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Abstract

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ON THE MECHANISM OF REGENERATION OF PORPHYRINS AFTER THE PHOTOREDUCTION REACTION

The photochemical properties of chlorophyll and related compounds have attracted the attention of many investigators (1–3). Most works concern the study, by spectral-luminescence methods, of the reaction of reversible photoreduction. The reaction of regeneration of the initial porphyrin molecules after photoreduction has been studied much less. The present work is devoted precisely to this reverse reaction. The essence of this reaction consists in the conversion of the photoreduction products of porphyrins into the initial porphyrin molecules as a result of admitting air and allowing the solution to stand in the dark for several (6—8) hours. At the same time, intense illumination of the reaction mixture after admission of air leads to instantaneous regeneration of the initial porphyrin. The experiments were carried out with porphyrins previously investigated in our laboratory: protoporphyrin, mesoporphyrin, tetraphenylporphyrin, and tetraazaporphin, with various reducing agents (4,5).

The most convenient medium, in which the direct and reverse light reactions proceed readily, proved to be a mixture of alcohol with pyridine in a ratio of 7:1. The porphyrin concentration was chosen to be of the order of $2—3 \cdot 10^{-5}$ mole/l. As the reducing agent, ascorbic acid was used at a concentration of $5—6 \cdot 10^{-2}$ mole/l. The photoreactions were carried out in vacuum cuvettes adapted for measurements on an SF-10. The solution, evacuated of atmospheric oxygen by repeated pumping on a fore-vacuum pump with preliminary freezing, was illuminated in the focus of the condenser with a 500 W incandescent lamp.

The kinetics of the direct and reverse light reactions, measured from the change in the absorption coefficient of the solution at the maximum of the absorption band ($\lambda = 745$ mμ) of the product of the direct and reverse reactions for mesoporphyrin, is given in Fig. 1. Upon irradiation of mesoporphyrin with the total light of an incandescent lamp, the direct reaction proceeds practically to completion in about 4 min. At first the process proceeds very rapidly. Then the reaction rate begins to slow down, which is reflected on the graph by the transition from an almost straight-line portion to a curve. After four minutes of illumination the concentration of the photoproduct reaches a maximum, and

Figure 1

Figure 1: Figure 1

with further illumination the concentration begins to decrease as a result of destruction of the photoreduced product and formation of an irreversible product, which can be followed from the spectra of the solutions and from the reversibility of the products. It was found that the reverse reaction proceeds considerably more efficiently than the direct one, and in order to increase the accuracy of the measurements it was necessary to supply the lamp with a reduced voltage (70 V instead of 127). The solution was illuminated with small portions of light for 5, 10, and, toward the end of the reaction, for 20-30 sec. Under such an attenuated regime, complete return to the initial porphyrin was observed after approximately 1.5 min of illumination with nonmonochromatic light. Thus, the rate of the reverse light reaction is considerably greater than that of the direct one. At the end of illumination, as in the first case, a decrease in the rate of regeneration of the initial product is observed. There are reports in the literature of reverse reactions proceeding under the action of light (^6). Excitation in the region is active ···

absorption of the reductant. Under our conditions, the long-wavelength absorption maximum of ascorbic acid lies at 304 mμ, whereas the absorption maxima of the products of mesoporphyrin photoreduction are located at 445 and 745 mμ. Such a large difference in the position of the absorption maxima of the reductant and of the reduced porphyrin makes it possible to attempt to carry out the photoreaction with excitation in the absorption region only of the reduced porphyrin. For this purpose, the reverse reaction was carried out with excitation in the red absorption band of the product formed, which does not overlap with the long-wavelength absorption bands of the initial porphyrin and the reductant (a KS-18 light filter was used, which does not transmit visible and ultraviolet light). In accordance with the decrease in the number of incident quanta, the time required for the photoproduct to return to the initial state increased to 8.7 min. At the same time, the amount of irreversible reaction products decreased.* (Approximately 98% of the photoreduced product returns to the initial state.)

Fig. 1. *a*—absorption spectra of mesoporphyrin: 1—initial; 2—after illumination for 4 min; 3—after regeneration of the initial porphyrin; *b*—kinetics of photoreduction of mesoporphyrin: 1—direct reaction, 2—reverse reaction.

In addition, using an SS-8 light filter, excitation was carried out at the absorption maximum of the product formed at 445 mμ. Under these conditions the reaction can be carried out in both the forward and reverse directions. To achieve the maximum concentration of the photoreduction product, 48 min were required. The reverse reaction proceeds in 5.5 min, and in this case both absorption bands of the photoproduct, 445 and 745 mμ, disappear simultaneously. The reversibility is less complete than in the case of using the KS-18 light filter. A product remains with an absorption maximum at 645 mμ.

Fig. 2. Spectra of triplet-triplet absorption of tetraphenylporphyrin: 1 —before reduction; 2 —after reduction

Figure 2: Fig. 2. Spectra of triplet-triplet absorption of tetraphenylporphyrin: 1 —before reduction; 2 —after reduction

Tetraphenylporphin is apparently somewhat less active than mesoporphyrin. Its reversibility in this case is also somewhat poorer. The photoreduction reaction proceeds in 12.7 min, i.e., 3 times more slowly than with mesoporphyrin (without allowance for the difference in absorptivity). Study of the reverse reaction yielded nothing fundamentally new.

Similar results in the study of the reverse reaction were also obtained for protoporphyrin and tetraazoporphyrin. H_2S was used as the reductant for tetraazoporphyrin.

Establishing the main features of the direct and reverse photochemical reactions of porphyrins, leading to photoreduction and then to regeneration of the initial porphyrins suggests a commonality of the mechanisms of these reactions, which apparently proceed at the level of the triplet states of the initial and photoreduced porphyrins. From this point of view it was essential to confirm experimentally the presence of triplet states in photoreduced porphyrins. The presence of triplet states and some of their properties for ordinary unreduced porphyrins have been shown in a number of works (7-9), including works from our laboratory.

In the present work we obtained spectra of triplet-triplet absorption of tetraphenylporphyrin in isobutyl alcohol and in a mixture of ethyl alcohol + pyridine (Fig. 2). Under the action of light pulses, absorption bands arise at 420 and 710 mμ, while the former absorption bands disappear. It is assumed that in the course of the photochemical reaction the pigment molecule passes into an excited state, and then by a radiationless transition into a metastable state. Such an active "biradical" molecule adds protons and gives the photoreduced product. We investigated the action of powerful light pulses on the photoreduced form. The investigations were carried out both under the action of light pulses and in the stationary regime upon excitation by a DKSSH-1000 xenon lamp*. A thoroughly evacuated photoreduced solution of tetraphenylporphyrin showed the reversible short-term appearance of absorption bands at 470 and 780 mμ. The former absorption bands of the photoreduction product decreased noticeably. Upon admitting air and illuminating, the reduced pigment was practically completely converted back into the initial tetraphenylporphyrin.

Fig. 2. Spectra of triplet-triplet absorption of tetraphenylporphyrin: 1 —before

* It is interesting to note that, simultaneously with the maximum at 745 mμ, the absorption maximum at 445 mμ also disappears, which indicates that both absorption maxima belong to one and the same photoreduced product.

reduction; 2 —after reduction

The data obtained apparently indicate that not only the direct photoreduction reaction, but also the reverse reaction, proceeds through an excited triplet state.

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* Measurement of absorption spectra under the action of powerful light pulses was carried out on a pulsed apparatus (9). The energy of the photolytic flash was of the order of 1600 J. The duration of the flash was $\sim 10^{-3}$ sec. As the spectrophotometric light source, a 400 W motion-picture lamp powered by accumulators was used. As a monochromator, an ISP-51 spectrograph was used with a photomultiplier installed at the fixed exit slit and adapted for taking spectra by the photoelectric method. The spectra were recorded with an S1-19 oscilloscope. Measurements of absorption spectra were carried out in vacuum cuvettes. The solutions were repeatedly pumped out with preliminary freezing to 10^{-5} mm Hg. Measurements were carried out in the region from 400 to 1000 mμ.

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