[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

Photochemical Reactions of Leuco Dyes in Rigid Solvents. Quantum Efficiency of Photo-oxidation

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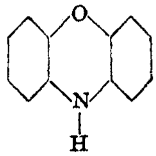
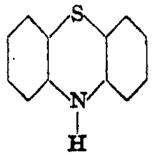
In previous papers[1,2] on photodissociation in rigid solvents, we have not dealt with the large class of leuco dyes such as the triphenylmethane and diphenylamine types. Products obtained by illuminating these substances in rigid solvents will be here discussed.

Oxazine and Thiazine.—These two substances with the formulas may, in accordance with



I
Oxazine



II
Thiazine

previous nomenclature,[3] be designated as the DH forms. Michaelis, Granick and Schubert[4] obtained the absorption spectra of the semiquinone forms of these two substances when they were partially oxidized in strongly acid solutions.[5] These semiquinone forms derived from the parent substance merely by loss of an electron may be represented by the symbol DH$^+$. These authors have been so kind as to give us samples of the two bases actually used in their studies and these we have illuminated with ultraviolet light in EPA (5 ether, 5 isopentane, 2 ethanol by volume)[1] at the temperature of liquid air. The absorption spectra of the resulting colored solutions are shown in Figs. 1 and 2. Curve 1 of each figure shows the absorption of the DH$^+$ form. Michaelis, Granick and Schubert found a single band for oxazine at room temperature at the position marked by an arrow in Fig. 1, while in the case of thiazine they found a series of sharp bands, the one of lowest frequency being at the position marked by the arrow in Fig. 2. It is evident that in spite of the great difference in solvent and in temperature our results are in close agreement with theirs.

Since Michaelis, Granick and Schubert worked in strong acids they could not obtain the other semiquinone form, D, derived from DH$^+$ merely by the loss of a proton. In our solvent, however, we found that the solutions which gave curves 1 of Figs. 1 and 2 changed on standing at a temperature of about 100°K., the DH$^+$ band disappearing and another band increasing. The latter is shown as curve 2 in each figure. We ascribe these bands to the D forms. The case is similar to that of diphenylamine.[1] In addition to the bands shown in Figs. 1 and 2, there is, even immediately after illumination, another band rising rapidly in the violet and also in the case of thiazine faint bands at 15300 and 16500 cm.$^{-1}$. These bands were not

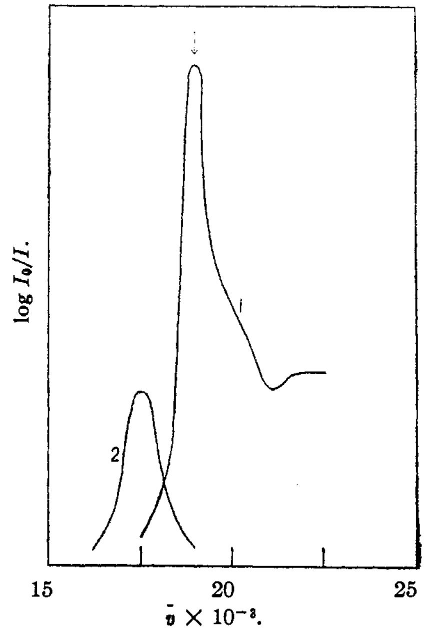


Fig. 1.—Absorption spectrum of illuminated oxazine in EPA at 90°K.: (1) is for the form DH$^+$ and the arrow shows the maximum obtained by Michaelis, Granick and Schubert[4] at room temperature; Curve (2) is for the D form.

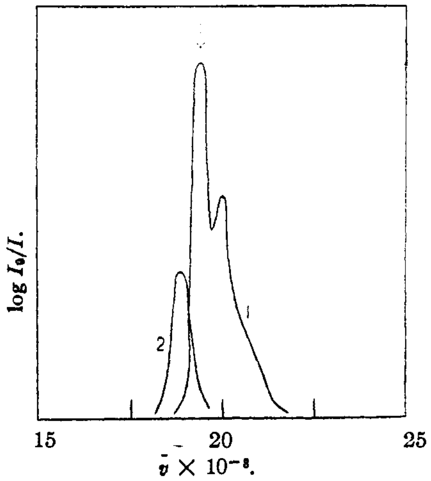


Fig. 2.—Absorption spectrum of illuminated thiazine; same comments as for Fig. 1.

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(1) Lewis and Lipkin, THIS JOURNAL, 64, 2801 (1942).

(2) Lewis and Bigeleisen, *ibid.*, 65, 520 (1943).

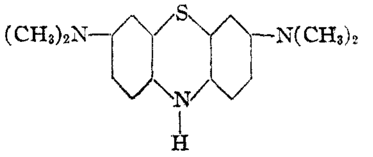
(3) Lewis and Bigeleisen, *ibid.*, 65, 1144 (1943).

(4) Michaelis, Granick and Schubert, *ibid.*, 63, 351 (1941).

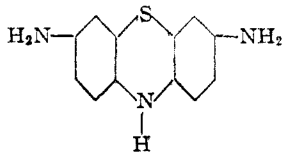
(5) The DH$^+$ form of oxazine is remarkably stable. Oxazine was dissolved in 12 M H_2SO_4 and exposed to air. The semiquinone formed rapidly and, after exposure to air for a year, underwent no appreciable change.

investigated further since we turned our attention at once to the more interesting and more complex phenomena found with the leuco bases of the true dyes.

Methylene Blue, Thionine and Capri Blue.—When we consider the possible products obtainable by the ejection of electrons from leuco methylene blue (III) and leuco thionine (IV)



III



IV

we might expect to get semiquinone and completely oxidized forms. Representing the leuco form by DH (and, in acid solutions, DH_2^+ and DH_3^{++}) we might expect the semiquinone forms D and DH^+ and the totally oxidized forms D^+ and perhaps DH^{++}.

From the work of Epstein, Karush and Rabinowitch[6] and from our own observations[3] we know the absorption spectra of these two completely oxidized forms (and also of DH_2^{+++}). The two semiquinone forms D and DH^+ will not be identical with those obtained by Granick, Michaelis and Schubert[7] for they were working in acid so strong that their semiquinones were of the form DH_3^{+++}, which gave the same spectra as simple thiazine.

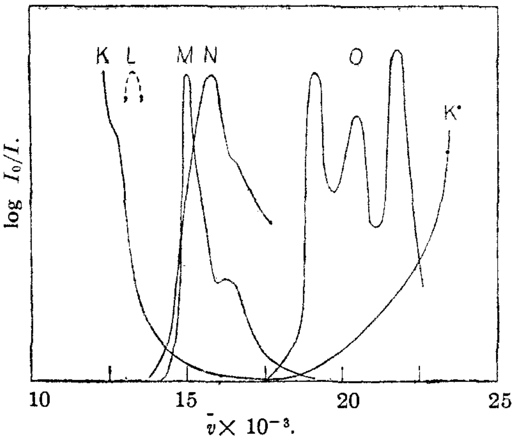


Fig. 3.—Analysis of various spectrograms of illuminated leuco methylene blue. The ordinates are in arbitrary units.

Our first experiments on the illumination of the two leuco bases (DH) in EPA at liquid air temperature gave a more complicated spectrum than was expected. Many further experiments, using different concentrations in a variety of solvents and studying the change in the absorption spectrum on standing at 100°K., were necessary before the whole spectrum could be analyzed. The results of the analysis for leuco methylene blue are given in Fig. 3. Immediately after illumination in EPA the absorption is due almost entirely to the two substances whose bands are designated arbitrarily by the letters K and O. The K substance has a band in the infrared, K, and one in the violet, K′, both of which disappear gradually and together, showing that the two bands belong to the same substance. The O band showing considerable vibrational resolution strongly resembles the DH^+ band for thiazine shown in Fig. 2 but displaced toward the red. We have no hesitation in assigning the O band to the molecule DH^+. The M band is obviously due to D^+, the ion of methylene blue. In fact the curve is identical with the one that we have previously obtained[8] for methylene blue at low temperature in alcohol, extrapolated to infinite dilution. This M band, which may be hardly discernible immediately after illumination, rose prodigiously on standing until, on account of the high extinction coefficient of methylene blue, it dominates the whole spectrogram. Its growth is concomitant with the disappearance of K.

The band marked N is ordinarily obscured by the neighboring bands but fortunately in a solvent consisting of 1 part isopentane and 1 to 3 parts of methylcyclohexane we were able to obtain this band almost alone. In this pure hydrocarbon solvent electrons return far more rapidly[1] to a positive ion than in EPA, thus leaving the uncharged substance N, which we therefore ascribe to the simplest semiquinone form D. The D band lies to the left of the DH^+ band as in the corresponding cases of thiazine and oxazine, but the difference is about 1000 Å. in this case as compared to about 300 Å. for those cases. The corresponding difference between $\lambda_{max.}$ for the ion of diphenylamine and for diphenyl nitrogen[1] is 700 Å.

We looked carefully for the known band of DH^{++}, but there is no evidence of its occurrence. It is presumably so strong an acid that, if formed, it loses a proton at once to the ether or alcohol. We have thus only one of the totally oxidized forms, D^+, and the two semiquinone forms D and DH^+. It remains to account for the K band and also the L band, which was faint in the case of leuco methylene blue, but very prominent in the case of leuco thionine.

Before attempting to identify these bands we may show in Fig. 4 two curves for the actual measured absorption of leuco thionine after illu-

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(6) Epstein, Karush and Rabinowitch, *J. Opt. Soc. Am.*, **31**, 77 (1941).

(7) Granick, Michaelis and Schubert, THIS JOURNAL, **62**, 1802 (1940).

(8) Lewis, Goldschmid, Magel and Bigeleisen, *ibid.*, **65**, 1150 (1943).

mination. The solid curve was obtained immediately after illumination and shows chiefly the K bands and the O, or DH^+, band. There is, however, a trace of the L, M and N bands. The dotted curve shows the absorption of the same sample after standing one hour at about 100°K. The band system at the left, that is, the K band, together with its small subsidiary vibrational band, has largely disappeared. So probably has the O band. But the L, M and N bands have greatly increased. The last, which we identify with the molecular species D, may have been produced partly from DH^+ by the loss of a proton and partly from the substance which gives the K band. On the other hand, from this and similar experiments with methylene blue it is certain that the M band is built up at the expense of the K substance alone.

This is a remarkable phenomenon, for the M band is that of the ordinary ion of the dye, obtained from the leuco dye by two stages of oxidation. We are going to show that in the brief illuminations that we employed it is impossible to assume that the double oxidation is due to the successive action of two photons. Instead, we are forced to the conclusion that a single photon produces the two stage oxidation.

The two substances that give the bands designated as K and L seemed at first very mysterious. The absorption spectra of all of the fully oxidized and semiquinone forms derivable from DH are now known, and none of the absorption bands correspond to these two new ones. A clue was obtained when we found that in all the true leuco dyes the amount of coloration produced by a given amount of absorbed light diminishes rapidly with increasing dilution. This suggests polymerization at low temperature of the parent leuco dye, and we are going to give evidence that in the case of methylene blue the dimer D_2H_2 is responsible for most, if not all, of the photochemical reaction.

When the molecule D_2H_2 is illuminated, a small amount of DH^+ is formed directly or indirectly, but the main substance produced is the one that gives the K band. In forming this substance a two-fold oxidation has occurred, either[9] by the loss of two electrons to form $D_2H_2^{++}$, or by the loss of one electron and one hydrogen atom to form D_2H^+. Since the first of these processes would require very much more energy than the second, and the ion produced would probably lose a proton at once, we shall assign the K band to D_2H^+. This substance on standing might undergo the reactions

$$D_2H^+ + e^- = D_2H \qquad (1)$$

$$D_2H^+ = DH^+ + D \qquad (2)$$

$$D_2H^+ = D + DH \qquad (3)$$

$$D_2H^+ = D_2{}^* + H^+ \qquad (4)$$

$$D_2H^+ = 2D + H^+ \qquad (5)$$

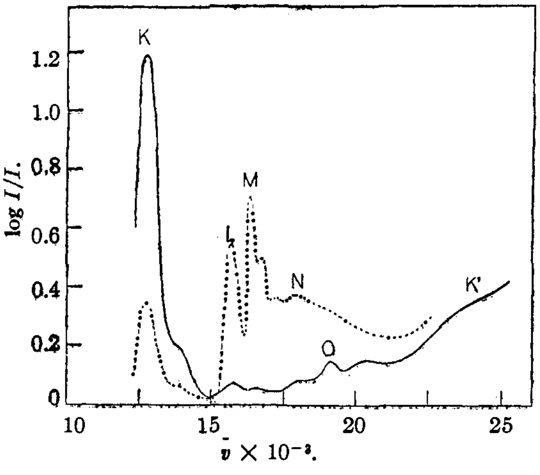

Fig. 4.—Spectrogram of illuminated leuco thionine in EPA at 90°K. The full curve was obtained immediately; the dotted curve after the sample had been warmed for forty-five minutes to about 110°K.

The first of these reactions we are inclined to discard, since, although no quantitative measurements were made, the rate of disappearance of D_2H^+ seems to be more rapid than the return of an electron to an ion that we have found in other cases.

The second reaction we also eliminate since DH^+ does not increase but diminishes with time. All the last three reactions we believe to go concurrently, giving D^+, D and the L substance $D_2{}^*$. The asterisk is used to indicate that the substance is not the ordinary dimer formed by the addition at the nitrogens of two of the odd molecules D. To account for its color it must be assumed to be a peculiar form of dimer, probably a biradical.

In the case of methylene blue in EPA reaction (3) is by far the most prominent, but with thionine reactions (4) and (5) seem to predominate. It will be interesting to study the rates of these reactions in different solvents at different temperatures.

We can say little regarding the absolute extinction coefficients of the various substances formed in these photochemical and follow reactions. From an inspection of all our curves it appears probable that the value of ϵ diminishes in the order D^+, D_2H^+, DH^+, $D_2{}^*$ and D.

The results obtained with leuco capri blue are so nearly identical with those with leuco methylene blue that we do not give a separate figure. The corresponding bands are mostly displaced toward higher frequencies as shown in the following table, which lists the absorption maximum (cm.$^{-1}$), or, in case of several vibration bands, the absorption maximum of lowest frequency, for the various molecular species.

Leuco Malachite Green, Leuco Crystal Violet and Michler's Hydride.—These three substances belonging to the triphenyl and diphenylmethane series appear to give a simpler spectrum on illu-

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[9] Formally we could also write the reaction $D_2H_2 = D_2H^+ + H^-$ but we do not know whether hydride ion would be capable of existence under our conditions.

TABLE I

	D_2H^+	D_2^*	D^+	D	DH^+
Methylene blue	(11500)[a]	13400	14950	15710	19100
Thionine	12740	15710	16330	18000	19100
Capri blue	(11700)[a]	13400	15130	16770	21780

[a] The values in parentheses are estimated, since these maxima fall just outside the reach of our photometer.

mination, but the processes are probably as complex as those found in the preceding group. The amount of color produced by a given amount of light absorbed increases greatly with the concentration and in no case is any great amount of color produced. Once more the concentration effect indicates that a dimer or other polymer exists, and there is always some absorption in the infrared.

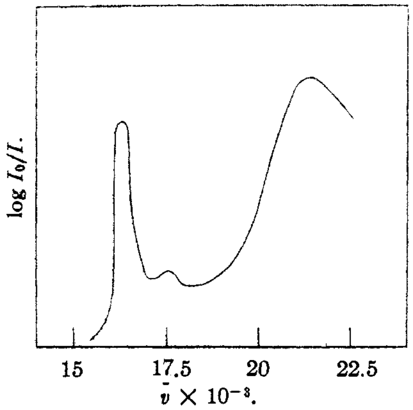

Fig. 5.—Spectrogram in EPA of illuminated Michler's hydride, measured at 90°K.

The prominent bands, however, are those belonging to D^+, D and DH^+, designating the leuco base once more as DH. The absorption spectrum of Michler's hydride after illumination is shown in Fig. 5. The first band at 16330 cm.$^{-1}$ is that of D^+. It coincides entirely with that of Michler's hydrol in acid solution. The second band is that of D and the third that of DH^+. On standing, the last band nearly disappears, the small infrared band (not shown in the figure) also disappears and D^+ and D bands increase in intensity by about 50%. For the products of illumination of these leuco dyes, $\nu_{\max.}$, is given in Table II.[10]

Table II

	D^+	D	DH^+
Leuco crystal violet	16330	17480	21040
Leuco malachite green	15700	17480	20700
Michler's hydride	16330	17480	21400

The Quantum Yield of Photo-oxidation in Rigid Solvents.—In all of our experiments we know qualitatively that during illumination color is produced, rapidly at first and then more slowly until finally further illumination produces very little increase in color. In a thin layer of a dilute solution the limit would be reached when all of the parent substance had been used up. However, under ordinary circumstances an apparent limit to the amount of color is reached when only a part of the parent substance has been affected. In such cases the front face of the reaction cell is strongly colored while the other side appears colorless.

A decrease of quantum efficiency with amount of illumination of the type illustrated in Fig. 6 is the common thing. For even if, as in our present cases, the solvent does not absorb, and even if there are no other substances present except the parent substance and its photochemical product, the former will gradually disappear at the illuminated face and the latter will be built up to form an absorbing screen, the effectiveness of which will depend upon the relative amounts and extinctions of the two substances. However, if the photochemical reaction required the absorption of two successive photons the curve would be quite different, starting at zero illumination with zero slope.

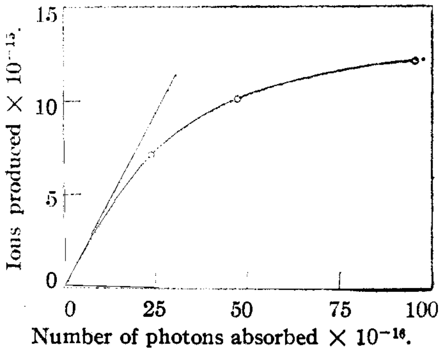

Fig. 6.—Showing the relation, in illumination of leuco methylene blue, between the number of methylene blue ions produced and the number of photons absorbed.

Our preliminary experiments on quantum efficiency were made with the base of Wurster's blue, using a small spectral region centered at 3660 Å., and giving about 10^{17} photons per sq. cm., per minute. Plotting the number of ions produced against the number of entering photons, a curve similar to that of Fig. 6 was obtained. Estimating the slope at the origin as 0.07, this would be the initial quantum yield, except that in this experiment some of the entering light passed through the cell. Estimating the average transparency as 30%, the true initial quantum yield is about 0.10. This is a large yield when we consider the brilliant fluorescence of the parent substance, which indicates that a large fraction of the excited molecules lose their energy by reemission.

Our next experiments were with leuco methylene blue, using the same spectral region as before. The dependence of quantum yield upon amount of illumination is shown in Fig. 6, where the ordinate

[10] Wieland, Popper and Seefried (*Ber.* 55, 1816 (1922)) expressed surprise that the substances believed to be free radicals, obtained by chemical reduction of dyes, have only an orange color. If our D forms are the true radicals, then the substances produced by ordinary reduction are something else—perhaps abnormal dimers of quinoidal character.

is the number of methylene blue ions obtained by illuminating and then allowing the sample to stand at about 100°K until all the K band had disappeared. The abscissa is the number of photons absorbed, which in this case coincides with the number entering the cell. The tangent of the curve at the origin, the initial quantum yield, is about 0.04. Since some of the substance giving the K band goes to other things than D^+, the quantum yield for the production of what we have taken to be D_2H^+ is still higher. It is evident that this high quantum yield and the shape of the curve of Fig. 6 both preclude the possibility of activation by two successive photons. It is therefore certain that the two stage oxidation is produced by a single photon.

Even at the beginning of illumination of leuco methylene blue there is a competition for the photons between the monomer and the associated form. Three concentrations of leuco methylene blue (calculated for the monomer), 9.16×10^{-5}, 4.66×10^{-5} and 1.50×10^{-5} M, were illuminated for the same length of time in a beam of the same intensity. The relative quantum yields were 1.00, 0.74 and 0.38. Assuming that the quantum yield is proportional to the fraction of the light absorbed by the associated form, it could be possible, with an accurate series of such measurements, to determine the concentrations of the two forms and their relative extinction coefficients. Unfortunately, in the present case the cell was not deep enough to absorb all the light, so that with cells of infinite depth the three quantum yields would have been closer together. For this reason and on account of the small number of observations we can make no quantitative calculations. Yet a rough examination shows that the data can hardly be compatible with the existence of any higher polymer than the dimer.

The three leuco bases with central carbons showed no photochemical action at wave lengths longer than about 2700 Å. The quantum yield was not measured but once more increases rapidly with the concentration, showing again that the simple monomer is not the chief reactant.

Experimental

The leuco bases of crystal violet, malachite green and Michler's hydrol employed were commercial samples. The leuco bases of methylene blue, thionine and Capri blue were obtained by reducing the dyes by aqueous sodium hydrosulfite. The water was pumped off on the vacuum line and the solvent EPA distilled in, all in the dark. The concentrations of the solutions were later determined by oxidation and determination of the resulting dye by spectrophotometric methods. The base of Wurster's blue was purified by fractional distillation *in vacuo*.

The spectrophotometer was the one used in previous investigations.[11] In the quantum yield determinations the intensity of the light was determined by the method of Leighton and Forbes.[12] The cell containing uranyl oxalate was placed in the same position and inside the same Dewar used for the illumination at low temperatures. The beam of light was uniform and illuminated only the central portion of the cell. The source of light was the high pressure mercury arc used in preceding investigations.[4]

Summary

When oxazine and thiazine are illuminated in a rigid solvent, each gives two semiquinone forms. The first is produced simply by the ejection of an electron, the second grows from the first on standing, by the loss of a proton. When the leuco bases of methylene blue, thionine and Capri blue are similarly illuminated, very complex spectrograms are obtained. By using different solvents and by observations of the changes on standing, it has been possible to analyze the spectra and show the presence of five different substances. Two of these are the semiquinone forms. One is identified with the completely oxidized ion of the dye. The remaining two are derived from the dimer of the leuco base, which is shown to be the main substance that is photo-oxidized. In this process, one photon produces double oxidation. Leuco crystal violet, leuco malachite green, and Michler's hydride behave similarly. The absorption maxima of their two semiquinone forms are given.

To begin the study of the quantum yield of photo-oxidation, experiments were made with the base of Wurster's blue. The quantum yield of Wurster's blue ions is found to be 0.10 near the beginning of illumination. When leuco methylene blue is illuminated, the quantum yield of the methylene blue ions increases with the concentration of the leuco base and diminishes with increasing illumination. In concentrated solutions the initial quantum yield is about 0.04. From the effect of concentration and time of illumination, it is shown that a dimer of the leuco base exists and is responsible for most of the photo-chemical products.

BERKELEY, CALIFORNIA RECEIVED SEPTEMBER 13, 1943

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(11) Lewis, Lipkin and Magel, THIS JOURNAL, **63**, 3005 (1941).

(12) Leighton and Forbes, *ibid.*, **52**, 3139 (1930).