Physical Chemistry

P. A. Shakhverdov, Academician A. N. Terenin

1965

SovietRxiv

Abstract

Full Text

Physical Chemistry

P. A. Shakhverdov, Academician A. N. Terenin

Deactivation of the Fluorescent and Phosphorescent States of Tetrapyrrole Pigments in Liquid Solutions

When a powerful light pulse acts on solutions of tetrapyrrole pigments, in particular phthalocyanines, a short-lived reversible change in their absorption spectra is observed—the disappearance of known bands and the appearance of new ones as a result of the transition of part of the molecules to the triplet level (*1*). The lifetime of the newly appearing absorption is several hundred microseconds. During this time the triplet molecule, possessing an excess of energy and unpaired electrons, is capable of reacting with the solvent and with other molecules present in the solution. In (*2*) it was shown that, in the spectrum of a mixture of magnesium phthalocyanine with electron donors under intense pulsed illumination, along with the usual triplet-triplet (T—T') absorption there is observed the appearance of new bands, which were interpreted as absorption bands of the positive ion of the donor molecule and the negative ion (semiquinone) of phthalocyanine $[MgPhc]^-$. At the same time, the question remained open whether the latter ion is formed from the excited singlet or triplet level of the pigment.

In the present work a comparison was made of the effects of various molecular donors, as well as electron acceptors, on the decay kinetics of T—T' absorption, on the one hand, and the fluorescence intensity of magnesium phthalocyanine (MgPhc), on the other. As electron donors, as in (*2*), phenol and diphenylamine were chosen, and as acceptors—benzoquinone and nitrobenzene. Measurements were carried out in dioxane solutions.

Experimental Part

Materials. Magnesium phthalocyanine from the English firm ICI, diphenylamine of "analytical reagent" grade, and phenol of "chemically pure" grade were not subjected to additional purification. Nitrobenzene was distilled in vacuum, and benzoquinone was purified by sublimation. The solvent—dioxane—was subjected to fractional distillation.

Apparatus. The spectrokinetic apparatus was constructed according to the generally accepted scheme (*2, 3*). The electrical energy of the flash of the exciting source (a capillary discharge in air) was 500 J (capacitance of the capacitor bank 5 μF at a voltage of 10 kV). The flash duration was 5 μsec. A gas-discharge

Fig. 1

Figure 1: Fig. 1

lamp of the DKSP-200 type was used as the probing source. A feature of the apparatus used in this work is the small dimensions of the luminous part of the exciting source (4 mm), which made it possible to shorten considerably the length of the cuvette with the irradiated solution, bringing it to 10 mm. The remaining parameters of the apparatus were unchanged (*2*). Irradiation was carried out through a KS-10 filter in the region of the absorption band of MgPhc. Registration was performed with the aid of an ZMR-3 mirror monochromator with an FEU-18A photomultiplier. To reduce scattered light from the exciting source and to cut off the ultraviolet radiation of the DKSP-200 lamp, light filters SZS-18 and ZhS-12 were placed in front of the cuvette in the measuring beam. Kinetic curves were recorded on oscillographs of types SI-4 and SI-15 and processed according to the method described in (*3*). The concentration of MgPhc was of the order of 10^{-4} M and was kept constant in all experiments. Removal of oxygen from the solution was carried out by—

air was carried out by 5-6 repeated cycles of freezing and thawing, followed by evacuation to 10^{-5} mm Hg.

The quenching of the fluorescence of the solutions was measured on a photoelectric setup with a double monochromator, DF-12. For excitation, the mercury line at 578 mμ was used; it was isolated by means of a high-luminosity monochromator with a diffraction grating and a light filter.

Results and Discussion

When a solution of MgPhc in dioxane is irradiated under vacuum conditions, a short-lived appearance of a new absorption band is observed, the maximum of which is at 470 mμ. This band corresponds to absorption

Fig. 1. *a*—quenching of the triplet state of magnesium phthalocyanine by nitrobenzene. Quencher concentration: 1—without quencher; 2—10^{-4}; 3—10^{-3}; 4—10^{-1} M; *b*—quenching of the triplet state of magnesium phthalocyanine by diphenylamine. Diphenylamine concentration: 1—10^{-1}; 2—10^{-2}; 3—10^{-4} M.

(T—T') from the triplet level ([1,2]). Measurements of the decay of triplet absorption were performed only at this wavelength.

After illumination of a solution of MgPhc alone, the absorption at 470 mμ disappears strictly according to an exponential law, obeying the equation:

$$-d[C_{\mathrm{T}}]/dt = k[C_{\mathrm{T}}],$$

where $[C_{\mathrm{T}}]$ is the concentration of triplet molecules, and k is a constant equal to $0.9 \cdot 10^4$ s^{-1}. These results are illustrated in Fig. 1a, where the ordinate

gives the relative change with time after the pulse in the optical density of the solution, $\ln(\Delta D_0/\Delta D)$, at the wavelength 470 mμ.

Addition to MgPhc solutions of electron acceptors—benzoquinone and nitrobenzene—leads to a shortening of the lifetime of triplet absorption, while the decay law remains exponential (Fig. 1a). From the slopes of the straight lines for different acceptor concentrations, the decay constants $k = 1/\tau$ were calculated; from these, the constants of deactivation of the triplet state were then determined. These constants are given in Table 1, which also gives the fluorescence-quenching constants of MgPhc by the same compounds, reduced to the lifetime of the excited state*.

Figure 2 presents the results of measurements of the quenching of MgPhc fluorescence by benzoquinone, *m*-dinitrobenzene, trinitrobenzene, and nitrobenzene. The quenching obeys the linear Stern–Volmer relation. The fluorescence-quenching constants, also given in Table 1, were determined from this relation, taking into account the lifetime of MgPhc molecules in the excited (singlet) state ([4]).

It follows from the data of Table 1 that quenchers with a greater electron affinity ([10]) exert a stronger quenching effect, as was observed earlier also for the quenching of chlorophyll fluorescence ([4]). We found that fluorescence quenching by reducing agents—phenol and diphenylamine—is insignificant, as was also observed in the case of chlorophylls ([6,7]).

* The authors thank O. D. Dmitrievskii for providing the data measured by him on the quenching of MgPhc fluorescence by some electron acceptors.

Further, from the data of Table 1 it follows that the deactivation constants of the triplet state of MgPc are approximately three orders of magnitude smaller than the fluorescence-quenching constants. The efficiency of deactivation by benzoquinone is an order of magnitude greater than by nitrobenzene, in accordance with the greater electron affinity of benzoquinone. Comparison with known data on the quenching of the triplet state of chlorophyll ([8]) shows that the triplet state of its analogue—MgPc—is quenched by benzoquinone two orders of magnitude more weakly, and is comparable with the quenching of the triplet state of anthracene ([9]).

Fig. 2. Quenching of magnesium phthalocyanine fluorescence by various electron acceptors: **1**—nitrobenzene; **2**—*m*-dinitrobenzene; **3**—trinitrobenzene; **4**—benzoquinone.

Irradiation by a flash lamp of MgPc solutions in the presence of the electron donors phenol and diphenylamine also leads to deactivation of the triplet state, but with more complex kinetics. A clear deviation of the decay-curve form from an exponential is observed, and irreversible changes occur in the absorption spectra. Figure 1*b* shows the time decay of the triplet-triplet absorption of an MgPc solution at various concentrations of the quencher—diphenylamine. Analogous results were also obtained for phenol. Meanwhile, as was stated

above, quenching of fluorescence by these electron donors was not observed, and it may be assumed that in the present case the triplet state is more reactive.

Table 1

Fluorescent compound	Quencher	Deactivation constant of the triplet state (M^{-1} sec^{-1})	Fluorescence-quenching constant (M^{-1} sec^{-1})
Magnesium phthalocyanine (MgPc)	Benzoquinone	$4.0 \cdot 10^7$	$2.7 \cdot 10^{10}$
Magnesium phthalocyanine (MgPc)	Trinitrobenzene		$1.1 \cdot 10^{10}$
Magnesium phthalocyanine (MgPc)	*m*-Dinitrobenzene		$4.3 \cdot 10^9$
Magnesium phthalocyanine (MgPc)	Nitrobenzene	$1.7 \cdot 10^6$	$1.0 \cdot 10^9$
Chlorophyll	Benzoquinone	$2.4 \cdot 10^9$ ([8])	
Anthracene	Benzoquinone	$2.0 \cdot 10^7$ ([9])	

Thus, both electron acceptors and electron donors interact with MgPc molecules in the triplet state; however, for electron acceptors the efficiency of the interaction is very small in comparison with the efficiency of interaction with the singlet excited state. For electron donors—reducing agents—the opposite relationship is observed.

The authors express their gratitude to V. L. Ermolaev for providing his apparatus for measuring fluorescence quenching.

Received
3 X 1964

REFERENCES

1. R. Livingston, E. Fujimori, *J. Am. Chem. Soc.*, **80**, 5610 (1958).
2. P. A. Shakhverdov, A. N. Terenin, *DAN*, **150**, 1311 (1963).
3. H. Linschitz, K. Sarkanen, *J. Am. Chem. Soc.*, **80**, 4826 (1958).
4. O. D. Dmitrievskii, V. L. Ermolaev, A. N. Terenin, *DAN*, **114**, 751 (1957).

5. I. I. Dilung, I. N. Chernov, *DAN*, **140**, 162 (1961).

6. V. B. Evstigneev, A. A. Krasnovskii, *DAN*, **60**, 623 (1948).

7. R. Livingston, A. C. P. Pugh, *Nature*, **186**, 969 (1960).

8. E. Fujimori, R. Livingston, *Nature*, **180**, 1036 (1957).

9. R. Livingston, O. Tanner, *Trans. Farad. Soc.*, **54**, 765 (1958).

10. M. Batley, L. E. Lyons, *Nature*, **196**, 573 (1962).

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