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Fig. 1

Figure 1: Fig. 1

Abstract

Full Text

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PHYSICAL CHEMISTRY

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INVESTIGATION OF PROCESSES OF INTERMOLECULAR ELECTRON TRANSFER UNDER PULSED ILLUMINATION

The binary molecular systems considered in the preceding communication consisted of tetrapyrrole pigments (Mg-phthalocyanine, methyl chlorophyllide, hematoporphyrin), subjected to pulsed photoexcitation, and such hydrogen (electron) donors as phenol, diphenylamine, and triphenylamine, which under the pulse revealed the spectral band of the corresponding positive ion ([1]). The spectrum of the negative ion for tetrapyrrole pigments, known only in the case of Mg-phthalocyanine ([2]), was not clearly detected in these experiments.

Therefore it became necessary to turn to other electron acceptors that give a distinct spectrum of the negative ion in the accessible region. In this respect, among the acenes, perylene is especially favorable; according to the work of Leonhardt and Weller ([3]), upon pulsed photoexcitation it exhibits the characteristic spectrum of its negative ion as a result of electron transfer from aromatic amines (aniline, dimethylaniline, diethylaniline, triethylamine).

Fig. 1. *a* —appearance of the oscillogram of the emission spectrum of the illuminating pulsed source (IFK-2000) in the region 740-460 mμ. Recording time 40 μsec. *b* —absorption band at 580 mμ of the ion Π^-, arising during illumination by a photopulse (400 J) of a solution of perylene (10^{-4} M) with dimethylaniline (10^{-1} M) in dimethylformamide.

In the present work the absorption spectra of labile intermediate products arising during the photopulse were recorded photoelectrically not by the usual, very laborious method of repeated oscillograms with stepwise change of wavelengths ([1]), but during a single light pulse. For this purpose, in the laboratory one of the authors developed a high-speed photoelectric spectrometer, which makes it

Fig. 2

Figure 2: Fig. 2

possible to obtain on the oscillograph OK-17 M a recording of the absorption spectrum from 460 mμ to 700 mμ in 40 μsec, i.e., during the flash time of the lamps. A description of the spectrometer will be published elsewhere. For pulsed illumination of the solution, two IFK-2000 lamps were used, with an (electrical) energy of 400 J and a flash duration of 40 μsec, placed in a "boiler"with scattering walls. The beam of light illuminating the solution and entering the spectrometer is produced by a third IFK-2000 lamp, whose flash is synchronized with the first two. The solution of the binary system under study, freed from dissolved air by pumping during repeated thawing and freezing, was transferred under vacuum into a glass cuvette 85 mm long and 20 mm in diameter with flat windows, which was placed for measurements in the light "boiler." The photographs of oscillograms of spectra given below reproduce the spectral distribution of the intensity of the illuminating source without correction for the spectral sensitivity of the receiver (FEU-27). In Fig. 1 copies of oscillograms of spectra are given, and in Fig. 2

authentic prints of the photographs. The notches on the curve in the source spectrum (Figs. 1a and 2a) belong to the intense Xe lines 541.9; 529.2; 484.4 mμ ($18.45 \cdot 10^3$; $18.87 \cdot 10^3$; $20.64 \cdot 10^3$ cm^{-1}), which are useful as wavelength markers. The spectral width of the spectrometer slit in these experiments was from 10 to 5 mμ (100-50 cm^{-1}). Calibration was carried out using the absorption bands of didymium glass (PS-7). The absorption bands arising in the solution under the photo-pulse appear against the background of the source distribution as distinct minima. Thus, in Fig. 1b, for a binary solution of perylene P(10^{-4} M) and dimethylaniline (0.1 M), the appearance of an absorption band at 580 mμ ($17.4 \cdot 10^3$ cm^{-1}) is visible; this band coincides with the band of the perylene anion (P^-), observed in work ([3]). In addition to dimethylformamide, methanol and acetone were used as solvents with identical results. However, in ethanol, ether, dioxane, cyclohexanone, and pyridine the ion P^- is not detected in the presence of dimethylaniline as donor. An analogous negative result was obtained in work ([3]) when benzene and methylcyclohexane were used as solvents; only solvents with a high dielectric permeability (dimethylformamide, acetonitrile) were favorable.

Fig. 2. *a* —oscillogram of the emission spectrum of the illuminating pulsed lamp. Recording time 40 μsec; *b* —absorption band at 535 mμ of the ion P^+, arising during illumination by a photo-pulse (400 J) of a perylene solution (10^{-4} M) with chloranil (10^{-3} M) in nitromethane.

With subsequent illuminating flashes without a photo-pulse, the 580 mμ band disappears from the spectrum. Measurement of the time of its existence, carried out on the oscillographic setup described in work ([1]), gave about $2 \cdot 10^{-4}$ sec.

At the next stage of the work the problem was posed of detecting under a photo-pulse not the anion, but the perylene cation (P^+), by selecting a suitable electron acceptor. Indeed, in solutions of perylene in nitromethane or acetone ($0.5 \cdot 10^{-4}$, $1.0 \cdot 10^{-4}$ M), upon addition to the solution of *p*-benzoquinone or chloranil, the appearance under the photo-pulse of a band at 535 mμ ($18.70 \cdot 10^3$ cm^{-1}) is observed (Fig. 2). Dissolved oxygen from the air was not removed in these experiments. The maximum of the perylene ion P^+ band is observed at 556.0 mμ ($18 \cdot 10^3$ cm^{-1}) in concentrated sulfuric acid or in nitrobenzene and chloroform in the presence of $SbCl_5$ ([4]). The discrepancy is evidently caused by the difference in medium. In the case of benzoquinone, in order to obtain an appreciable concentration of P^+, a concentration of $3 \cdot 10^{-3}$ M is necessary, whereas for chloranil $1 \cdot 10^{-4}$–$3 \cdot 10^{-4}$ M is sufficient, which corresponds to the greater electron affinity of the latter ([5]).

In contrast to the conditions for obtaining P^-, here the absorption spectra of the acceptors (benzoquinone and chloranil) are superimposed on the spectrum of the perylene molecules. With the aid of two BS-7 light filters placed between the cuvette and the lamps in the "cauldron," it is possible to eliminate the light action on the maximum of the absorption spectrum of chloranil. This did not produce any noticeable change in the 535 mμ absorption band that arose under the photo-pulse. The BS-8 light filter, which partially screens the radiation in the short-wavelength region of the P band spectrum, somewhat reduced the P^+ band both in the case of chloranil and of benzoquinone. These experiments show that excitation of the acceptor for

of electron transfer is of no significance. Removal of the 722 mμ region in the spectrum of the photopulse by means of an SZS-7 light filter does not affect the appearance of the P^+ band. In this region lies the electron-transfer spectral band in the *P*-chloranil complex ([6]). This result rules out an explanation of the phenomenon by photodissociation of this complex into P^++ chloranil$^-$. In addition, the spectral measurements carried out showed that the 722 mμ band of the *P*-chloranil complex in the nitromethane solutions used, at concentrations of P 0.5—$1.0 \cdot 10^{-4}$ M and chloranil $1 \cdot 10^{-4}$—$3 \cdot 10^{-4}$ M, is extremely weak. The oscillographically measured lifetime of P^+ is from $2 \cdot 10^{-5}$ to $10 \cdot 10^{-5}$ sec. Increasing the concentration of the acceptor by an order of magnitude has no appreciable effect on the lifetime or on the intensity of the P^+ band, which is also observed in the presence of oxygen in the solution. The latter completely eliminated the participation of triplet perylene molecules in the process under consideration. For this reason the triplet absorption band at 490 mμ ([3]) was absent from the spectrum.

The abstraction of an electron by the acceptor evidently occurs from the P molecule in the excited singlet state.

Fluorescence of perylene is absent in nitromethane; in acetone it is present and is quenched by chloranil.

In the second part of the work I. Shaganov took an active part.

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CITED LITERATURE

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