On the Question of the Structure of the Products of Photochemical Reactions of Porphyrins

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Abstract

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CHEMISTRY

Elucidation of the structure of the products of the reaction of photochemical reduction of chlorophyll and related compounds, discovered by Krasnov (1,2), has attracted the attention of many investigators (3-7). At the same time, it has not yet been possible to resolve this question definitively. Our previous studies made it possible to somewhat reduce the number of possible hypotheses (6,7) and to express an opinion concerning the symmetry of the reaction products. The present work is the next step in this direction.

It is assumed that, as a result of the photoreduction reaction, two hydrogen atoms are added to the pigment molecule (ˆ2). In principle, several variants of hydrogenation of the double bonds of the molecule are possible. The first possibility consists in hydrogenation of the central C = N bonds and addition, to the nitrogen atoms at the sites of hydrogenation, of two hydrogen atoms (ˆ3). The second possibility consists in hydrogenation of the C = C bonds of the methine bridges, with addition of one hydrogen atom to the broken bridge and the second to the N atom at the center of the molecule (ˆ5). And, finally, the last variant consists in hydrogenation of the double bonds of the pyrrole rings. In all these cases, a corresponding redistribution of the conjugated system must occur.

Infrared spectroscopy offers rich possibilities for clarifying this question. At present, the infrared spectra of the photoreduced forms of a number of porphyrins are known (3,4,ˆ8). However, it is not possible to draw from them an unambiguous conclusion about the site of localization of the hydrogen atoms. This is connected primarily with the complexity of the infrared spectra of porphyrins and the absence of a reliable interpretation of the spectra. In order to refine the information concerning the possible hypotheses, we undertook a study of the infrared spectra of the photoreduced form of tetraazoporphin. This porphyrin* is the simplest in its structure and differs from porphin by the presence of four nitrogen atoms instead of CH on the methine bridges. In this connection, tetraazoporphin is a convenient compound for determining the participation or nonparticipation of the methine bridges in the photoreduction reaction. Indeed, if as a result of the reaction the hydrogen atoms are added to the nitrogen atoms on the methine bridges, then an intense band corresponding to NH stretching vibrations should appear in the infrared spectrum. The absence of this band

Figure 1 graph: absorption spectra of tetraazoporphin

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would indicate the nonparticipation of the bridge nitrogen atoms directly in the reaction.

As is known (ˆ7), tetraazoporphin is much more efficient with respect to photochemical transformations than other porphyrins. On the other hand, the reverse process—the oxidation of its photoreduced form in the presence of atmospheric oxygen—also proceeds very rapidly. This creates considerable difficulties in obtaining the fully photoreduced form of tetraazoporphin during washing out of ascorbic acid. Therefore, unlike in our previous studies of mesoporphyrin and tetraphenylporphin, where the reduction was carried out in mixtures of various media, and as the reducing agent ascorbic acid was used; the photoreduction of tetraazoporphin was carried out in pyridine, and the reducing agent was H_2S, used by the authors of papers (3, 4). The use of a gaseous reducing agent makes it possible to avoid washing out the reducing agent and to avoid the danger of the reduced porphyrin returning to its initial state. At the same time, the greater efficiency of photoreduction of tetraazoporphin leads to the fact that, when air is evacuated from the solution, partial reduction of tetraazoporphin occurs without illumination. Comparison of the electronic spectra of the reaction products of photoreduction by ascorbic acid and by H_2S shows the equivalence of these products. Photoreduction was carried out in vacuum at a concentration of tetraazoporphin in pyridine of $3 \cdot 10^{-4}$ mole/l in the presence of KBr powder. After reduction the solvent was evaporated under vacuum. Spectral measurements were carried out on an SF-10 in the visible region and on a UR-10 in the infrared.

Fig. 1. Absorption spectrum of tetraazoporphin in pyridine (1), spectrum of reduced tetraazoporphin in the same solvent (2), and spectrum of the same compound after admission of air (3)

The infrared spectra of both the initial and the reduced tetraazoporphin were studied in pressed KBr pellets.

As a result of photoreduction of tetraazoporphin, a product is formed with a maximum in the visible region at 450 mμ (Fig. 1). Thus, this compound differs from all other porphyrins not only in the efficiency of photoreduction, but also in the number and position of the bands arising in the reaction. If the spectra of all other porphyrins change only slightly upon reduction and the principal

* This compound was synthesized in our laboratory by A. M. Shulga and S. M. Tauter by the method of R. P. Linstead, M. Whalley (ˆ9). The authors express their sincere gratitude for the provision of the preparations and for assistance in the work.

Fig. 2. IR spectrum of tetraazoporphin in KBr before reduction (1), after reduction (2), and differential spectrum (3)

Figure 2: Fig. 2. IR spectrum of tetraazoporphin in KBr before reduction (1), after reduction (2), and differential spectrum (3)

band lies in the red region, then the spectrum of tetraazoporphin differs fundamentally, and the band that appears lies in the green region. Photoreduction of tetraazoporphin in pyridine with ascorbic acid gives exactly the same spectrum; it also does not change if the reduction is carried out in other solvents. With a sufficient amount of reducing agent, the bands of the initial tetraazoporphin disappear completely. After air is admitted into the cuvette, almost complete regeneration of the initial tetraazoporphin is observed. The differences in the positions of the electronic spectra of photoreduced porphyrins and aza-substituted porphyrins are apparently not connected with a different structure of the products, since other compounds as well (chlorins and other porphyrins with an intense long-wavelength absorption band) give photoreduction products in the green region of the spectrum. This feature, as noted in (7), is probably connected with features of the structure of the π-electron cloud of the molecule.

Figure 2 presents the infrared spectra of the initial tetraazoporphin, its photoreduced form, and the differential spectrum showing the changes that occurred as a result of the photochemical reaction. From the data presented it is evident that the spectrum changes strongly upon photoreduction. These changes can be reduced to the following. In the far infrared region a band at 615 cm^{-1} appears, while the 635 cm^{-1} band disappears upon reduction. Large changes are observed in the 700-800 cm^{-1} region; the intense 803 cm^{-1} band in the spectrum of the reduced product practically disappears, and the 940 cm band sharply decreases. The 1200-1600 region changes considerably: the bands at 1340, 1510, and 1558 cm^{-1} almost completely disappear, while very intense bands at 1280, 1380, and 1460 cm^{-1} arise. Absorption increases in the 2800-3000 cm^{-1} region; the intense band disappears

3085 cm^{-1} and a weak band at 3300 cm^{-1}, which is interpreted as an NH vibration (10). If, during reduction, hydrogenation of the double bonds of the methine bridges occurs with localization of one of the hydrogen atoms on the broken bridge, then in the spectrum of the reduced tetraazoporphin, along with the band at 3300 cm^{-1} corresponding to the NH group located at the center of the molecule, one more band should appear, characterizing the NH group formed on the methine bridge as a result of reduction.

Fig. 2. IR spectrum of tetraazoporphin in KBr before reduction (1), after reduction (2), and differential spectrum (3)

In fact, a second such band in the region where NH groups appear is not observed; moreover, the previously present band at 3300 cm^{-1} disappears. Apparently, the redistribution of the conjugated system that occurs during photoreduction affects the central NH groups, while hydrogenation of the double bonds of the methine bridges does not occur. Changes in the bands at 803 and 940 cm^{-1} (^{10}) possibly indicate that, during photoreduction of tetraazoporphin, the CH groups of the pyrrole rings are affected. The bands that arise in the region 1300–1500 cm^{-1}, and the increase in absorption at 2800–3000 cm^{-1}, apparently belong to the CH group formed as a result of reduction at the site of hydrogenation of the double bonds.

The data obtained make it possible to suppose that, during photoreduction—at least of tetraazoporphin—hydrogen atoms do not add to the bridging nitrogen atoms. The site of localization of the excess hydrogen atoms is probably the pyrrole rings.

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