Physical Chemistry

A. N. SIDOROV, V. G. VOROB' EV, Academician A. N. TERENIN

1963

SovietRxiv

Abstract

Full Text

Physical Chemistry

A. N. SIDOROV, V. G. VOROB' EV, Academician A. N. TERENIN

SPECTRAL STUDY OF THE PHOTOREDUCTION OF TETRAPHENYLPORPHIN

In a previous work we obtained the IR spectra of the photoreduced form of pheophytin *a*, formed upon irradiation of a pyridine solution of the pigment in the presence of H_2S (1). Study of the spectra obtained made it possible to suggest that, as a result of the photoreduction reaction, 2 H atoms add to the N atoms of the pyrrole nuclei of the pigment molecule. At the same time, recent reports by Woodward on the possible existence of compounds of the chlorin and isochlorin series (2) suggest that, in the photoreduction of compounds of the porphin series, the H atoms adding to the molecule may also be localized at the C atoms of the methine bridges. In this connection we carried out a series of experiments on the spectral study, in the visible and IR regions, of the photoreduction reaction of tetraphenylporphin (TPP), which differs from pheophytin and most other compounds of the porphin series by the relative simplicity of its molecular structure.

TPP was synthesized and purified by the method of Rothemund and Menotti (3). The visible and IR spectra of the TPP studied by us coincide with the spectra of TPP published earlier by other investigators (4–6). The photoreduction reaction was carried out in a vacuum cuvette (7) in deoxygenated pyridine at pigment concentrations of 10^{-4}—10^{-5} mol/l in the presence of hydrazine (concentration up to 1 mol/l) or H_2S. The equilibrium pressure of H_2S above the solution was 200-300 mm Hg, which, according to rough estimates, corresponds to a concentration of its molecules in the solution of several tenths of a mole/l. Illumination was performed with a 500-W incandescent lamp with reflector and condenser. During illumination the cuvette with the solution was placed in a glass jacket with running water. Spectral measurements were carried out on SF-10 and UR-10 instruments.

Upon irradiation of a TPP solution in the presence of hydrazine, absorption at 705 mμ and at 540 mμ initially increases (Fig. 1). As the exposure is increased, the intensity of the 705 mμ band rapidly reaches a maximum and begins to decrease, while the intensity of the 540 mμ band continues to increase. The reaction proceeds to completion, and one hour after the start of irradiation both the bands of the initial TPP and the 705 mμ band disappear. Only an intense broad 540 mμ band remains in the spectrum (Fig. 1), and the solution acquires a pink color. If the resulting solution is left standing under vacuum conditions in the dark, the intensity of the 540 mμ band slowly decreases and the 705 mμ

Fig. 1

Figure 1: Fig. 1

band again grows. Upon irradiation of a TPP solution in the presence of H_2S, only one 705 mμ band appears (Fig. 1), as a result of which the solution acquires a green color. In what follows, for brevity, we shall refer to the products with bands at 540 and 705 mμ as the pink and green photoreduced forms of TPP.

Both the pink and the green forms, by evacuating the solvent and the reducing agent (H_2S or hydrazine) from the vacuum cuvette, can be deposited as solid layers directly on the cuvette windows transparent in the IR region, which makes it possible to obtain their IR spectra. Redissolution of the solid layers of the photoreduced forms in pyridine completely regenerates the initial spectrum of the corresponding pink

or green form. This shows that both the pink and the green forms can be converted to the solid state without a change in molecular structure.

When solid layers of the pink and green forms are dissolved in CCl_4 (under vacuum conditions), their spectra change markedly (Fig. 1). The pink form in CCl_4 gradually changes into the green form with an absorption band at 684 mμ. When the green form obtained in this way is transferred into pyridine (under vacuum conditions), the 684 mμ band shifts to 705 mμ. The conversion of the pink form into the green is accelerated considerably if air is admitted into the cuvette containing the solution. It is practically completed within a few minutes, during which no substantial regeneration of the original TPP has yet had time to occur. Regeneration of TPP after conversion of the pink form into the green can be stopped by evacuating the air from the cuvette.

The kinetics of photoreduction of TPP show that formation of the pink form requires a greater light exposure than formation of the green form.

Fig. 1. **A**—absorption spectra of TPP in pyridine with hydrazine. **1**—initial solution; **2**—after 7 min of illumination; **3**—after 1 h of illumination; **4**—after evacuation of the solvent, transfer of the resulting precipitate into CCl_4, and holding of the resulting solution in the dark under vacuum for 15 h. **B**—absorption spectra of TPP in pyridine with H_2S. **1**—initial solution; **2**—after 5 h of illumination; **3**—after transfer of the photoreduced form into CCl_4.

On interaction of TPP with H_2S, the pink form is not formed at all. In the presence of hydrazine, the green form under irradiation changes into the pink form, which is richer in stored energy. The latter is less stable than the green form and changes into the green form.

When air is admitted into the cuvette containing a solution of the pink or green form, gradual regeneration of the original TPP occurs (over several hours), as may be judged from the intensity of the TPP absorption bands at 519, 552, 594, and 652 mμ. The completeness of regeneration depends substantially on the

Fig. 2. IR spectra of solid films: 1 –TPP; 2 –pink photoreduced form of TPP; 3 –green form obtained by reaction with hydrazine; 4 –green form obtained by reaction with H2S; 5 –TPP hydrochloride. Dashed curves depict the spectra of films of the corresponding deuterated pigments.

Figure 2: Fig. 2. IR spectra of solid films: 1 –TPP; 2 –pink photoreduced form of TPP; 3 –green form obtained by reaction with hydrazine; 4 –green form obtained by reaction with H2S; 5 –TPP hydrochloride. Dashed curves depict the spectra of films of the corresponding deuterated pigments.

duration and conditions of storage of the photoreduced forms, which gradually decompose irreversibly.

Figure 2 shows the IR absorption spectra of solid films of TPP, its photoreduced forms, and its hydrochloride, as well as of the corresponding deuterated pigments. The green form, whose spectrum is shown by curve 3 in Fig. 2, was obtained from the pink form by dissolving the latter in CCl_4 and admitting air into the cuvette containing the solution for 15 min, after which the air was evacuated and the CCl_4 was evaporated off. TPP hydrochloride was obtained by holding a TPP film in gaseous HCl, followed by evacuation of excess gas. Deuteration of the pigments was carried out by redepositing their films from solutions in pyridine containing 2% D_2O. Deuteration of the hydrochloride was carried out by holding its film in D_2O vapor (at $p = 4$ mm Hg) for several hours.

Most vibrations of the TPP molecule, because of its complexity, are not characteristic and as yet cannot be identified with sufficient reliability in the IR spectrum. Nevertheless, even a single comparison of the -

shown in Fig. 2 with one another makes it possible to put forward certain assumptions about the structure of the photoreduced forms of TPP. A comparison of the spectrum of the original TPP with the spectrum of its pink and green forms shows that photoreduction leads to profound changes in the structure of the molecule. In particular, the appearance of comparatively intense absorption in the region characteristic of the frequencies of –C=C–bonds (1550-1600 cm^{-1}) indicates a rupture of conjugation in the closed tetrapyrrole cycle of conjugated bonds. The bands of the imino groups NH of the TPP molecule also change significantly upon photoreduction (Fig. 2).

Fig. 2. IR spectra of solid films: **1** –TPP; **2** –pink photoreduced form of TPP; **3** –green form obtained by reaction with hydrazine; **4** –green form obtained by reaction with H_2S; **5** –TPP hydrochloride. Dashed curves depict the spectra of films of the corresponding deuterated pigments.

The spectral differences between the pink and green photoreduced forms, on the one hand, and between their deuterated analogs, on the other, are practically identical (curves 2, 3, Fig. 2). In other words, deuteration of the photoreduced form does not affect those functional groups in the molecule whose changes determine the conversion of the green form into the pink form and back. Hence it follows that these two forms differ not by the addition to any one of them of an extra H atom (which–

ry, being labile, should have been able readily to exchange for D), but by some structural transformations of the molecular skeleton. This, in particular, is confirmed by the similarity of the spectra of the pink and green forms in the region of the stretching frequencies of the NH and CH bonds and by differences in the region of the bonds –C=C–: the pink form has 2 bands in this region, whereas the green form has 4.

In the spectra of both photoreduced forms of TPP an absorption band of medium intensity is observed near 2600 cm^{-1}, which, upon contact of the pigment with D_2O, shifts to 1945 cm^{-1} (Fig. 2). Taking into account the position of this band in the spectrum, it can most probably be assigned to stretching vibrations of some CH bonds with a labile H atom readily exchanged for D. Absorption bands of CH bonds with a labile H atom in approximately this same region of the spectrum have been observed in the IR spectrum of ascorbic acid ([8]). It may be assumed that in the photoreduction of TPP, as in the case of the formation of phlorins ([2]), H atoms add to the C atoms of the methine bridges of the molecule, accompanied by rupture of conjugation at the sites of H addition. The CH bonds thereby formed correspond to the absorption band at 2600 cm^{-1}, and the C=C bonds to absorption in the region 1550-1600 cm^{-1}. The question of the number of H atoms added remains open.

When the spectra of TPP hydrochloride and of its green form, obtained upon irradiation in the presence of H_2S (curves 4 and 5, Fig. 2), are compared, the similarity of a number of details in these spectra is striking: the absorption bands in the region of the stretching frequencies of NH (ND), the bands in the region 650-800 cm^{-1}, and a number of others. It is especially interesting to note the similarity of the spectral changes of these forms of TPP that occur upon their deuteration.

It is known ([9]) that, upon formation of porphyrin hydrochlorides, two protons add to the central N atoms of the pigment molecule. The similarity of the spectra of the green form of TPP and of its hydrochloride suggests that, during photoreduction of TPP, H atoms add not only to the C atoms of the methine bridges but also to the central N atoms. The presence in the spectra of the photoreduced forms of TPP of broad absorption bands in the region of the stretching frequencies of NH (ND), similar to the corresponding bands in the spectrum of the hydrochloride, serves as an argument confirming this assumption.

Finally, it should be noted that there is a difference between the IR spectra of the green forms of TPP obtained upon photoreduction of the pigment by hydrazine and by hydrogen sulfide (curves 3 and 4, Fig. 2). Each of these spectra has its own characteristic absorption bands: the bands at 3260, 1123, and 1098 cm^{-1} upon photoreduction by hydrazine, and the bands at 1330 and 1280 cm^{-1} upon photoreduction by H_2S, as well as a number of other bands. All these bands shift upon deuteration. Evidently, during photoreduction, not only H atoms but also a residue of the reducing-agent molecule is added to the TPP molecule, as, for example, in the formation of quasi-leuco bases of dyes ([10]).

Received
8 VII 1963

CITED LITERATURE

1. A. N. Sidorov, A. N. Terenin, DAN, **145**, 1092 (1962).
2. R. B. Woodward, Zhurn. Vsesoyuzn. khim. obshch. im. D. I. Mendeleeva, **7**, 384 (1962).
3. P. Rothemund, A. R. Menotti, J. Am. Chem. Soc., **63**, 267 (1941).
4. R. H. Ball, G. D. Dorough, M. Calvin, J. Am. Chem. Soc., **68**, 2278 (1946).
5. S. F. Mason, J. Chem. Soc., **1958**, 976.
6. D. W. Thomas, A. E. Martell, J. Am. Chem. Soc., **81**, 5111 (1959).
7. A. N. Terenin, A. N. Sidorov, Optiko-mekhanich. promyshlennost, No. 1, 1 (1959).
8. J. W. Weigl, Anal. Chem., **24**, 1483 (1952).
9. G. P. Gurinovich, A. N. Sevchenko, K. N. Solov' ev, UFN, **79**, 173 (1963).
10. A. T. Vartanyan, ZhFKh, **36**, 2118 (1962).

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

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.