hours; curve 3, for ten hours; curve 4, for fifteen hours.

authors made no absorption measurements on the faded solutions, but refer to the colored solution as the photo compound. It will be observed that the maximum log ϵ of the faded solution between 3400 and 3700 Å. as given in Fig. 3 is about 3.8, whereas for the colored product (the photo compound of Harris, Kaminsky and Simard) at 3700 Å. in Fig. 1 it is only 3.5. This discrepancy is probably real and can hardly be accounted for by the lack of accuracy for the faded solutions at low extinction values since in this neighborhood the values are close together, the curves crossing almost at right angles. The inaccuracy of readings at low extinction would be in the horizontal direction (wave length) and not in the vertical direction (log ϵ). A comparison of curves 1 and 5 of Fig. 2 shows that our curve for the 5×10^{-5} M leucocyanide agrees with that of Harris, Kaminsky and Simard to within 50 Å. in all but point log ϵ 3.778 and wave length 2990, even at low extinction values.

When the faded solutions of A were treated with dilute hydrochloric acid they became uniformly dark green. No difference in intensity of color was apparent to the eye. The four solutions of B with similar treatment showed differences in intensities ranging from a very light green for the solution irradiated for one hour to a moderately deep green for the solution irradiated for fifteen hours. The depth of color was in the same order as the time of radiation. The darkest solution was not as heavily colored as the acidified portions of A. The solutions of C became uniformly dark green when acidified.

Discussion

The treatment of the irradiated and faded solutions with hydrochloric acid would seem to indicate that the neutralization of the alcohol used as a solvent had not changed the results previously reported in unneutralized alcohol,[2] except possibly in 84.6% alcohol.

The trend of the absorption curves as well as the results obtained with hydrochloric acid make it seem likely that the proposal of Lifschitz for the dark reaction would still be valid in 100% ethyl alcohol. In the presence of water, however, the end-product could not be the leucocyanide, the leucocarbinol, nor the photo-compound, since all of them show minima in their absorption curves at 3500 Å.

The experiment indicates that the end-product of the dark reaction of the photolysis of malachite green leucocyanide in ethyl alcohol containing some water has the following properties: (a) It is colorless, but has a peak in its absorption curve in the neighborhood of 3600 Å. (b) It is formed more easily as the amount of water in the solution increases, but it is unstable in as much as 15% water. (c) It is not as stable as the leucocyanide, being decomposed by dilute hydrochloric acid or excess water to produce the colored ion of malachite green. (d) When irradiated with ultraviolet light, it produces the colored ion of malachite green. (e) Although derived from the malachite green ion and easily reproducing this same ion, its absorption curve shows it to have a structure essentially different from the leucocyanide and leucocarbinol.

These properties would indicate that the end-product of the dark reaction must be the result of some reaction between the solvent and the malachite green ion. In analogy with the mechanism proposed by Villiger and Kopetschni,[3] this end-product might be the ether form: $Ar_3C{\cdot}OC_2H_5$. However, such a compound would be expected to be more stable than the substance produced here. Further investigation is necessary before the true identity of this end-product is established.

Summary

Absorption studies of photolyzed and subsequently faded solutions of malachite green leucocyanide in alcohol containing some water have shown that the dark reaction does not regenerate the leucocyanide as an end-product. The end-product is also shown not to be the leucocarbinol. The final product of the dark reaction is a colorless, light-sensitive substance with a peak in its absorption curve in the nieghborhood of 3500 Å. This end-product is decomposed by dilute hydrochloric acid to form a green solution similar to that of malachite green salts.

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