

SPECTRAL STUDY OF THE PHOTOREDUCTION OF HYDROGENATED DERIVATIVES OF TETRAPHENYLPOR- PHIN

![Fig. 1. Absorption spectra](image)

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Abstract

Full Text

CHEMISTRY

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SPECTRAL STUDY OF THE PHOTOREDUCTION OF HYDROGENATED DERIVATIVES OF TETRAPHENYLPORPHIN

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Continuing the spectral study of the photoreduction reactions of pigments of the porphin series (¹⁻³), we studied the photochemical interaction of hydrogenated derivatives of TPP*, namely: TPC and the trans-isomer of TPBC—with hydrazine, as well as the interaction of TPC with H₂S. The pigments were prepared by hydrogenating TPP with hydrazine and were purified chromatographically by the method described previously (⁴). The experimental procedure in studying the photochemical interactions of the pigments was the same as in the study of the photoreduction of TPP (²).

Fig. 1. Absorption spectra of a solution of tetraphenylchlorin (10^{-4} mol/l) in pyridine with hydrazine (2 mol/l) under vacuum conditions: **1**—initial solution; **2, 3**—after illumination for 15 and 30 min; **4**—after keeping the illuminated solution in the dark for 30 h.

TPC. Illumination of a pyridine solution of TPC in the presence of hydrazine leads to the disappearance of all its initial absorption bands in the visible region of the spectrum and to the appearance of a new broad band at $550\text{ m}\mu$ with a poorly resolved structure. Upon further illumination the intensity of this band decreases, and then increases again when the solution is left standing in the dark (Fig. 1). When air is admitted into the cuvette, regeneration of the initial TPC occurs with a yield of 90% or more. The absence of analogous spectral changes in the control solution without hydrazine, and the ability of the product of the photochemical interaction of TPC with hydrazine to regenerate in air to the initial pigment, make it possible to conclude that, as a result of this reaction, photoreduction of TPC takes place. Drawing an analogy with the photoreduction reactions of chlorophyll and porphyrins (^{5,6}), it may be assumed that the product of photoreduction of TPC, characterized by an absorption band at $550\text{ m}\mu$, is the result of addition of two H atoms to the molecule of the initial pigment. The reaction does not end with the addition of only two H atoms and,

Fig. 2. IR absorption spectra of solid films of tetraphenylchlorin (TPhCh), its hydrochloride (TPhChH), the photoreduced form (ph. TPhCh), and the corresponding deuterated compounds (-d).

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as the exposure is increased, apparently two more H atoms are added, as a result of which a colorless photoreduced product is formed. The latter is unstable and even under vacuum conditions in the dark passes into the photoreduced product with a band at $550\text{ m}\mu$.

Upon illumination of a pyridine solution of TPC in the presence of H_2S (equilibrium pressure about 500 mm Hg) under vacuum conditions for 15 min, no spectral changes in the visible region are detected—

* As before, we use the abbreviations: TPP —tetraphenylporphin, TPC —tetraphenylchlorin (tetraphenyldihydroporphin), TPBC —tetraphenylbacteriochlorin (tetraphenyltetrahydroporphin).

was found, with the exception of a slight decrease in the intensity of the pigment absorption bands, evidently caused by irreversible photodecomposition of the pigment, which also occurs in the absence of reducing agents in the solution.

To elucidate the features of the molecular structure of the photoreduced form of TPhCh, characterized by an absorption band at $550\text{ m}\mu$, its IR absorption spectra were obtained. The sample was prepared in the form of a solid film deposited from solution directly onto

Fig. 2. IR absorption spectra of solid films of tetraphenylchlorin (TPhCh), its hydrochloride (TPhChH), the photoreduced form (ph. TPhCh), and the corresponding deuterated compounds (-d).

the window of a vacuum cuvette, similarly to the way this was done in spectral measurements of photoreduced TPhP (²). For comparison, the IR spectrum was also obtained of a layer of the original TPhCh prepared by sublimating the pigment at $290\text{--}300^\circ$ onto a sylvine plate in vacuum, the IR spectrum of TPhCh hydrochloride obtained by exposing a sublimed layer of TPhCh to gaseous HCl, and the IR spectra of the corresponding deuterated pigments obtained by exposing layers of the original samples to D_2O vapor for several hours (Fig. 2).

An experiment was also carried out on the photoreduction of TPhCh with deuteriohydrazine N_2D_4 (95% deuterium enrichment). It was found that, in the region $650\text{--}4000\text{ cm}^{-1}$, the IR spectra of TPhCh reduced with N_2D_4 and of TPhCh reduced with N_2H_4 followed by exposure of the photoproduct to D_2O vapor are similar. Exactly the same similarity is observed between the spectra

of TPhCh reduced with N_2H_4 and TPhCh reduced with N_2D_4 followed by exposure of the photoproduct to H_2O vapor. Hence one can draw the unambiguous conclusion that all H atoms added to the TPhCh molecule as a result of the photoreaction

with hydrazine, readily exchange for deuterium with molecules of D_2O .

Comparison of the spectrograms in Fig. 2 shows that the changes in the IR spectrum of TPhCh that occur upon formation of the hydrochloride and upon photoreduction of the pigment have a certain similarity. Upon photoreduction the absorption bands at 948, 819, and 658 cm^{-1} disappear and bands at 1540, 1495, and 1204 cm^{-1} appear. Upon formation of the hydrochloride the same bands disappear and new ones appear at 1534, 1489, and 1230 cm^{-1} . A similarity of the changes is also observed in the frequency region of the stretching vibrations of NH bonds and in the regions 950–1000 and $700\text{--}800\text{ cm}^{-1}$. Moreover, the changes occurring in the IR spectra of the photoreduced form of TPhCh and of its hydrochloride when the samples are deuterated in D_2O vapor also prove to be similar (Fig. 2). These similarities make it possible to suppose that there is an analogy between the molecular structures of the photoreduced form of TPhCh and of its hydrochloride. Of course, this analogy cannot be complete, since the hydrochloride molecule has an ionic structure and, accordingly, a different electron-shell structure in comparison with the molecule of the photoreduced form of TPhCh. The difference in the structure of the electron shells evidently also determines the differences between the IR spectra of the hydrochloride and the photoreduced form (Fig. 2). It is noteworthy, however, that those absorption bands which distinguish the spectrum of the photoreduced form from the spectrum of TPhCh hydrochloride do not change upon deuteration of the samples. This means that they most likely correspond to vibrations of the molecular skeleton and are not directly associated with vibrations of the H atoms that add to the TPhCh molecule upon photoreduction. (These atoms, as shown above, readily exchange for deuterium.)

Thus, it may be thought that, just as protons do in the formation of the hydrochloride molecule (⁷), the H atoms in the photoreduction of the TPhCh molecule add to the two central atoms of the pigment molecule. That is, the molecule of the photoreduced form of TPhCh has a structure similar to the structure we proposed for the molecule of the photoreduced form of pheophytin (¹). Additional arguments supporting such a structure are: 1) the presence in the spectrum of the photoreduced form of TPhCh of characteristic absorption bands in the frequency region of stretching vibrations of NH bonds (Fig. 2); 2) the ease of replacement by deuterium of the H atoms added as a result of the photoreactions. The possibility of some other interpretation of the spectral changes occurring during transformations of the TPhCh molecule is not excluded, however, and therefore the molecular structure we propose for the photoreduced form of TPhCh cannot yet be considered definitive.

Despite a certain ambiguity in the interpretation of the spectra and of the spectral changes characterizing the photochemical transformations of TPhP and

Fig. 3. Absorption spectra of a solution of tetraphenylbacteriochlorin in pyridine with hydrazine (1.5 mol/liter) under vacuum conditions: 1 —initial solution; 2 —after 2 min illumination; 3 —1.5 h after air was admitted into the cuvette

Figure 3: Fig. 3. Absorption spectra of a solution of tetraphenylbacteriochlorin in pyridine with hydrazine (1.5 mol/liter) under vacuum conditions: 1 —initial solution; 2 —after 2 min illumination; 3 —1.5 h after air was admitted into the cuvette

TPhCh molecules, it can be asserted that the molecular structures of the photoreduction products of these pigments are different. The point is that in the spectrum of the photoreduced form of TPhP (when reduced with both hydrazine and H_2S) there is an absorption band at 2600 cm^{-1} , which we assigned to stretching vibrations of CH bonds arising as a result of addition of an H atom to the methine bridges of TPhP molecules (²). In the spectrum of the photoreduced form of TPhCh, as in the spectrum of the photoreduced form of pheophytin, there is no such absorption band. Consequently, the localization of the H atoms that have added to TPhP and TPhCh molecules as a result of their photoreduction is different. The question of whether this difference is common to all porphyrins and chlorins remains open. It is thought that differences may exist between the structures of the photoreduced products of metal-free pigments and of their complexes with metals.

TFBCh. Like TPP and TPhCh, TFBCh is capable of photochemical reduction by hydrazine, as a result of which a colorless product is obtained that regenerates to the initial pigment when air is admitted into the cuvette (Fig. 3). Unfortunately, because of the difficulty of preparing pure TFBCh in sufficient quantity, we were unable to obtain the IR spectrum of its photoreduced form. The spectral changes in the visible region make it possible to suppose that, as in the case of TPP and TPhCh, photoreduction of TFBCh involves disruption of conjugation in the tetrapyrrole ring of the pigment molecule. Since the photoreduced form of TFBCh has no absorption bands in the visible region, it may be asserted that, in comparison with the cyclic system of bonds of the porphin molecule, the conjugation in the molecule of photoreduced TFBCh is more strongly disrupted than in the molecules of photoreduced TPP and TPhCh. This was to be expected, because, owing to the presence of two hydrogenated pyrrole rings, the dimensions of the ring of conjugated bonds already in the initial TFBCh molecule are smaller than those in the molecules of TPP and TPhCh.

Fig. 3. Absorption spectra of a solution of tetraphenylbacteriochlorin in pyridine with hydrazine (1.5 mol/liter) under vacuum conditions: 1 —initial solution; 2 —after 2 min illumination; 3 —1.5 h after air was admitted into the cuvette.

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