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PHOTOSENSITIZED REDUCTION OF THIAZINE DYES ON SOLS AND IN SOLUTIONS

Photoreduction leading to the formation of a colorless leuco form is typical of thiazine dyes, for example, methylene blue (hereafter MB) (^1). As a result of irradiation of an oxygen-free solution in the absorption band of the dye, more or less rapid bleaching of the latter is observed.

Such a phenomenon is observed even in media that do not possess reducing ability in the usual sense, for example in solutions in pyridine (^2), formamide (^3), and also in adsorbates of this dye on silicic-acid sols (^4). After air is admitted, the color of the solution regenerates with the same or an altered spectrum. The change in the spectrum is associated with the irreversible demethylation reaction, which in a number of cases occurs during photoreduction of MB, as a result of which the decrease in optical density is accompanied by a shift of the absorption band toward shorter wavelengths ($^{2-}$5). The absorption of thionine (T) decreases upon photoreduction without a shift of the absorption band. In these experiments the active wavelengths causing the photoreaction are concentrated in the region of the visible absorption band of the dye ($\lambda_{\max} = 660$ mμ for MB and 605 mμ for T).

In the work of Karyakin and Terenin (^6), experiments are described in which, for a combined adsorbate of two dyes—acriflavine* (A) and MB—on a silicate adsorbent, bleaching of MB is also caused by light absorbed only by A (filters GG-13 and BG-25, transmitting the region 375-500 mμ). The phenomenon was attributed to transfer of excitation energy from A to MB molecules by the known inductive mechanism, realized when two molecules are sufficiently close and have partially overlapping absorption spectra (^7).

It could be expected that an analogous phenomenon would also be observed in solutions containing MB (or T) and another dye in sufficiently high concentrations. In this connection, experiments were carried out on irradiation of an aqueous silicic-acid sol bearing MB, and also of solutions of MB (and T) in formamide, pyridine, and in a viscous sucrose solution ($C = 3\ M$) in the absorption region of a second dye, adsorbed or dissolved together with the thiazine dye. In all cases the reducing agent is the medium itself.

Fig. 1

Figure 1: Fig. 1

Method. Removal of oxygen from solutions in formamide and in pyridine was carried out by repeated freezing and subsequent pumping. This procedure is described in detail in (^2, ^3). The procedure for working with solutions of silicic-acid sols is described in (^4). To remove oxygen from viscous sucrose solutions, pumping was carried out without freezing, and at the end of the procedure even with heating to 30-40°. To restore the initial concentration of dye and sucrose, which changes as a result of pumping, water was frozen out in the cuvette under vacuum conditions from an additional side arm of the cuvette. The amount introduced was controlled by the magnitude of the optical density of the solution.

The concentration of dyes in solution was varied within the range from $2.4 \cdot 10^{-6}$ M to $9.4 \cdot 10^{-5}$ M. Absorption spectra were measured on an SF-2M recording spectrophotometer.

* Acriflavine in the cited work is called trypaflavine.

Illumination was carried out with focused light from a PZh 100 W projection lamp. To isolate individual regions of the spectrum, light filters from Lenzos colored-glass catalog were used. To account for the intrafilter effect in mixed solutions, when illuminating an MB solution without the second dye, an additional cuvette containing a solution of the second dye was placed in front of the sample. When mixtures were illuminated, solvent was placed in this cuvette.

Fig. 1. Absorption spectrum of an aqueous solution of methylene blue ($5.0 \cdot 10^{-5}$ M) in the presence of silica sol. Solid curves—upon addition of acriflavine ($7.0 \cdot 10^{-5}$ M). Dashed curves—without acriflavine. The band with a maximum at 450 mμ belongs to the latter. 1—before illumination; 2—after 10 min illumination in the region 360-540 mμ; 3, 3′—after 40 min illumination; 4—after 4 h illumination; 5—after repeated illumination and subsequent admission of air.

Results. Figure 1 shows absorption curves of an aqueous solution of silica sol ($C = 1.0$ g/l); on the latter, either MB ($C = 5.0 \cdot 10^{-5}$ M) and A ($C = 7.0 \cdot 10^{-5}$) were coadsorbed (solid curves), or only MB (dashed curves).* As shown in Fig. 1, 3, illumination in the region 360-540 mμ (SZS-12 filter), outside the absorption band of MB, does not cause any change in the absorption spectrum of a sol containing only MB during exposure times up to 40 min. In the presence of A, however, the light absorbed by it (λ_{max}450 mμ), isolated by the SZS-12 light filter, causes a lowering of the absorption curve of the second component—MB. As a result of 40-minute illumination, the optical density of MB decreases by approximately 35% (Fig. 1, 3). More prolonged illumination leads to a further decrease in the magnitude of absorption (Fig. 1, 4). Upon subsequent admission of air, the regenerating absorption band of MB shifts to the position of the absorption band of azure (Fig. 1, 6), as occurred upon illumination of

Fig. 2

Figure 2: Fig. 2

Fig. 3

Figure 3: Fig. 3

similar solutions of MB alone in the absorption band of the latter (4).

Fig. 2. Absorption spectrum of methylene blue in formamide. Solid curves for $9.4 \cdot 10^{-5}$ M, dashed curves for $2.4 \cdot 10^{-5}$ M. 1, 1′—before illumination; 2, 2a—after 4 min illumination in the region 360-540 mμ of solutions not containing the second dye; 2′, 2a′—the same, but in the presence of an equimolecular amount of acriflavine.

Thus, on silica sol, MB undergoes the same bleaching as a result of photoreduction upon absorption of light by another dye (A) as was observed on porous glass (6).

Similar photosensitized reduction of MB and T also occurs in solutions. However, in solutions of formamide and pyridine, some decrease

* The different appearance of the absorption curves of unilluminated MB solutions in the presence of A and without it is associated with binary association of the two dyes, leading to a decrease in the dimerization of MB, i.e., to a decrease in the maximum at 610 mμ (8).

a decrease in the density in the absorption band of this dye occurs upon illumination in the region 360-540 mμ, i.e., outside the absorption band, and without the presence of a second dye. This is evidently caused by absorption on the short-wavelength slope of the curve. But the introduction of A into such a solution substantially intensifies bleaching under the action of short-wavelength light absorbed by A.

In Fig. 2 are shown the absorption spectra of solutions of MG and mixtures of MG and A (of the same concentrations) in formamide, subjected to illumination by light in the region 360-540 mμ, absorbed by A. It is seen from the figure that the presence of A very substantially intensifies the process of photoreduction both for the concentrated and for the diluted solution.

Fig. 3. Absorption spectrum of thionine ($5 \cdot 10^{-5}$ M) in a sucrose solution. Solid curves—in the presence of acriflavine ($5 \cdot 10^{-5}$ M), dashed curves—without it. 1—before illumination; 2, 2′—after 1 min of illumination in the region 360-540 mμ, 3, 3′—after 5 min of illumination, 4—after admission of air

A similar effect is also observed in a viscous reducing solvent. In Fig. 3 are given the absorption curves of T in a sucrose solution ($C \simeq 3M$), illuminated through an SZS-12 filter in the presence of A and without it. If without A the decrease in the magnitude of absorption of T after 1 min of illumination is less

Fig. 4

Figure 4: Fig. 4

than 3%, then the presence of the second dye increases it to 12%; after 5 min of illumination these values are, respectively, 12 and 28%.

Fig. 4. Absorption spectrum of an aqueous solution of thionine ($5 \cdot 10^{-5}$ M) in the presence of Trilon-B and acriflavine ($5 \cdot 10^{-5}$ M). 1—before illumination, 2—after illumination for 1 min at wavelengths shorter than 500 mμ, 3—after 5 min of illumination, 4—after 10 min of illumination, 5—after admission of air. Solid curves—in the presence of acriflavine ($5 \cdot 10^{-5}$ M); dashed curves—without acriflavine

In addition to A, acridine yellow, acridine orange, safranin T, eosin, and other dyes also possess the ability to sensitize.

An even more striking sensitization effect is obtained by using not a weakly reducing medium, but a typical reducing agent. As such, the disodium salt of ethylenediaminetetraacetic acid-5 (Trilon-B) was used. In the presence of the latter, reversible bleaching of an aqueous solution, for example of T, readily occurs upon illumination in the absorption band of the dye. But upon illumination with blue light (SS-5 light filter) only an insignificant photoreaction is observed. However, if the dye A is additionally introduced into the solution of T, then upon illumination with the same light, now absorbed by the latter, rapid bleaching of T occurs, reversible upon admission of air (Fig. 4).

Sensitizer A also undergoes slight reversible bleaching in this case.* It is interesting that nonluminescent dyes (tartrazine, orange II) do not photosensitize the reductive bleaching of MG and T.

The fact that photosensitization is also observed in very dilute solutions (Fig. 2, 2a′), i.e., in cases where the distance between the molecules of the two dyes is sufficiently large (about 400 Å), makes it possible to suppose that transfer of excitation energy is possible even in very dilute solutions.

Indeed, the formation of intermolecular complexes, by which the observed phenomenon could be explained, occurs, as a rule, in those media for which ordinary aggregation of dyes is characteristic. In the cases considered by us it takes place only on sols of silicic acid, which is reflected in the absorption spectra of the adsorbed dyes (Fig. 1). Some interaction of the two dyes may also be admitted in concentrated solutions in sucrose. However, neither in formamide nor, especially, in pyridine, which, as is known, prevent aggregation (^9), is complex formation possible.

One might have expected that the reduction of thiazine dyes occurs as a result of the formation of some photoproducts of A (or of another photosensitizing dye), as in the case of riboflavin and lumichrome. To test this, porous solutions of A and MG in formamide were placed in different side arms of a vacuum cuvette. After removal of oxygen from the cuvette, the side arm with A was illuminated in its own absorption band. Then this solution, under vacuum conditions, was combined with the MG solution. However, no changes in the absorption spectrum of the latter were observed.

Energy transfer most probably occurs from triplet molecules of A, which convert molecules of MG or T into the triplet state (or into the excited singlet state), and these are reduced, since the triplet level of A is undoubtedly located higher than even the singlet levels of MG and T (^10, ^11). Energy transfer may occur during diffusional encounters of molecules of the two dyes.

To test this assumption, experiments with pulsed photoexcitation of dyes are planned for the future.

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CITED LITERATURE

^1 G. Holst, *Zur Photochemie der reversiblen Redox Prozesse*, Lund, 1938; G. Oster, W. Wotherspoon, *J. Chem. Phys.*, **22**, 157 (1954).
^2 Kh. L. Arvan, D. N. Glebovskii, *ZhFKh*, **35**, 2822 (1961).
^3 Kh. L. Arvan, N. V. Ivanova, *ZhFKh*, **35**, 1215 (1961).
^4 Kh. L. Arvan, G. A. Korsunovskii, Yu. S. Gledev, *DAN*, **139**, 402 (1961).
^5 N. Wotherspoon, G. Oster, *J. Am. Chem. Soc.*, **79**, 3992, 4836 (1957).
^6 A. V. Karyakin, A. N. Terenin, *ZhFKh*, **36**, 2286 (1962).
^7 M. G. Galanin, *Tr. Fiz. inst. im. P. N. Lebedeva*, **12**, 3 (1960).
^8 Kh. L. Arvan, *DAN*, **121**, 123 (1958).
^9 Kh. L. Arvan, *Izv. AN SSSR, ser. fiz.*, **20**, 443 (1956).
^10 A. N. Terenin, V. L. Ermolaev, *Izv. AN SSSR*, **26**, 21 (1962).
^11 V. L. Ermolaev, E. B. Sveshnikova, *DAN*, **149**, 1295 (1963).
^12 N. Takeyama, *Nature*, **191**, 1359 (1961).
^13 A. A. Krasnovskii, *DAN*, **61**, 91 (1948); V. B. Evstigneev, V. A. Gavrilova, *DAN*, **98**, 1017 (1954); **100**, 131 (1955).

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* The reduction of MG by ascorbic acid or phenylhydrazine, photosensitized by uranyl, is mentioned in article (^12). Earlier, reactions of the reduction of safranine, methylene red, etc., photosensitized by chlorophyll and its analogs (^13), proceeding through an explicit stage of photoreduction of the sensitizer, were studied.

Note: Figure translations are in progress. See original paper for figures.

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