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Abstract

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STUDY OF INTERMOLECULAR ELECTRON TRANSFER IN TETRAPYRROLE PIGMENTS UNDER PULSED ILLUMINATION

In studies of the action of powerful pulsed illumination on tetrapyrrole pigments of the porphyrin, chlorophyll, and phthalocyanine types in solutions, the main attention has usually been directed to the absorption spectrum of triplet molecules ([1]). Meanwhile, in some solvents, in the absence of typical hydrogen donors, the appearance under a light pulse of absorption bands belonging to unstable products similar to the leuco-reduced forms of the original pigments is observed ([2]). In the fundamental works of Krasnovsky and Evstigneev ([3]) on the photoreduction of tetrapyrrole pigments with ordinary light sources, and in reproductions of these works abroad, compounds were used as reducing agents whose radicals and positive ion-radicals do not possess characteristic absorption bands in the accessible spectral region. The aim of the present work was an attempt to separate H-atom transfer from electron transfer in the primary photoreduction reaction. For this purpose phenol, diphenylamine, triphenylamine, and benzidine were used as reducing agents; the spectra of the radicals and positive ion-radicals of these compounds are well known from studies ([4], [5]), including those that did not employ pulse techniques ([6]).

Experimental Part

In the present work a pulsed apparatus was used, analogous to that described in the literature ([7]), with improved time resolution. At an energy of 350 J the flash duration was reduced to 2.5 μsec by decreasing the inductance of the discharge circuit to 0.05 μH. As the probing source of constant light, an IFK-2000 flash lamp was used with a luminous flux stabilized during the observation time; this made it possible to extend the spectral measurements to 250 mμ and to improve the signal-to-noise ratio.

The recording part of the apparatus consisted of a ZMR-3 monochromator and FEU-18 and FEU-22 photomultipliers, the signal from which was fed through a cathode follower to an OK-17M pulse oscilloscope having a passband up to 10 MHz. The linearity of the measuring channel was checked with neutral light filters. The spectral width of the monochromator slits was varied from 0.5 mμ for the ultraviolet to 10 mμ for the infrared region of the spectrum.

Fig. 1

Figure 1: Fig. 1

Removal of dissolved oxygen from the solution was carried out by 5-6-fold alternate freezing and thawing in a vacuum of 10^{-5} mm Hg, after which it was poured in vacuum into a cylindrical quartz cuvette 150 mm long and 20 mm in diameter. First, for a given wavelength of the monochromator, an oscillogram was photographed during the flash of only the probing lamp, with a duration of 1000 μsec. Then the probing lamp was flashed and, with a delay of 10 μsec, the flash of two straight pulsed lamps placed parallel to the cuvette, with the energy and duration indicated above. Since at the output of the monochromator there was practically no scattered light from the exciting light pulse, the signal from it was not recorded separately. The photograph of the oscillograms was projected onto the screen of a P-10 projector, graduated in millimeters. After repeated measurements at different wavelengths, graphs were constructed of the relative changes in the transmittance of the solution, $\Delta I/I_0$, under the action of the light pulse as a function of wavelength. The values of $\Delta I/I_0$ were plotted upward from the zero line when additional absorption appeared, and downward when the original absorption disappeared.

Irradiation by the flash was carried out in the absorption band of the dye: for magnesium phthalocyanine (MgPhc), Schott OG-2 light filters were inserted between the lamps and the cuvette, transmitting wavelengths above 600 mμ and cutting off wavelengths shorter than 360 mμ; for hematoporphyrin (HP), BS-7 light filters were used, cutting off wavelengths shorter than 360 mμ. Crystalline HP was kindly supplied by the Institute of Blood Transfusion; MgPhc was supplied by the English firm ICI. The solvents—pyridine, dioxane, dimethylformamide, ethanol—were subjected to fractional distillation. Acetone from "Reanal" was not subjected to additional purification. MgPhc was also introduced into styrene and polystyrene. Phenol, diphenylamine, triphenylamine, and benzidine were preliminarily sublimed in vacuum. The pigment concentrations were usually $1.0 \cdot 10^{-6}$–$2.5 \cdot 10^{-6}$ M, and those of the compounds introduced into the solution were of the order of $10^{-3} M$.

Fig. 1. Relative changes in the absorption spectra of solutions of magnesium phthalocyanine (MgPhc). 1 –MgPhc in pyridine (10^{-6} M); 2 –MgPhc in pyridine (Livingston data); 3 –MgPhc 10^{-6} M + phenol (10^{-3} M) in pyridine; 4 –MgPhc (10^{-6} M) + phenol (10^{-2} M) in dioxane. The dotted curve is the initial spectrum

Figures 1 and 2 give the complete spectral pictures of the changes in the initial absorption spectrum of the pigments, shown by the dashed curve. The spectral curves located below the zero line indicate the practically complete disappearance of the normal absorption bands (these curves are for the most part not given). The spectral curves above the zero line belong to new bands of labile short-lived products arising under the action of the flash.

Figure 2

Figure 2: Figure 2

In a solution of MgPhc alone in pyridine there are maxima at 400 and 500 mμ, approximately coinciding with the triplet absorption band found by Livingston and Fujimori by the photographic method (8), but with the inverse ratio of heights (Fig. 1, 1, 2)*. In the presence of dissolved phenol (Fig. 1, 3, 4), along with them a new sharp intense absorption maximum appears at 450 mμ. The same new maximum appears at 440 mμ in the presence of benzidine (10^{-3} M in acetone solution) and, consequently, it cannot be attributed to any phenol radical, for example Ph—O·, the band maximum of which is located at 382 mμ (5). Indeed, in our apparatus, upon irradiation by a flash without exclusion of the UV radiation of a solution of phenol in ethanol (10^{-3} M), a broad band at 370–410 mμ is obtained, evidently due to such a radical.

In the spectrum of the stable negative ion-radical MgPhC, a maximum at 420 mμ was also previously found (9), along with maxima at 950 and 640 mμ. This suggests that the new maximum obtained here in another solvent may possibly belong to an MgPhC molecule that has accepted an electron from phenol, i.e., to the MgPhC^- ion-radical.

In dioxane in the presence of phenol, together with maxima at 400 and 500 mμ belonging to the triplet state, there is also a most intense maximum at 450–460 mμ, which we assign to the radical anion of the pigment (Fig. 1, 4).

Fig. 2. Relative changes in the absorption spectra of hematoporphyrin (HP). 1 –HP ($2.5 \cdot 10^{-6}$ M) in pyridine; 2 –HP ($2 \cdot 10^{-6}$ M) in dimethylformamide; 3 –(HP) ($2.5 \cdot 10^{-6}$ M) + diphenylamine (10^{-3} M) in pyridine; 4 –HP (10^{-6} M) + diphenylamine (10^{-3} M) in dioxane; 5 –HP (10^{-6} M) + triphenylamine (10^{-3} M) in acetone. The dashed curve is the initial spectrum.

In order to refine and extend the work (2), experiments were carried out on pulsed photoexcitation of HP (hematoporphyrin) in various solvents in the presence of diphenylamine (DPA) and triphenylamine (TPA) as electron donors. Illumination was performed through BS-7 light filters, which excluded photoexcitation of the latter compounds. In Fig. 2 some of the results obtained are compared. As in Fig. 1, first of all there is an almost complete disappearance of the bands at 425, 505, 540, 580, and 630 mμ of the pigment' s own absorption during the pulse; this is shown in the figure only for the 425 mμ band by the segments of curves 1 and 3, plotted downward from the zero line and occupying the region 370–430 mμ. In addition, however, new bands appear in pyridine and dimethylformamide, with maxima at 470 and 330* mμ for the pigment without

* In the first work (2) on pulsed photoaction on pigments, carried out on an imperfect apparatus, only a broad unresolved band appeared, occupying the region 470–580 mμ.

additives (Fig. 2, 1 and 2). The additional maxima at 520 (weak), 605, and 660 mμ found in the previous work (2) were not reproduced in the present work, but the maximum at 660 mμ is observed at a high pigment concentration. The appearance of the 470 mμ band was associated in (2) with the formation, under the photo-pulse, of the primary semi-reduced form of HP, discovered by Evstigneev under ordinary illumination conditions (10). In (2) it was suggested that the solvents used have a reducing function, being capable of reversibly donating an electron with the formation of a short-lived HP$^-$ ion.** In dioxane, together with the reversible disappearance of the intrinsic absorption bands, no new bands appeared. When an electron donor—DPA—is introduced into dioxane, a 470 mμ band appears (Figs. 2, 4). The same band also appears upon addition of DPA or TPA (10^{-3} M) to a pyridine or acetone solution of HP (10^{-6} M), Figs. 2, 3, 5. In their presence, moreover, a band for DPA appears with a maximum at 650–660 mμ (curves 3 and 4) in dioxane and pyridine, and with a maximum at 650 mμ for TPA in acetone (curve 5). The absorption maxima of positive ions of DPA at 680 mμ and of TPA at 570 and 656 mμ, obtained by photoionization in frozen glassy solvents, are well known (6). It may be concluded with confidence that, under the photo-pulse, positive ions of the indicated amines are detected in the given binary solution. The shift of the bands is caused by the difference between the solvent media. The decay time of the new bands is 500–800 μsec and differs little from the duration of the bleached state of the pigment, evidently due mainly to conversion to the triplet state. The absence of absorption bands that could be ascribed to triplet molecules is in agreement with the results of studies (7, 8) with protoporphyrin and tetraphenylporphin. In these, a single selective maximum at 450 mμ was observed, accompanied by a rapid uniform decline to 800 mμ, where a considerably weaker absorption maximum occurred. The possibility of ascribing the 470 mμ HP maximum observed by us to absorption by triplet molecules is contradicted by its prolonged existence under ordinary conditions in the typical photoreduction reaction (10). The absence of the 470 mμ HP maximum in dioxane in the presence of ordinary reversible pulsed photobleaching is also inconsistent with such an interpretation. Further measurements with other objects will make it possible to broaden this range of observations.

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* In dimethylformamide the intense maximum is located at 310 mμ (Fig. 2, 2).

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** It should be noted that the reducing activity of pyridine and dimethylformamide is also manifested in the rapid reversible photobleaching of thiazine dyes under ordinary illumination (11).

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