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Abstract

Full Text

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REVERSIBLE PHOTOCHEMICAL REDUCTION OF POLYMETHINE DYES

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In studying the action of polymethine compounds on the reaction of reversible photoreduction of chlorophyll by ascorbic acid, we found that some polymethine dyes undergo photosensitized reduction in this process ([1]). These observations indicated the possibility of direct photoreduction of dyes of this class. We succeeded in finding conditions under which reversible photoreduction of these compounds by ascorbic acid and cysteine is observed, and photosensitized reduction of the azo dye methyl red occurs. The results obtained indicate that the photosensitizing action of such dyes in solutions (as also in the case of chlorophyll and its analogs ([2])) is associated with their ability to undergo the reaction of reversible photoreduction. The results of the investigation are briefly described in this article.

Photoreduction. Thiocarbocyanines differing from one another in the length of the polymethine chain (I, II, III, IV) were used in the work.

Of greatest interest to us were compounds III and IV, which have absorption maxima in the red (III) and near-infrared region of the spectrum (IV), where the absorption maxima of chlorophyll and bacteriochlorophyll are located. A solution of the dye in pyridine at a concentration of about 10^{-5} M/l was introduced into a Tunberg vacuum tube of special form, adapted for measuring absorption spectra on an SF-4 spectrophotometer. Chemically pure reagent-grade pyridine was used, distilled within the range 112-114°, to which 5% water was added. Ascorbic acid was introduced into the tube in the form of an aqueous or pyridine (freshly prepared) solution; the air was pumped out of the tube with an oil vacuum pump with vigorous shaking for three minutes, and the mixture was illuminated at the focus of the condenser of the illuminator (300 W lamp), usually through a red KS-13 light filter (about 10^5 erg/cm$^2\cdot$sec). The total volume

Figure 1

Figure 2: Figure 1

of the mixture after removal of the air was 4 ml. During illumination, a decrease in optical density (D) at the absorption maximum of the dyes and a reversible increase of D in the dark (the tube was placed in the spectrophotometer cell holder) were observed for various periods of illumination.

After the period of illumination, 15-20 sec usually elapsed before the time of measurement; during this time the reverse reaction partially proceeded. Thus the figures show the course of the reverse reaction that was observed after an initial period of 15 sec to 2-3 min. In those cases where no obvious reverse reaction in the dark was observed (experiments with cysteine), the possibility remained that the reverse reaction occurred during the 15 sec required to begin measurement on the spectrophotometer. After the experiment, air was admitted into the tube and the course of the reaction in the dark was again measured. In this case a slower regeneration of the dye from the reduced forms was observed. Experiments at low temperature (down to -50°) were carried out in a transparent Dewar vessel containing a mixture of alcohol with solid carbon dioxide. A Tunberg tube was immersed in the transparent cooled alcohol and illuminated under the usual conditions. The reverse reaction was observed at the same temperature.

Fig. 1. Photoreduction of thiacarbocyanines (II, III, IV) by ascorbic acid (A) (K—control experiments without ascorbic acid) and by cysteine (B) in pyridine (K—control experiment without cysteine). Reversible change in optical density (D) at the absorption maxima at 565 mμ (II), at 660 mμ (III), and at 770 mμ (IV). D of the dyes at the maxima about 1; ascorbic acid 0.25 mg, cysteine 0.1 mg, water 5%, final volume of the mixture after evacuation of air 4 ml. Illumination through a red light filter KS-13 in experiments with III and IV and without a light filter with II. Temperature $+20^\circ$. Evacuation of air 3 min. Periods: illumination 0.5 min. (C), darkness 2 min. (T), air—20 min.

Investigation of the effect of the concentration of the reducing agent—ascorbic acid and cysteine—on the reaction rate showed that, within the studied range of reducing-agent concentrations from 10^{-4} to 10^{-2} M, no substantial changes in the rate of the photoreactions are observed. The reversibility of the process is most clearly observed at reducing-agent concentrations of 10^{-3}–10^{-4} M. In experiments with ascorbic acid at room temperature, reversibility of the reaction in the dark (without access of air) was observed against the background of a gradual decrease in optical density (D) caused by the simultaneous process of destructive (irreversible) photoreduction (Fig. 1A). In experiments with cysteine, some reversibility was observed only after admitting air, which oxidized the products of photoreduction (Fig. 1B); in the control experiment (Fig. 1B, K) (dye solution without reducing agent), no changes in the dye upon illumination were observed. Under the given experimental conditions, compound I is

Fig. 2 and Fig. 3

Figure 3: Fig. 2 and Fig. 3

reduced neither by ascorbic acid nor by cysteine.

Investigation of the effect of temperature on the rate of the process in the range from +20° to −25° showed that, when the temperature is lowered to −25°, the reaction is not slowed down in comparison with room temperature, which indicates the possibility of formation of a complex of the dye with the reducing agent. In the presence of ascorbic acid and cysteine it is not possible to observe changes in the absorption and fluorescence spectra of the dyes (Fig. 2), which may indicate the absence of interaction of the reducing agent with the singlet excited state of the dye. At the same time, the possibility of interaction with the triplet excited state remains. Preliminary formation of a complex may also not be accompanied by a change in the absorption spectrum. The fluorescence spectrum was measured by Yu. E. Erokhin

(under excitation by the blue mercury lines isolated by a ZS-3 light filter) on an apparatus described elsewhere (⌢3).

Photosensitization. In studying photosensitized oxidation-reduction reactions in solutions, it is very convenient to use an irreversibly reducible electron acceptor, which makes it possible to observe the result of the sensitized reaction after a period of illumination. Azo dyes are often used as such a terminal electron acceptor (⌢4).

Fig. 2. Absorption and fluorescence spectra of thiacarbocyanines. *1, 2* – absorption spectra of the dyes in the presence and absence of ascorbic acid and cysteine: *1* –dye III, *2* –dye IV; *3, 4* –fluorescence spectra of the dyes in the presence and absence of ascorbic acid: *3* –dye III, *4* –dye IV. Fluorescence is in relative units.

Fig. 3. Photosensitized reduction of methyl red by thiacarbocyanine. *1, 2* – change in the optical density at the absorption maximum of thiacarbocyanine at 660 mμ. *1* –thiacarbocyanine + methyl red + ascorbic acid; *2* –thiacarbocyanine + methyl red; *3, 4, 5* –change in optical density at the absorption maximum of methyl red at 425 mμ. *3* –methyl red + thiacarbocyanine + ascorbic acid; *4* –methyl red + thiacarbocyanine; *5* –methyl red + ascorbic acid (C –light, T –darkness).

We carried out the reactions in the ternary system under the following conditions: to 4 ml of a pyridine solution of dye (III) at a concentration of about 10^{-5} M (D at 660 mμ about 1) we added 0.25 mg of ascorbic acid (0.1 ml of an aqueous solution) and methyl red (0.01 ml of an aqueous solution), calculated so that its optical density (D) at 425 mμ was 0.6 (in this region the sensitizers practically do not absorb light). After removal of air, the solution was illuminated through a red KS-13 light filter, and the optical density was measured in the red absorption maximum of the sensitizer and in the region of the methyl red maximum at 425 mμ. A rapid photosensitized reduction of methyl red was observed, characterized by a decrease in optical density at 425 mμ. At this stage of the process D at the absorption maximum of the sensitizer remained unchanged, since complete regeneration of the sensitizer occurred through interaction of its photoreduced form with methyl red. After the methyl red had been "sensitized" and reduced, photoreduction of the sensitizer occurred, with reversibility effects in the dark (Fig. 3).

On the basis of these experiments and by analogy with the behavior of chlorophyll in solutions, the reaction mechanism may be represented by the following hypothetical scheme:

Preliminary interaction of the sensitizing dye and the reducing agent

$$\mathrm{K} + \mathrm{AH} \rightleftarrows \mathrm{K} \cdot \mathrm{AH}. \tag{1}$$

Phototransfer of an electron in the complex $\mathrm{K} \cdot \mathrm{AH}$ and "separation" of the ion-radicals formed

$$\mathrm{K} \cdot \mathrm{AH} \rightleftarrows \mathrm{K}^{-} \cdot \mathrm{AH}^{+} \rightleftarrows \cdot\mathrm{K}^{-} + \cdot\mathrm{AH}^{+}. \tag{2}$$

"Dark" interaction of the semiquinone of the photoreduced sensitizer with an electron acceptor, with regeneration of the sensitizing dye

$$\cdot\mathrm{K}^{-} + \mathrm{MK} \rightarrow \mathrm{K} + \cdot\mathrm{MK}^{-}. \tag{3}$$

This is followed by the stages of proton addition and radical dismutation with the formation of valence-saturated compounds.

As is known, both monomeric and aggregated forms of dyes adsorbed on silver bromide possess sensitizing action. Carroll and West (^{5}) indicate that sensitization by "monomeric" molecules, randomly adsorbed on the surface of silver bromide, is usually more effective than sensitization by aggregated forms of the dye. The literature has repeatedly pointed out the possibility of the participation of dyes in processes of photochemical electron transfer from a reducing agent (for example, from SH groups of gelatin) to a silver ion in the silver bromide lattice (^{6,7}). It is possible that the described ability of polymethine dyes for reversible electron uptake (photoreduction) may be connected with the mechanism of their participation in the photosensitized decomposition of silver bromide. We are far from likening the reactions occurring in dye solutions (where comparatively long-lived intermediate photoproducts are formed) to the reactions occurring under conditions of adsorption of monomeric and aggregated forms of dyes on silver bromide crystals. In this case the elementary photoprocess is possibly not connected with diffusion of intermediate photoproducts. However, the ability of sensitizing dyes for reversible photoreduction (observed in solution) may also manifest itself on silver bromide, where phototransformations of dyes may be limited by reversible electron uptake from the donor component and its transfer to the electron-acceptor component of the system.

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